CAPTURING RADIATION-INDUCED MICROSTRUCTURE EVOLUTION
IN SITU THROUGH DIRECT PROPERTY MONITORING

by

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Abstract

Advanced materials development for nuclear systems is currently a time and resource intensive process relying on many iterations of material exposure and destructive testing. There exist few methods for characterizing irradiated material performance in situ, during exposure. Techniques such as in situ TEM or in situ Raman spectroscopy can provide local structural information during irradiation, but no current methods can continuously monitor bulk thermal and mechanical properties. Such a tool would provide the ability to map dose-property relationships at a resolution not previously possible, enhancing mechanistic understanding of irradiation-induced evolution. These methods could also be used to identify the onset of emergent irradiation-induced effects such as the transition from incubation to steady-state void swelling.

For this purpose, we have identified transient grating spectroscopy (TGS) as an appropriate technique to obtain these dose-property relationships during irradiation. This method, by optically inducing and monitoring monochromatic surface acoustic waves on materials under investigation, is able to determine the elastic and thermal transport properties of a microns-thick layer at the surface of a sample, the same depth to which ion beams can impose damage. First, we demonstrated that this method is sensitive enough to measure changes in material properties induced by radiation. Afterwards, we designed new optical geometries which enable second-scale time-resolved TGS measurements on dynamically changing materials. In addition, we developed new analytical methods through which multiple material properties, acoustic wave speed and thermal transport properties, may be extracted simultaneously from single-shot measurements. As proof-of-principle experiments, ion irradiation-induced property changes have been measured post-irradiation on pure, single crystal copper. In these copper samples, TGS measurements indicate the presence of volumetric void swelling, which is confirmed with scanning transmission electron microscopy (STEM). These developments together show that TGS is capable of capturing irradiation-induced evolution in real time and motivate the design and commissioning of an in situ experiment for ion beam irradiation and TGS monitoring.

To this end, an in situ TGS beamline experiment for concurrent ion beam irradiation and property monitoring has been developed on the 6 MV tandem accelerator at the Ion Beam Laboratory at Sandia National Laboratories. The in situ ion irradiation TGS (I3TGS) facility has the ability to monitor material evolution at high temperatures in real time under ion bombardment. Using high-energy self-ions, we are studying radiation damage effects on the thermomechanical properties of pure metals. In these experiments, irradiation-induced void swelling has been monitored at an orders-of-magnitude finer dose resolution than is possible with traditional methods. This tool has allowed the onset of swelling to be pinpointed in applied dose, a key consideration when developing new materials for use in nuclear systems, on the timescale of days rather than months or years. We are now able to provide the type of rapid, engineering-relevant data necessary to speed the innovation cycle in nuclear materials development. Moving forward, these methods can be used as a screening tool to expedite the design and testing process for advanced nuclear materials.

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“The scientific enterprise as a whole does from time to time prove useful, open up new territory, display order, and test long-accepted belief. Nevertheless, the individual on a normal research problem is almost never doing any one of these things. Once engaged, his motivation is of a rather different sort. What then challenges him is the conviction that, if only he is skillful enough, he will succeed in solving a puzzle that no one before has solved or solved so well. Many of the greatest scientific minds have devoted all of their professional attention to demanding puzzles of this sort. On most occasions any particular field of specialization offers nothing else to do, a fact that makes it no less fascinating to the proper sort of addict.”

– T.S. Kuhn

The structure of scientific revolutions
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Chapter 1

Introduction

Materials which experience high levels of radiation exposure often undergo unique and dramatic forms of microstructure evolution and degradation not seen under any other extreme conditions. The archetypal example of such a system is, of course, the commercial nuclear fission power plant. Others include space and satellite systems, weapons systems, future fusion reactor systems, as well as innumerable scientific instruments and devices. In all such systems, radiation-induced or -enhanced degradation may take many forms including but not limited to precipitation, segregation, particle dissolution, disordering, void swelling, stress corrosion cracking, and a myriad of others [1,2]. These changes in microstructure often cause changes in the thermophysical properties on which engineering-scale components rely for safe operation. For example, the formation of copper-rich precipitates during irradiation in low-alloy steel used for reactor pressure vessels causes life-limiting embrittlement [3,4]. In stainless steels, radiation-induced segregation of passivating chromium away from grain boundaries increases the chances of stress corrosion cracking [5,6]. Ni-based superalloys may experience irradiation disordering or dissolution of desired $\gamma'$ precipitates, dramatically decreasing total hardness [7].

In this work, we have chose one of these modes in particular, volumetric void swelling, as our canonical mode of interest in seeking to develop advanced instrumentation and methodologies to observe these evolution processes. This degradation mode initiates with the generation of a net supersaturation of vacancies during irradiation due to preferential sinking of highly-mobile interstitials. With this net supersaturation, vacancies will tend to agglomerate into large, vacuum-filled defect clusters. The presence of insoluble gas in the crystal matrix, particularly He, often serves to stabilize initial void formation and, if the gas concentration is high enough, can lead to pressurized bubble formation as opposed to void formation. Fig. 1-1 shows both the micro- and macro-scale effects of void swelling in two different materials. On the micro-scale, the inclusion of this high level of porosity may drastically affect thermal transport, dislocation mobility, neutron transport, and, most importantly, may lead to a near-complete loss of ductility at levels of around 10% swelling. On the macro-scale, the physical size change of components associated with large amounts of swelling can easily place systems out of engineering specification. This degradation mode is commonly observed in austenitic steels used for structural applications in high neutron environments [9], although eventually almost all materials will undergo void swelling given a combination of sufficiently high dose and insoluble gas generation [10]. Materials being designed for this application in future reactors must either be stable against swelling and other types of radiation-induced degradation over decades or have extremely well-characterized evolution.
Figure 1-1: (a) High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image of self-ion induced void swelling in pure copper. Here, the crystal matrix appears light where the faceted voids appear dark. This image was captured as part of this thesis and will be discussed in detail later. (b) Photograph of 316 austenitic stainless steel cladding having undergone physical dimension change as a result of neutron exposure [8].

The driving motivator for this work is precisely that materials design process which must take place before new materials are placed into service. A standard iterative materials design protocol is presented in Fig. 1-2. This protocol begins with some material design including alloying composition, processing, and fabrication. To test how the microstructure and properties of this material will evolve in operando, they must be placed in some out-of-equilibrium condition including but not limited to temperature, corrosive fluids, pressure, and radiation for some length of time to emulate the conditions they will see in service. Following this exposure, samples are tested, normally destructively, to determine what evolution has occurred. Standard types of testing techniques include electron microscopy for structure characterization and methods such as tensile or impact testing to determine mechanical properties [11,12]. However, to ensure reliability throughout an operation lifetime, many exposures to different equivalent lengths of service must be carried out, ideally on identical samples. Based on the results from these tests, a larger iteration in materials design, in minor alloying, for example, may be carried out to combat whatever degradation modes are identified in the initial design point. The cycle will then repeat until a material with suitable performance is identified.

This doubly-iterative design process, colloquially referred to as a “cook and look” development scheme, is exceptionally time and resource intensive. Compounding these challenges are the limited availability of and extra time associated with conducting direct neutron exposures of materials under development. Exposures of this type incur an extra time penalty as materials will often become activated during neutron exposure and must be allowed to cool before post-irradiation examination (PIE) may take place. A complete materials development program using this type of protocol is commonly a many-year undertaking. As a result of all these constraints, very few materials in total are qualified for service. Despite the variety of different environments present in a commercial power reactor, only on the order of ten different metals and alloys are put into service in these large systems [13].

For the last several decades, ion beam irradiation has been and is being increasingly utilized to combat the cost incurred from direct neutron exposure [14,15]. Using particular conditions of temperature and dose rate, exposure to levels equivalent to decades in service may be carried out in days instead of months. However, even with this
time savings, the reliance on destructive PIE results in time-consuming studies with coarsely-sampled data. Example data generated from this type of development process is shown in Fig. 1-3, which shows the high-dose void swelling resistance of several radiation-tolerant steels under ion beam irradiation. The major conclusion of Getto and coworkers from this particular study is that both alloy T91 and T92 perform very well under exposures equivalent to end-of-life conditions in advanced fast reactor concepts [16]. However, as noted on the plot, at high doses these data are sampled with a resolution in dose of approximately 100 dpa (displacements per atom). In the long term response regime where these materials are expected to swell linearly proportionally to the total dose applied, this coarse sampling may be of no great concern despite being equivalent to years in service. However, in the lower-dose regime where a drastic transition from incubation to steady-state void swelling is expected, this coarseness may be missing critical evolutionary states.

Data like those presented in Fig. 1-3 directly motivate the work carried out in this thesis. Here, we ask: can dose-property correlations for volumetric swelling (and possibly other degradation modes) be captured at much finer resolution, much more rapidly, than the current state of the art? If so, then we can use whatever these new methods may be as rapid down-selection tools to drastically speed the innovation cycle in nuclear materials development. The goal is to put new materials into service which are not just ‘good enough’ but specifically optimized for their particular use cases.

To generate highly-resolved dose-property correlations efficiently, the inner loop of the iterative development cycle in Fig. 1-2 must be broken through the use of *in situ* testing. Characterizing continuously (or nearly so) during the exposure step in the material development framework is advantageous for several important reasons. Foremost, *in situ* testing the resolution in processing space is restricted only by the physical processes being used to interrogate the material. The challenge, however, comes in designing and implementing characterization methods that can suitably operate in these extreme out-of-equilibrium conditions. If successful, *in situ* testing recovers these out-of-equilibrium properties, ideally similar to *operando* conditions, rather than those measured post-exposure at ambient conditions. Importantly for the case of radiation effects, equilibrium point defect concentrations vary drastically between beam-on and beam-off conditions [17], creating a challenge in extrapolating results from PIE to in-service conditions. Finally, *in situ* testing has the advantage of eliminating issues related to sample-to-sample variation that often plague experiments collected with small data sets.
For all these reasons, *in situ* testing has been utilized in some form in the field of radiation effects for the past several decades. Specifically, methods such as *in situ* TEM [18] and *in situ* Raman spectroscopy [19] have been utilized, and, in some cases, turned into popular user facilities. However, the current state of the art still relies on characterization of material structure during irradiation, as opposed to direct material property evaluation. In those studies, highly-resolved dose-structure relationships still rely on previously determined structure-property relationships to infer how material performance will be affected. The goal of this thesis is to short-circuit this procedure and measure dose-property relationships directly during *in situ* testing. Such a capability would simultaneously provide a means through which new emergent radiation-induced effects may be uncovered while also allowing for property evolution to be monitored with orders-of-magnitude finer resolution in dose.

Here, several *in situ* structural characterization methods are described in detail in Chapter 2. Afterwards, several possible interrogation methods are described which could be utilized as an *in situ* property and performance diagnostic. Of these, we choose to implement a specific method called transient grating spectroscopy (TGS), which will be the sole focus of the remainder of the thesis. The mechanics of this particular methodology are described in brief in Chapter 2 as well, although discussions at various levels of detail are presented throughout this work as necessary. In Chapter 3, the ability of this methodology to detect mesoscale radiation-induced microstructural evolution is explored and proven through sensitivity experiments and molecular dynamics simulations. Following this determination, a matrix of pure, single crystal copper specimens are analyzed post-irradiation using TGS to observe the effects of self-ion induced void swelling in Chapter 4. Significant swelling is confirmed in these samples using high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and image analysis. Taken together, Chapter 3 and Chapter 4 show conclusively that the TGS methodology is appropriate for monitoring this particular mode of
radiation-induced evolution.

Previous implementations of this methodology have been restricted to static material systems, where no material evolution is ongoing. To fully utilize this method as an in situ diagnostic, new optical implementations are designed to allow for time-resolved characterization of materials undergoing dynamic evolution. This new geometry is detailed and its performance characterized in Chapter 5. In addition, TGS measurements on static systems have the advantage of being able to use two distinct signal collection modes to extract different material properties from the sample in question (thermal and elastic). For in situ experiments, a multi-modal measurement technique is desired to extract as much information as possible in a single-shot measurement. To this end, a signal collection and analysis method is presented in Chapter 6 which allows for both of these properties to be extracted simultaneously.

With these capabilities (sensitivity, time-resolution, and multi-modality) in hand, Chapter 7 describes the complete in situ ion irradiation transient grating spectroscopy (I^3TGS) facility which has been designed, constructed, and tested as the major goal of this work. This facility operates on a 6 MV tandem ion accelerator at the Ion Beam Laboratory at Sandia National Laboratories and is capable of conducting high-temperature ion beam irradiations with continuous TGS property monitoring. Chapter 7 describes only the initial testing of this facility, while Chapter 8 describes further experimental campaigns conducted after the facility was commissioned. In addition, Chapter 8 provides a discussion of the assignment of a ‘dose’ to materials non-uniformly damaged using energetic ions and non-uniformly sampled used TGS. A physics-inspired dose calculation is proposed, but remains to be validated. Future studies are described which will be necessary to prove whether TGS measurements on materials with different spatially varying microstructures may be compared quantitatively.

Finally, Chapter 9 draws conclusions from this work in total and proposes additional steps for future research. These steps include both impactful systems on which the capabilities developed herein should be immediately targeted as well as developmental steps which should be carried out to increase both the utility and versatility of the suite of tools presented.

Note: Much of the work presented in this thesis has been peer-reviewed and published in a variety of technical journals. Specifically, Chapters 3–7 each draw directly from particular publications. In introducing these chapters, full citations will be provided to their published counterparts. The publishers of these journals (Elsevier, the American Institute of Physics, and the American Physical Society) all grant access for authors to reproduce their own work as part of theses and dissertations.
Chapter 2

Current and possible *in situ* diagnostics

The initial scoping for a new real-time property monitoring diagnostic suitable for ion beam irradiations in this thesis is conducted in two major parts. First, methods of *in situ* radiation response monitoring that are currently in use are reviewed. These methods are found to be, in general, focused on structural characterization of materials as they are exposed to radiation and are unable to directly access engineering-relevant properties. Second, a set of characteristics describing the ideal performance monitoring tool is constructed. From these desired characteristics, two broad classes of techniques are identified as the most promising: mechanical spectroscopy and thermal wave microscopy. Some advantages and disadvantages of different implementations of each are discussed, following and expanding on the analysis made by Short et al., [20]. Of these many possible techniques, transient grating spectroscopy (TGS) is chosen as the ideal candidate to develop for *in situ* property monitoring during ion beam irradiation.

Before proceeding, a passage from Hinks, in a review on TEM facilities with *in situ* ion irradiation capabilities, is instructive in considering the goals of any such work with ion beams. Hinks states, “...it is not always possible to extrapolate directly from the results of ion irradiation experiments to the neutron case. However insofar as neutron irradiation damage is concerned, the real strength of TEM with *in situ* ion irradiation does not necessarily lie in its ability to directly reproduce the same responses in materials but rather in its unique capacity to image the internal microstructure and gain insight into the underlying mechanisms at work – a knowledge of which can then be used to help explain and predict the consequences of neutron irradiation” [21]. The work presented here largely ascribes to the same principle. However, while accepting this inability to directly match the neutron case with ions, one can still seek to observe radiation-induced evolution through a lens that comes as close as possible to interrogating the performance characteristics on which safe operation relies [14,15].

2.1 Current *in situ* ion irradiation diagnostics

The inception of the field of *in situ* radiation damage monitoring was centered around the transmission electron microscope (TEM). In 1961, Pashley and coworkers noted the generation of spots and dislocation loops in gold films studied in the TEM from what were eventually identified as O⁻ ions produced by oxidation of the tungsten filament in the electron gun [21,22]. In the abstract of their original report on the matter, Pashley et al. state: “The ion damage is assumed to be very similar in character to that produced by primary knock-ons resulting from irradiation
by other particles (e.g. neutrons),” likely becoming one of the first to note the utility of emulating neutron damage with ions [22]. Since that time, several methods in addition to electron microscopy have come to be commonly (or relatively commonly) utilized for in situ radiation damage evaluation. These methods have in common a focus on structural material characterization. In this context, structural characterization denotes either direct imaging of the material atomic structure or microstructure, measurements of electronic or phononic structure, or measurements of local atomic disordering. Such structural characterization stands in contrast to property or performance characterization which returns macro- or meso-scale mechanical, thermal, and electronic properties which are important design criteria for engineering-scale components. Although many methods of structural characterization of this type exist, relatively few have been adapted to be used as in situ tools for radiation-induced evolution given the challenges of coupling complex diagnostics to complex processing chambers for ion beam irradiation. Here, three of these methods – in situ TEM, in situ Raman spectroscopy, and Rutherford backscatter spectroscopy and ion channeling (RBS/channeling) – will be described briefly. For each, an experimental implementation will be shown, representative data for common experiments presented, and broad classes of materials identified for which the techniques are most useful. In particular, the experimental implementations of these methods are of interest as they provide insight into common issues like coincidence positioning and dosimetry that will need to be addressed in the new diagnostic under development here. In all cases these methods are non-contact evaluation techniques, relying on the interaction of some probe, electrons, lasers, or ions, with the material undergoing ion exposure to return meaningful structural information. This lack of contact is desirable for an in situ irradiation probe as it reduces the effect of testing on the radiation-affected material evolution taking place. This criterion will be considered a necessity as different methods of property and performance testing are considered.

2.1.1 In situ transmission electron microscopy (TEM) The general goal of in situ imaging with a TEM during ion beam irradiation is to observe directly the accumulation, agglomeration, and evolution of structural defects caused by radiation. To do this, samples must be prepared as electron-transparent films, around 100 nm thick, necessary for imaging. Defect characterization and identification in samples of this geometry is a well-developed science; a concise review specific to radiation-induced defects is given by Jenkis and Kirk in their book [23]. The specific type of imaging conditions used during in situ exposure can vary from experiment to experiment, but most commonly, real-time videos are captured in standard bright-field imaging conditions. In these highly time-resolved videos, frames are most often collected at relatively low magnifications due to effects such as sample drifting. Example in situ TEM data from Li and coworkers are presented in Fig. 2-1. Snapshots from videos such as these can be processed via image analysis to generate plots of defect accumulation such as that presented in Fig. 2-1(g). At these resolutions, defect identification is only possible with knowledge of the common types of formations in the material of interest; the resolution available rarely allows for direct identification based on structure and orientation relationships. In situ TEM experiments are also often conducted in an interrupted mode where the irradiating beam will be blocked for some length of time during the exposure to allow high-resolution imaging to take place. While not continuously monitoring the material evolution in these cases, and possibly affecting the defect accumulation dynamics
in the ion-beam-off periods, this protocol has the advantage of being able to recover more detailed information while continually interrogating one region of interest. Imaging techniques such as under- and over-focused image series to identify nanoscale bubble or void formation can be conducted in this protocol to identify defects that are otherwise unobservable [23–25]. In experiment, irradiating ion energies can be chosen either to pass entirely through thin foil samples, leading to no effects from chemistry change, or be implanted at very low energies – 10’s of keV – to impart the maximum amount of displacement damage into the thin foil [18].

The geometric coupling between an ion beamline and a TEM is a challenge which has been approached in several different ways around the world. In almost all cases the ion beam is brought into the TEM column between or near the upper and lower pole pieces of the objective lens. In this geometry, the ion beam can be introduced approximately normal to the TEM column direction, requiring a relatively large tilt angle to be introduced between the sample and the column to allow simultaneous imaging and irradiation [18,21]. This geometry allows the physical microscope and beamline to operate on the same building level. An example of such a facility is the I^3TEM at Sandia National Laboratories, shown schematically in Fig. 2-2. The high irradiation and imaging angles are shown in Fig. 2-2(b). An alternative geometry option is to introduce the ion beam at some high angle to reduce the absolute tilt necessary during in situ experiments. This option often requires the microscope and ion accelerator to be located at different vertical levels, i.e. different floors of the building in question, and can also require an additional separation of the objective pole pieces [21]. Examples of facilities taking this approach are the Intermediate Voltage Electron Microscope (IVEM) at Argonne National Laboratory and the MIAMI (Microscopes and Ion Accelerators for Materials Investigation) facilities at the University of Huddersfield. The final possibility is to use electrostatic deflection within the TEM column to control ion beam positioning [21]. Such methods are more challenging due to space constraints and the introduction of additional fields within the column.

In addition to solely sampling structural defects in materials being exposed to high levels of radiation, in situ TEM experiments must address questions regarding the length scale of specimens used for such testing. The thin, electron transparent films necessary for electron microscopy in this form provide large, essentially infinite defect sinks in
Figure 2-2: (a) Schematic of the *in situ* ion irradiation TEM (I3TEM) facility location at Sandia National Laboratories. Capable of dual-ion irradiation, this facility contains many standard ion beam control and diagnostic components upstream of the target located inside the TEM column. (b) TEM sample geometry showing the relative beam paths of heavy ions from the tandem accelerator (MeV), light ions from the Colutron (keV), the imaging electrons (e\(^{-}\)), illumination optical pathway (\(h\nu_{B-C}\)), and optical imaging pathway (\(h\nu_{D-F}\)). Both figures from [18].

samples where active defect generation is ongoing. These large sinks cause the accumulated defect dynamics to differ from exposures of bulk materials. Li et al. undertook a systematic study to show the effects of sample thickness during *in situ* TEM experiments at the IVEM and concluded that the effects may be successfully taken into account using a combination of thickness-dependent experiments and coordinated modeling to recover fundamental defect accumulation properties [27]. However, in essence, that study serves to reinforce the care that must be taken in the interpretation of *in situ* TEM studies in light of the requirements on sample geometry, and adds yet another experimental step when seeking to extract meaningful information about a given material.

### 2.1.2 *In situ* Raman spectroscopy

In the context of measuring the effects of radiation, Raman spectroscopy can be used as an identification tool to measure the presence and extent of changes in structure or disordering induced by radiation. In brief, the measurement physics relies on inelastic scattering of monochromatic light from low-frequency phonon vibrational modes. Incident monochromatic light, normally from visible-wavelength lasers, will either elastically scatter, retaining individual photon energy, or be shifted in wavelength through Stokes or anti-Stokes scattering processes from virtual vibrational states [28]. Scattered light from samples under interrogation is focused and collected in a spectrometer designed to reject the majority of the elastically-scattered intensity. These measurements are most useful in systems that undergo phase transitions or amorphization during irradiation such as ceramics, ordered compounds, or glasses [19,29,30]. It is possible to achieve some amount of depth resolution in ion-irradiated samples using confocal Raman [31], however this mode is not commonly implemented for *in situ* experiments.

Example *in situ* Raman spectra collected on 6H-SiC as a function of applied Au ion fluence are shown in Fig. 2-3. In the low fluence regime, a decrease in intensity for the sharp phonon peaks is correlated with increasing disorder or amorphization of the structure [19]. The disappearance of these peaks at a certain fluence level is therefore taken to mean that the radiation-affected layer has been completely amorphized. At higher fluences, broad bands associated
with disordered sp$^2$ carbon bonding are observed and eventually those evolve into signatures of fully mixed sp$^2$ and sp$^3$ coordinated C-C bonds. Similar to TEM investigations, the interpretation of these data relies heavily either on prior experiments in similar material systems or modeling for the interpretation of the structural signatures that are generated. These data in particular are collected in an interrupted mode; for each representative fluence the ion beam exposure is halted and the Raman collection carried out for 150 sec [19]. The particular facility used for this study, at JANUUS-Saclay, has the ability to operate both the spectrometer and ion beam concurrently, yet their standard collection time is long enough that the instrument is most routinely operated in this interrupted mode.

Implementing in situ Raman spectroscopy during ion beam irradiation has been accomplished in a smaller number of facilities worldwide than in situ TEMs, with only a handful of facilities operating (primarily in Europe). These facilities generally operate in one of two modes, tilting or non-tilting. In tilting mode experiments, two distinct sample positions are maintained within the target chamber, one for ion beam exposure and one for Raman collection. Facilities operating in this mode must by design operate using interrupted exposures and true in situ measurements are not possible. An example of a non-tilting geometry is shown in Fig. 2-4, which is implemented at the JANUUS-Saclay facility. This experiment has the ability to conduct triple-beam ion irradiations with each beam incident on the sample at approximately 15° off-normal, while maintaining line-of-sight access to the sample with the Raman interrogation diagnostic. This diagnostic head is fiber-coupled to a standard Raman spectrometer located away from the target chamber and has a working distance of 32 mm to the sample surface. This set point working distance is ultimately limited by geometric shadowing of the ion beams [19]. Experiences garnered from these experiments, specifically, coupling optical diagnostics to irradiation experiments, will be of use when considering the ultimate design of the optical in situ diagnostic implemented as the major goal of this work.

2.1.3 RBS/channeling

Thus far the in situ, or near in situ, techniques considered have used electrons and photons as the non-contact probe of the material experiencing some type of evolution. The final commonly-used technique instead uses additional ion beams to probe disordering effects induced by irradiation. Rutherford backscatter spectrometry and ion channeling
(RBS/channeling) exploits the phenomenon of ion beam channeling in well-oriented single crystal material, and specifically the degradation of such channeling behavior as crystal irregularities are induced, to monitor irradiation effects. A thorough review of RBS techniques generally is provided by Chu and coworkers [32]. In brief, if a single crystal material is exposed to ions along a low-index zone axis, the ions may “see” large, open-volume channels due to crystal symmetry. Along these zone axes, the number of measured recoils will be lower than that measured for amorphous materials as ion are able to penetrate further into the material. As the quality of these channels degrades with irradiation exposure, the total amount of backscatters will increase towards the fully amorphous level. Depth-dependent backscattering yields are assigned based on the amount of energy loss experienced from monoenergetic probing ions by the time they are detected.

Similar to in situ TEM experiments, RBS/channeling can be used to interrogate radiation-induced evolution in a wide variety of materials, both ceramic and metallic, provided that either single crystals may be produced or the grains of a polycrystal are large enough that a low-index area may be identified. Example RBS/channeling data from Zhang et al. on the disordering of single crystal Ni and two equiatomic solid-solution mixtures, NiFe and NiCo, are presented in Fig. 2-5. Data here are presented after a fixed level of exposure to 3 MeV Au ions, and not in a continuous in situ manner [33]. The damage-free level is indicative of all three samples and indicates a large amount of channeling, i.e. perfect crystallinity. Following exposure, the backscattering yield as a function of depth is increased due to the generation of small defect clusters. Backscattering yields in the form of Fig. 2-5(a) can be converted to a ‘dechanneling’ or ‘relative disorder’ parameter as a function of depth as in Fig. 2-5(b). As shown, the intensity of the relative disorder maps with the depth-dependent damage profile induced by heavy ions. In a relative sense, data of this type is useful as a screening tool to indicate that the solid-solution alloys retain many fewer radiation-induced defect clusters than the pure metal. However, in an absolute sense, this measure is still something which needs to be compared with microstructure characterization in the TEM and then correlated back to material performance through pre-determined structure-property relationships.

Historically, the capability to use an ion beam facility to target bulk irradiation damage has followed after the
implementation of a variety of ion beam analysis tools such as RBS/channeling. This being the case, RBS/channeling is often a tool readily available to use for the interrogation of ion-exposed samples. Experimentally, given a well-collimated source of light ions, usually He, implementing a channeling experiment requires only the ability to finely position the desired zone axis along the ion beam direction with a goniometer. A simplified geometry for such experiments is shown in Fig. 2-6. As light ions are necessary for these backscattering experiments and heavy ions – or some combinations of light and heavy ions for multi-beam exposure – are preferred to induce displacement damage, the species of ions being generated by the accelerator must be changed from a damaging species to an interrogating species for RBS. In practice, this requires that channeling experiments must again be used in an interrupted manner and not as a true in situ diagnostic in single-beam facilities. Facilities which have the capability to perform multi-beam irradiations are able to use both damaging and interrogating beams simultaneously. These experiments are difficult to implement and although they have been used, they are not conducted routinely [34,35].

Figure 2-6: Schematic of RBS/channeling experimental setup commonly employed on many ion beam analysis facilities. For “in situ” experiments, the incident beam of the ion accelerator can be changed from a damaging self-ion beam to a lighter-ion analysis beam immediately upon completion of an exposure. Diagram from [32].
2.1.4 Summary of current diagnostics

Having explored several currently implemented in situ, or near in situ, ion beam irradiation diagnostics, several commonalities may be noted between these implementations. Each method described above relies on prior knowledge, either experimental or modeling data, to interpret changes in the signatures noted during irradiation. This requirement is the weakest for TEM experiments, where such high-resolution comparison data can be generated by running interrupted experiments. For both Raman and RBS/channeling, high resolution TEM is commonly carried out in parallel to correlate measured responses to particular microstructural formations. This structural knowledge can then be translated to material performance using structure-property relationships. In the methods that we seek to develop here, one of these gaps will still exist. By sampling material performance characteristics directly, the methods put in place will also rely on other experimental or computational methods to infer material structure evolution. However, by starting from material properties directly, radiation-induced evolution which causes a significant degradation in system performance may be identified much more efficiently.

2.2 Possible in situ diagnostic methods

An evaluation technique which could be utilized for the purpose of direct material property evaluation during ion beam irradiation should ideally have a distinct set of characteristics. Short et al. [20] enumerate that a method used for this purpose would

- be non-destructive,
- be non-contact,
- collect data rapidly,
- have micron-scale resolution in order to match the length scale of damage imposed by ions,
- utilize non-electronic probes which won’t degrade with radiation exposure.

In addition, a second-order consideration would be to seek a method that not only returns material properties directly, but returns multi-property information simultaneously. For this application, material properties of interest which may be isolated non-destructively include thermal transport properties, elastic mechanical properties, magnetic properties, and electrical properties. It is generally the plastic, non-recoverable deformation properties such as ultimate tensile strength or fracture toughness that are the most relevant mechanical properties of interest to system performance. However, these properties cannot be accessed using a non-destructive methodology since by definition they are characteristics of irreversible processes. Therefore, the non-destructive interrogation of purely mechanical properties must be limited to the elastic properties governing reversible processes.

Table 2.1 delineates all of the currently used in situ techniques and all of the new techniques under consideration for in situ property monitoring during ion beam irradiation as a function of the criteria delineated above. Each of the new techniques can be classed into two primary groups: mechanical spectroscopy or thermal wave microscopy. The following sections will describe broad characteristics of each of these classes and provide comments on the particular strengths and weaknesses of each implementation. The result of that discussion is the selection of transient grating spectroscopy (TGS) – which includes characteristics of both mechanical spectroscopy and thermal wave microscopy techniques – as the most appropriate tool to develop for this purpose.
Table 2.1: A comparison of the commonly-utilized in situ ion beam irradiation measurement techniques with several methods which could be used for in situ property monitoring. Of the methods presented here, only time domain thermoreflectance (TDTR) and transient grating spectroscopy (TGS) provide multi-modal property data simultaneously, in both cases elastic and thermal transport properties. This table has been modified from the version appearing in Short et al. [20].
2.2.1 Mechanical spectroscopy

Mechanical spectroscopy, in the most general sense, utilizes the propagation and dissipation of mechanical energy to determine the properties of solid-state materials. In the crystalline materials of interest here, this energy propagation takes the form of acoustic wave propagation where information regarding material properties and defect structure may be extracted from propagation speeds, decay characteristics, and non-linearities [36,37]. Well-validated models of acoustic wave propagation as a function of fundamental material properties such as modulus and density exist such that the information returned from these techniques may be considered a ‘direct property evaluation.’ Due to the strict requirement of non-destructive interrogation for this purpose, techniques such as ablation spectroscopy will not be considered [38]. Instead, the methodologies of possible interest will be acoustic or ultrasonic methods which induce small mechanical actuations over a variety of frequency ranges that do not irreversibly deform the specimen under investigation. The techniques considered here use both bulk and surface acoustic wave (SAW) propagation and have induction and detection schemes which are contact, non-contact, or some combination thereof. None of these methods will provide multi-modal information about the material under investigation; they exclusively sample the mechanical response of the material in question.

The first broad class of techniques use some form of contact for acoustic wave induction or detection, and hence will not be suitable for the \textit{in situ} diagnostic under development. The most basic form of this testing is conventional contact ultrasonics in which bulk acoustic waves are induced in a sample using a piezoelectric oscillator. In physical contact with a sample, these acoustic waves may be detected using a second contact receiver on a different surface of the piece in question, measuring the characteristics of the transmitted acoustic wave. Similar methods can be constructed which use physically-contacted transducers and receivers on a single surface of a sample in question which are designed to induce only surface skimming Rayleigh wave or SAW modes [39]. A variation that does not require physical contact between the transducer and sample, but rather utilizes an intermediate working fluid to transport focused acoustic excitation from a distant source, is dubbed scanning acoustic microscopy (SAM) for its ability to raster the excitation and detection across a surface [40]. An example experimental configuration for a SAM experiment is shown in Fig. 2-7. More advanced methods continue to use contact ultrasonic transducers to induce acoustic waves, but use laser interferometry to detect through-sample propagation. These techniques, in a few variations, are referred to as scanning laser acoustic microscopy (SLAM) and although they have removed one sample contact point, they fail to be entirely non-contact and therefore will not be satisfactory for this use [41,42].

Moving away from piezoelectric acoustic wave induction, thermoelastic excitation is the other most commonly used form of mechanical wave generation mechanism used. By rapidly causing a local temperature rise through the use of a laser source, rapid thermal expansion will launch a strain wave in the surface of the material. Depending on the geometry of the excitation and the material properties and layering structure of the sample under interrogation, this strain wave will be exhibited as acoustic wave(s) of various characters [43]. Surface-localized excitations are of interest for this use case, as mentioned previously, as an ideal method would match the length scale of the surface imposed ion damage. These methods can generally be classified as laser-induced surface acoustic wave (LSAW) techniques. Ultimately, the method of choice considered in this work will fall into this class of methodologies. Thermoelastic excitation of this type provides a second major advantage when attempting to recover multi-property information, as well. Due to the presence of an out-of-equilibrium temperature field, experiments can be conceived such that the
dynamics of both mechanical and thermal energy propagation may be probed simultaneously.

There are several non-contact methods which may be used to detect the effects of thermoelastic surface excitations. A high-precision, yet time-consuming, method is surface Brillouin scattering (SBS). In opaque materials, SBS works by shining a low-power laser into the region which has been excited. Small ripples on the surface of the material due to acoustic wave displacement may cause Stokes or anti-Stokes scattering of the probing excitation laser [44]. These frequency shifts are generally detected using Fabry-Perot interferometry to isolate the acoustic wave speeds responsible for scattering. Despite the fine level of detail that SBS captures, the signal collection time, on the order of hours, is simply too long to be useful as an in situ diagnostic hoping to resolve property changes on the order of tens of seconds. Several other, less time-consuming, methods which may be employed to detect SAWs include interferometric methods, displacement or knife-edge detection, or reflectivity changes [43]. All three methods may be employed as separated source-receiver methods, where traveling SAWs are detected using laser probe as some distance from their excitation location [43,45]. Sources may be some kind of point, line, or periodic source depending on the application in question. The ultimate geometry chosen for this application will utilize a probing laser overlapped with a periodic source such that standing wave behavior is interrogated. However, before that method is described in detail, a separate class of techniques focusing on thermal property determination from similar laser excitations will be described briefly.

2.2.2 Thermal wave microscopy

Techniques falling into the class of thermal wave microscopy generally use the evolution of a impulse surface temperature rise to determine the thermal transport properties of the sample in question [46]. Although many geometries for this class of experiment exist, a commonly-used implementation is time-domain thermoreflectance (TDTR). Here, TDTR will be taken as the canonical example of such a technique and described in enough detail to rule it out for the purpose of an in situ diagnostic for use during ion beam irradiation.
TDTR is an optical pump-probe technique which measures the dynamic propagation of heat at short timescales. The description here relies on a recent review by Cahill, one of the pioneers of this methodology, and noted parameters are taken from his example [47]. The excitation and probing laser pathways are generated from a single Ti:sapphire source operating at 80 MHz with 200 fs pulses. The probing pulse train is path length delayed such that it reaches the sample on the picosecond timescale following the pump. Rapid temperature rise caused by the pump will induce changes in the temperature-dependent complex reflectivity of the sample in question. The small changes in reflected probe light due to these reflectivity modulations are monitored by adding an additional 10 MHz modulation to the probe train and using a lock-in amplifier to detect very small changes in intensity as measured on a photodiode. An example experimental configuration for this type of experiment is shown in Fig. 2-8.

Since this methodology requires a sufficient change in reflectivity to measure the thermal transport dynamics, it must ensure that 1) enough heat is imparted into the sample and 2) that the reflectivity dependence on temperature is strong enough to cause a measurable shift. For both of these reasons, samples under TDTR investigation are most commonly coated with an aluminum transducer film. Using a conductive metal for this purpose is preferred since all of the laser energy will be absorbed within one skin depth – on the order of 10 nm – and since aluminum has been found to have a sufficiently strong temperature dependence of reflectivity [47]. To completely block stray optical signals, this transducer film is normally around 50 nm thick. With the now-complex layered system under investigation, detailed models for heat transport in multi-layered systems as function of pumping frequency must be solved to extract the thermal conductivity of the layer of interest [48–50]. Most often, the material properties and thickness of the transducer film are taken as known quantities in this multi-parameter optimization method. This and similar methodologies have been used to study a wide range of materials and physics including but not limited to porous ceramics [51], thermal boundary resistance in semiconductor films [52], nanoscale ballistic heat conduction [53], and polycrystalline ceramic coatings on surrogate nuclear fuels [54], among many others.

Since the impulse used for this methodology is again a rapid temperature rise, thermal expansion will launch surface
acoustic waves of various characters in this layered system which may be used to determine system elastic properties, film thicknesses, or local microstructure [55,56]. In this way, TDTR is the first methodology discussed here which may be considered ‘multi-modal,’ in that thermal transport and elastic properties may be returned. However, due to the necessary transducer layer present in most experiments, TDTR fails to qualify for the ‘direct property measurement’ characteristic that has been identified as necessary for the purpose of in situ property monitoring. The major challenge of this transducer layer in a radiation environment is that the transducer layer itself, and its adherence to the sample of interest, may be affected by the imposed ion irradiation. This would call into question the literature values for transducer layer properties which are, if not required, at least extremely helpful in determining the material properties of the sample under exposure. Primarily for this reason, TDTR is unsuitable for the task at hand. This implementation restriction is common among most well-developed classes of thermal wave microscopy. However, the physics on which this methodology relies – namely, tracking changes in complex reflectivity as a measure of temperature evolution and therefore thermal transport – will still be utilized in the methodology which is selected in this work.

### 2.3 Transient grating spectroscopy (TGS)

Following consideration of the techniques described above, the transient grating spectroscopy (TGS) method is found to either have, or have the potential for, all of the requirements identified for an in situ multi-property monitoring methodology. TGS, or impulse stimulated thermal scattering (ISTS), is a type of laser-based, pump-probe spectroscopy which uses an excitation in the form of a 1-D periodic laser intensity profile. This pump profile is generated by crossing two laser pulses at the surface of the sample under interrogation at a fixed angle to create a spatially periodic interference pattern, as in Fig. 2-9(a). In the common ‘boxcar’ optical geometry, these two pulses are generated from a single source, split using a diffraction optic, and recombined at the sample surface using a 4f imaging system [57]. The periodic laser excitation will generate surface variations in temperature and displacement in the form of SAWs caused by thermal expansion, as in most LSAW techniques. Rather than using purely physical displacement or reflectivity techniques, this method exploits the periodicity of the excitation to use a diffraction method to monitor the dynamics of the induced excitations. To do so, a continuous wave (CW) probing laser is focused in the center of the excited area, as seen Fig. 2-9(b) and (c), and the intensity of the laser signal diffracted from the surface excitation is monitored to determine dynamics of the excitations’ propagation and decay, revealing material thermal transport properties and elastic mechanical properties. Optical heterodyne amplification schemes are implemented to allow for selective monitoring of different (thermal or displacement) dynamics [58,59]. This and similar methods have been used for several decades on a variety of static materials systems to study surface thermal transport [58], elastic mechanical performance [60], thin film properties [61–63], heterostructures [64], and ion-induced radiation damage [65–67], among many others [68–70].

The TGS methodology has several distinct advantages for the use-case under consideration here beyond simply meeting all of the criteria delineated above. Like all ultrasonic techniques, the measured acoustic wave velocities may be reliably related back to fundamental elastic material properties if enough information is provided. However, the 1-D nature of the excitation provides an extremely controllable method by which the penetration depth of the interrogating acoustic wave may be set. As will be discussed further in Chapter 4 and Chapter 7, this length scale may
be tuned to very closely match the thickness of the damaged layer induced by ion irradiation. Matching that scale in general was one of the criteria of interest, but the particular optical implementation used allows the excitation wavelength to be easily selected for a given experiment and in theory may be continuously tuned to achieve any acoustic wavelength desired [71]. Additionally, although changes in complex reflectivity are exploited to determine thermal transport properties, no optical transducer layer is strictly necessary in the TGS methodology. Rather, the method as it will be implemented here relies on direct laser energy absorption in the material under investigation. As the target materials of interest for this work are primarily metallic, this will pose no implementation problems. If, however, TGS were to be used on a transparent or highly absorbing material, a metallic transducer layer similar to that used in TDTR may still be necessary.

Although appearing to meet all of the necessary criteria for an in situ ion irradiation property diagnostic on the surface, several functionalities of the TGS technique must still be demonstrated before it can employed for this purpose. These functionalities may be stated broadly as the need for: theoretical sensitivity to radiation effects, demonstrated sensitivity to high-dose radiation effects, demonstrated time resolution, and demonstrated ability to extract both elastic and thermal parameters simultaneously. Most importantly, as all prior work had focused on static material systems and not those undergoing some dynamic evolution, new optical geometries will need to be designed that allow for dynamic systems to be monitored continuously. This new capability is described in detail in Chapter 5, and each of the other functionalities listed above are described in dedicated chapters as well.
Chapter 3

Bridging the gap to mesoscale property monitoring

In developing transient grating spectroscopy as an in situ ion irradiation diagnostic, the first functionality which needs to be demonstrated is a theoretical sensitivity limit which allows for the detection of radiation-induced defects through changes in material properties. In this chapter, that functionality is demonstrated by measuring the change in surface acoustic wave speed as a function of relative orientation on metallic single crystals and showing that the absolute sensitivity is appropriate for expected radiation-induced changes from the literature. This chapter also shows that properly-scaled classical molecular dynamics (MD) simulations can be used to accurately simulate orientation-based changes in surface acoustic wave speed on single crystal surfaces by comparing with experimental measurements and theoretical predictions. The agreement between theory, simulation, and experiment gives confidence in classical MD as a predictive tool to simulate defect-based changes in elastic properties which cannot yet be fully treated by theory. This ability is of critical importance for the informed use of TGS to measure material property changes induced by radiation damage, which may vary by amounts formerly too small for reliable in situ detection. Finally, the new MD simulation framework is used to study the effect of an imposed vacancy population on the acoustic response of several materials. The results of these studies indicate that TGS experiments are well-suited to the ex situ and in situ study of radiation-induced material property changes. The work presented in this chapter is largely sourced from Dennett et al., Phys. Rev. B 94 (2016) 214106 [72].

3.1 Introduction and background

In radiation materials science, quantities like the Young’s modulus must be reliably determined to hundreds of parts per million (ppm), as radiation-induced defects change elastic properties in well-defined, though small, amounts. Vacancies have been analytically and computationally shown to change elastic moduli on the same order of magnitude as their concentration [73,74]. Interstitial atoms are predicted to have an effect between two [73] and ten [74–76] times as strong. Thermal equilibrium populations of defects are found in levels from $10^{-10}$ to $10^{-4}$ atom fraction for vacancies from room temperature to the melting point, respectively, and at levels thousands of times lower for interstitials. Radiation damage can increase vacancy fractions to a theoretical maximum of one percent during intense irradiation [77]. Direct, ultrasonic measurements of defect effects on elastic moduli have been conducted by several authors [78–80]. Irradiation can also create dislocations, which non-linearly affect the Young’s modulus as compared to a perfectly annealed material [81]. High-dose irradiation may also induce void swelling, which is expected to reduce...
the Young’s modulus by a magnitude on the order of the void volume fraction [82]. In all cases, the ability to resolve changes of 1% and lower in the elastic constants is necessary in a mesoscale measurement technique sensitive to these properties for radiation damage.

TGS is identified here as a promising tool for these direct, mesoscale measurements [65,83]. This technique optically induces and monitors monochromatic surface acoustic waves (SAWs) with micron-scale wavelengths over an area on the order of 100 µm². Characterization of these waves allows direct mesoscale measurement of elastic constants and thermal diffusivity of the material in question. Robust repeatability of these measurements at the necessary sensitivity level is required to accurately analyze irradiation-induced changes to material properties. These material properties can be anisotropic in crystalline materials, such that knowing the precise surface-normal orientation and relative rotation of the crystal face (for single crystals) or grain size and texture (for polycrystals) are critical to the sensitivity of the measurement.

Elastic anisotropy causes the SAW speed to vary as a function of relative orientation on single crystal surfaces. Here, anisotropy is defined for cubic crystals by the Zener anisotropy ratio, A, as

\[ A = \frac{2C_{44}}{C_{11} - C_{12}} \]  

(3.1)

where \( C_{ij} \) are the components of the reduced elastic stiffness tensor in Voigt notation [84]. By rotating the orientation of induced SAWs on single crystal surfaces, one can measure a change in SAW speed. This variation provides a convenient method of validating both the sensitivity of the experimental technique as well as a new simulation framework using molecular dynamics (MD). The ultimate sensitivity test is to select materials with very low anisotropy, like aluminum (\( A = 1.22 \)), resulting in expected changes in SAW speed of fractions of a percent per degree of rotation. Only tungsten (\( A = 1.01 \)) has a lower anisotropy ratio [85]. The speed of measured SAWs, \( c_R \), can be shown to scale as

\[ c_R \propto \sqrt{E} \]  

(3.2)

where \( E \) is an effective elastic modulus for the direction and crystal orientation under investigation [86]. Orientation-based TGS measurements made on single crystal metallic samples can thus serve two purposes. First, they can be used to qualify the TGS technique for the study of fine changes in effective elastic modulus. Second, they can be used to set a lower bound on the systematic sensitivity of the TGS technique. In addition, correctly simulating these orientation-based changes in the acoustic response will validate classical MD on the tens of nanometer scale as a predictive tool for such small changes in effective elastic modulus.

In Chapter 2, TGS was proposed as a methodology for in situ property monitoring during ion beam irradiation. In this chapter, we show that this technique is sensitive to changes in SAW speed on the order of changes expected as a result of irradiation. Classical MD, scaled to an appropriate simulation size, is then shown to be able to predict the linear elastic response of materials by periodically exciting a simulation volume in the same manner as TGS experiments and monitoring the dynamic response. A lower size limit of \( \sim 50 \) nm for MD simulations is shown to retain excellent scaling in SAW speed with experiments. This imparts confidence in the ability of classical MD to predict the response of materials with mesoscale defect populations, such as those due to irradiation, where theory cannot yet describe them. As a proof of concept, the reduction in SAW speed with increasing vacancy fractions, up
Figure 3-1: Schematic of the induced surface excitation in experiment (a) and simulation (b). In experiment, crossed laser pulses create an interference pattern on the sample surface, causing spatially periodic heating and launching SAWs with fixed wavelength, $\Lambda$. A detailed description of the optical arrangement used in experiment can be found in [57]. In simulation, periodic boundary conditions are applied in all dimensions and a small vacuum gap is included within the periodic boundary in $\hat{z}$ to allow for the simulation of free surfaces. Emulation of the laser pulse is accomplished by increasing the temperature of atoms in the simulation periodically in the $\hat{z}$ direction.

$\text{to the theoretical maximum of } X_s = 10^{-2}, \text{ is simulated in single crystal copper and aluminum.}$

### 3.2 Methods

In the following sections, examples of the measurement, simulation, and analysis methods are given for explanation. All raw data files, processing scripts, output datasets, simulation input files, intermediate relaxed atom files, final atomic configurations, compiled/processed data files, and the code used to generate the slowness surfaces with input parameters are hosted permanently on a GitHub repository for the manuscript where this work was originally published [87].

#### 3.2.1 Experiment

Experimental TGS measurements are carried out on aluminum (Al) and copper (Cu) single crystals with \{001\} and \{111\} surface orientations purchased from the MTI Corporation. Aluminum samples are $>99.99\%$ pure, mechanically polished to $<10$ nm surface roughness, and have surface orientations within $\pm 2^\circ$ of the given index. Copper samples are $>99.99\%$ pure, mechanically polished to $<3$ nm surface roughness, and have surface orientations within $\pm 2^\circ$ of the given index. An \{001\} oriented sample of $99.99\%$ pure tungsten (W) with $\pm 0.1^\circ$ misorientation was used as a calibration standard for all measurements.

The photoacoustic excitation and detection process used in TGS proceeds as follows. Two excitation (pump) laser pulses are crossed at an angle $\theta$ at the surface of the sample under interrogation. These crossed beams project a spatially periodic intensity pattern, causing local, periodic thermal expansion with a fixed wavelength $\Lambda$. This thermal excitation launches monochromatic, counter-propagating acoustic waves with wavelength $\Lambda$. A schematic of this excitation process is shown in Fig. 3-1. These acoustic waves may take on several characters depending on the elastic constants, density, and layered structure (in the case of film-substrate systems) of the sample being measured [83]. For samples of thickness $d_{\text{sample}} \gg \Lambda$, the excited acoustic waves may take on two possible characters, either surface acoustic waves (SAWs) or pseudo-surface acoustic waves (PSAWs). SAW propagation is modeled as the
superposition of the three evanescent partial waves whose amplitude decays to zero at infinite depth into the sample. In contrast, PSAWs are comprised of two evanescent partial waves with a small bulk wave component which radiates energy away into the bulk of the sample [88]. Both SAW and PSAW character excitations are observed in this work. TGS measurements for these experiments are carried out using a passively Q-switched, 532 nm, solid-state laser with a pulse length of 300 ps, repetition rate of 1 kHz, spot size of 90 µm and pulse energy at the sample surface of 2.15 µJ for Al samples and 1.75 µJ for Cu samples. Pumping power was reduced for Cu samples to avoid oxidizing the sample surface.

Detection of the induced acoustic waves is accomplished using an optical heterodyne detection technique [57]. In brief, a quasi-continuous wave probe laser is diffracted from the thermally induced displacement and refractive index variation on the sample surface [58]. This diffracted probe signal is heterodyne mixed with a spatially-coincident reference beam and directed into a fast silicon avalanche photodetector with a 3dB bandwidth of 1.0 GHz. The probe used in this experiment is a 785 nm, CW diode laser modulated to a repetition rate of 1 kHz with a 20% duty cycle, a power at the sample surface of 3.36 mW, and a spot size of 150 µm. A more detailed description of an equivalent experimental setup can be found in [58]. The voltage output from the photodetector is recorded using a 5 GHz (20 GS/sec) bandwidth digital oscilloscope. Optical heterodyne detection increases the amplitude of the recorded traces by controlling the relative phase difference between probe and reference beams. For each measurement, two signals with a 180° heterodyne phase offset are recorded and subtracted from each other in the analysis process. This allows for an increased signal-to-noise ratio and also allows for the removal of any long-timescale detector response in the analyzed trace. A filtered power spectral density of these signals is taken and a peak-finding algorithm is used to determine the frequency of the dominant acoustic modes, \( f_{\text{TG}} \), of each measurement [87]. A characteristic measured trace and its corresponding power spectrum can be seen in Fig. 3-2. The initial spike in signal amplitude corresponds to thermal impulse of the pulsed excitation. SAW oscillations are imposed over the background of the non-exponential decay of this thermal spike, which is fitted and subtracted before the power spectrum of the trace is calculated [89].
Angular-dependent measurements are taken using a manual rotation stage with 2° gradations as a sample mount. All rotation measurements are carried out in air at ambient conditions using a nominal wavelength of $\Lambda = 4.80$ µm. As the actual projected transient grating spacing on the sample surface is a sensitive function of optical component placement [71], calibration measurements of the projected grating are taken before each measurement of interest. For calibration, a single crystal of {001} oriented W is measured. Since W is the least elastically-anisotropic pure metal, with an expected variation in SAW velocity on the surface of 0.1%, we use the experimentally-determined SAW frequency, $f_W$, and a reference SAW speed on the {001} surface of W of $c_W = 2665.9$ m/s to calculate the projected grating spacing for each measurement as

$$\Lambda = \frac{c_W}{f_W} \quad (3.3)$$

The calculation of the speed $c_W$ was carried out using an isotropic approximation [86] with elastic constants aggregated from [90–92]. Using the value for the calibrated grating spacing, the acoustic wave velocity corresponding to peaks in the power spectrum can be calculated as $c_{TG} = \Lambda f_{TG}$.

Four single crystal metallic samples are used in this study: {001} and {111} oriented Al and {001} and {111} oriented Cu. For each sample under investigation data are collected by manually rotating the sample face in 5° increments relative to the orientation of the induced SAW, as the absolute orientation of the SAW is fixed by the optical arrangement. The collection time for each measurement, averaging the response of 60000 laser pulses, is approximately five minutes. This time scale is primarily set by the necessity of manually changing the heterodyne phase once per measurement to be able to carry out background subtraction and signal amplification during processing.

### 3.2.2 Simulation

Molecular dynamics simulations using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) framework are used to emulate the SAW response that is observed in TGS experiments [93]. Simulations are carried out on volumes with dimensions $L_x \times L_y \times L_z$, where the $\hat{x}$ axis is oriented along the direction of wave propagation and the $\hat{z}$ axis is along the incident direction of laser pulse. To mimic the TGS experiment, we apply periodic boundary conditions in the directions of $\hat{x}$ and $\hat{y}$, whereas the top and bottom of the sample in $\hat{z}$ are free surfaces. The free surface is generated by making the thickness of the simulated layer, $L_z$, slightly smaller than the periodic boundary in $\hat{z}$, creating a vacuum boundary of 5–6 nm between periodic cells in that dimension. In this case, the dimension $L_x$ sets the length scale in the same manner as the experimental transient grating wavelength $\Lambda$. The imposed MD boundary conditions and the relation of the simulation excitation scheme to the experimental case can be seen in Fig. 3-1. The wavelength effects on acoustic wave speed were studied by changing the sample length $L_x$ and will be discussed in detail in Section 3.3.3. Single crystals of Al and Cu with surface orientations {001} and {111} are investigated by rotating the simulation cell such that the appropriate crystal face appears normal to the surface. Embedded atom method (EAM) type interatomic potentials are employed for Al [94] and Cu [95], both of which are tuned using ultrasonically measured elastic constants. These EAM potentials have been shown to accurately describe elastic and thermal properties of these materials, though the elastic constants for the Al potential differ more from experimental values at room temperature than those for the Cu potential.

Before laser energy is imparted into the simulation, the system is relaxed at zero pressure for 20 ps in the NPT
ensemble (constant number of atoms, pressure, and temperature) and then for another 20 ps in the NVT ensemble (constant number of atoms, volume, and temperature). The Nosé-Hoover thermostat is used in time integration and the time step is set to be 2 fs. This twice-relaxed lattice is used as the input for the laser-induced surface wave simulation, which is performed in the NVE (constant number of atoms, volume, and energy) ensemble.

The laser heating process is modeled using the Langevin thermostat by scaling the temperature of atoms as

$$T(x, z, t) = \begin{cases} 
T_0 + \delta T \left( \frac{2}{t_0} \right) \exp \left( \frac{z}{z_0} \right), & |x| \leq x_0 \\
T_0, & |x| > x_0 
\end{cases}$$  

(3.4)

where $t_0$ is the laser pulse duration, $T_0$ is the initial simulation temperature (at $t = 0$), taken as 300 K, $\delta T$ is the maximum temperature increase at the end of the laser pulse (time $t_0$) and the sample surface, $z$ is the depth into the material, $z_0$ is the electron conduction depth (here taken as 7.5 nm [96–98]), $x$ is the distance along the wave propagation direction, and $x_0$ is the half-width of the excitation pulse. For all simulations with $L_z > 15$ nm, the laser pulse, incident on the sample surface in the $\hat{z}$ direction, has a fixed width of 15 nm such that $x_0 = 7.5$ nm. For simulations with $L_z < 15$ nm, the pulse has a width of $L_z/2$ such that $x_0 = L_z/4$. Simulations with a Gaussian applied temperature profile in the $\hat{x}$ dimension were also tested on the Cu simulations, but the resulting acoustic spectrum was unchanged from the uniform profile described above. After the heating process is complete, the simulation is allowed to relax in the NVE ensemble.

The oscillations of the induced acoustic waves are recorded by tracking the $\hat{z}$ position of the center of mass of two small patches of atoms on the free surface of the simulation, one at the center of simulation volume and one located along the periodic boundary, $L_z/2$ away in the $\hat{x}$ direction from the first patch. The acoustic oscillations of interest, those with periodicity $L_z$, are $180^\circ$ out of phase between these two patches of atoms. By subtracting the $\hat{z}$ center of mass position of the second patch from the first, a representative trace can be generated from simulations which is equivalent to the photodetector signal recorded in experiment. The power spectrum of this trace can similarly be used to isolate the excited acoustic modes using processing identical to that used for experimental data. A representative trace from a simulation is shown in Fig. 3-2(b) along with the associated power spectrum as a comparison to the trace collected in an experiment.

Unlike experiments, for simulations $d_{\text{sample}} \sim \Lambda$ and as a consequence it is possible that the primary acoustic oscillation may not be at the same velocity as the SAWs observed in experiment. In this thin film regime the lowest order symmetric and anti-symmetric Lamb modes have not yet collapsed to the Rayleigh wave velocity at which we expect to observe SAW oscillations in “bulk” experimental samples, see Figure 11 in [83]. Therefore, a series of simulations are conducted to determine an appropriate simulation thickness, $L_z$, such that the Lamb modes have collapsed and the simulated SAW speed no longer varies as a function of thickness. These simulations show that the SAW and PSAW speeds do not vary once $L_z > 1.5 L_z$. Therefore, all the results presented in this work are obtained by setting sample thickness $L_z = 2L_z$, such that the simulation is thick enough to capture the SAW response while maintaining a small simulation volume to minimize computation time.
Table 3.1: Reference values of reduced elastic constants and Zener anisotropy ratio, $A$, used in analytic calculation of acoustic wave speeds as well as the values given from the atomic potentials used for MD simulations at 325K for Al and 300K for Cu. Elastic constant values are given in GPa.

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (ref.) [85]</td>
<td>107.3</td>
<td>60.9</td>
<td>28.3</td>
<td>1.22</td>
</tr>
<tr>
<td>Cu (ref.) [99]</td>
<td>168.4</td>
<td>121.4</td>
<td>75.4</td>
<td>3.23</td>
</tr>
<tr>
<td>Al (MD) [94]</td>
<td>107.7</td>
<td>57.9</td>
<td>26.2</td>
<td>1.05</td>
</tr>
<tr>
<td>Cu (MD) [95]</td>
<td>169.9</td>
<td>122.6</td>
<td>76.2</td>
<td>3.23</td>
</tr>
</tbody>
</table>

3.2.3 Analytical SAW velocity calculation

The expected velocity of acoustic waves excited in TGS experiments can be calculated by considering the elastic wave equation

$$\rho \frac{\partial^2 u_j}{\partial t^2} = C_{ijkl} \frac{\partial^2 u_k}{\partial x_i \partial x_j},$$  \( (3.5) \)

where $u_i$ are the components of the displacement vector, $x_i$ are the Cartesian axes, and $C_{ijkl}$ is the elastic stiffness tensor of the material in question. Solutions to this equation are sought in the form of plane waves

$$u_i = U_i \exp \left[ i (k \cdot x - \omega t) \right],$$  \( (3.6) \)

where $U_i$ are the components of the polarization vector, $k$ is the wave vector (with direction parallel to the wave normal), and $\omega$ is the angular frequency [36]. A useful method for exploring surface wave phenomena obeying this set of wave propagation equations is the Fourier-domain surface dynamic Green’s function $G_{ij}(k_\parallel, \omega)$ [88]. This function describes the $i^{th}$ component of the displacement response of a surface to a force acting in the $j$ direction as a function of the wave vector on the surface of the material, $k_\parallel$, and the temporal frequency $\omega$.

To a good approximation, measurements made using TGS are sensitive to displacements normal to the surface of a semi-infinite half-space induced by a forcing function normal to the surface. As the excitation depth of acoustic waves in the TGS experiment is approximated by the acoustic wavelength, $\Lambda$, this semi-infinite approximation is appropriate as long as the thickness of the sample is much greater than $\Lambda$. To calculate the acoustic wave speeds expected in an experiment, we consider an infinite half-space normal to $x_3$ occupying the domain $x_3 > 0$. By considering a force acting normal to this surface, the Green’s function $G_{33}(k_\parallel, \omega)$ can be calculated, as detailed in [88]. Allowed surface wave modes appear as poles in $G_{33}$ and can be visualized by plotting intensity maps of $\Im[G_{33}]$ as a function of the acoustic slowness (or inverse velocity), $s_\parallel = k_\parallel / \omega$. These “slowness surface” calculations can be carried out for materials of arbitrary crystal symmetry and surface orientation by proscribing the appropriate values for $C_{ijkl}$ and rotating the stiffness tensor such that the desired face is normal to $x_3$. All calculations of $\Im[G_{33}]$ presented in this work are conducted using an algorithm detailed in [88].

3.3 Results

Results from both TGS experiments and simulations on Al and Cu are presented in Fig. 3-3, overlaid on the slowness surfaces calculated with the reference elastic constant values in Table 3.1 for each of the four material and orientation
3.3.1 Theoretical predictions

In intensity plots of $\Im \left[ G_{33} \right]$ the poles corresponding to the Rayleigh-character SAWs appear as thin, dark lines bounding the bulk of the slowness surface. For very anisotropic materials such as Cu there are certain directions on certain crystal planes at which the polarization of the SAW can change from out-of-plane (along $x_3$), to in-plane (along $x_1$ and $x_2$). In these cases, the response is not captured in $G_{33}(k_3, \omega)$. This can be seen in the right of Fig. 3-3 on the $\{001\}$ surface near the $\langle 110 \rangle$ direction as the intensity of the SAW fades. PSAWs appear on these surfaces as similar dark bands, but at smaller values of slowness, and therefore higher speed, than the SAW excitations. The remainder (lighter gray areas) of these surfaces represent bulk acoustic modes captured in $G_{33}(k_3, \omega)$, but not excited in the TGS experiments.

3.3.2 Experimental results

The range of experimental data collection for each sample is chosen to match the periodicity of the expected acoustic response, namely over a range of 90° for $\{001\}$ oriented samples and 60° for $\{111\}$ oriented samples. Measured SAW speeds are inverted and projected along their relative directions to be plotted on the slowness surface such that each
data point has coordinates given by

\[(s_1, s_2) = \frac{1}{cT_G} \left(\sin \varphi, \cos \varphi\right),\]

(3.7)

where \(\varphi\) is the relative orientation of the induced acoustic wave vector on the sample surface. As the surface directions of the crystals is not known \textit{a priori}, the data presented in Fig. 3-3 includes an arbitrary phase shift with respect to the \(\langle 100 \rangle\) or \(\langle 1\overline{1}0 \rangle\) directions such that the maxima and minima of each data set are aligned with the correct position on the slowness surface.

The relative error in each SAW speed measurement, inclusive of that incurred by determining the grating spacing, \(\Lambda\), with a tungsten calibration sample and of the finite width of the peaks in the TGS power spectra, is on the order of 0.1% based on measured values. This order holds true for all experimental measurements taken as part of this study on both Al and Cu. The error incurred due to finite width peaks is taken as the 95% confidence interval on the value of the peak location parameter for each peak in a TGS power spectrum. The width of these peaks is consistently on the order of 15 MHz. The error bars on each measurement are not included in Fig. 3-3 as they are virtually indistinguishable given the marker size on the plot. The order of magnitude of the relative error makes the 1-2% change in SAW speed along different directions on the Al crystals easily distinguishable in the experimental measurements.

The small deviation in the absolute measured values from the values predicted using \(\mathbb{M}[G_{33}]\), for example along \(\langle 11\overline{2} \rangle\{111\}\) in Cu, is expected given the sensitivity of the calculation to the particular reference values chosen for the elastic constants. However, the expected periodicity is matched in experiment in all cases presented. Even for the case where the absolute agreement appears the worst, on the \(\{111\}\) surface of Cu, the ratio of the maximum measured SAW speed (along \(\langle 11\overline{2} \rangle\)) to the minimum measured SAW speed (along \(\langle 1\overline{1}0 \rangle\)) is 1.2171 where the values from the reference calculation give a ratio of 1.2178, giving a worst-case experimental error of 575 ppm. Given the level of agreement between calculated and measured slowness values, these experiments are clearly an accurate reflection of the physical properties of the single crystals under investigation.

### 3.3.3 Simulation results: pure materials

In addition to the convergence study used to determine the minimum appropriate value of \(L_z\), a set of simulations is carried out varying \(L_x\) to determine the minimum acoustic wavelength necessary to accurately capture the experimental SAW response. These simulations are oriented along the \(\langle 100 \rangle\{001\}\) and \(\langle 110 \rangle\{001\}\) directions using the aforementioned EAM Al potential. Fig. 3-4 shows simulated and measured SAW speeds for the \(\langle 100 \rangle\{001\}\) direction over several orders of magnitude in excitation wavelength. Simulations are run with wavelengths ranging from 2.4 nm to 203 nm; experimental measurements using \(\Lambda\) from 2.05 to 4.82 \(\mu\)m are included as a reference and illustrate the excellent scaling behavior of the simulations. As is clear from Fig. 3-4, at very small \(L_x\) the continuum elasticity approximation that is used to calculate SAW speeds breaks down. This approximation is valid for the mesoscale excitations that are being induced in experiment, but surface phonon dispersion effects become apparent in small simulations [100]. In the range of \(L_x = 40 – 100\) nm, simulations have a small and fairly consistent deviation from the calculated SAW speed in that direction. Therefore, for all other simulations besides those on \(\{001\}\) Al, a target wavelength of 40-50 nm is chosen for expedited computation time without sacrificing accuracy.

For both Al and Cu, the following crystal orientation and directions are simulated: \(\langle 100 \rangle\{001\}\), \(\langle 110 \rangle\{001\}\), \(\langle 1\overline{1}0 \rangle\{111\}\),
Figure 3-4: Dependence of the measured SAW velocity in experiment (blue squares) and simulation (open red circles) on wavelength for SAWs induced along the ⟨100⟩ direction on {001} crystals of aluminum. The analytically predicted SAW speed for this orientation and direction, 2941.2 m/s, is plotted as the dashed line. At very small wavelengths there is a significant deviation between the predicted and simulated SAW speeds.

As is apparent from Fig. 3-3, the simulated TGS response agrees very well with the calculated and measured SAW and PSAW speeds for the {001} orientations of both Al and Cu. The additional ⟨120⟩ direction on the Cu surface shows that not only are the magnitudes of the responses close to the expected values, but also the simulations are able to capture the dynamic response on intermediate crystal directions. It is noteworthy that this intermediate behavior is captured accurately even along a direction at which the polarization of the SAW has almost undergone the transition from normal-to-the-surface to parallel-to-the-surface and both SAW and PSAW modes are identifiable in the response.

As Fig. 3-3 also shows, the simulated responses match less well on the {111} surfaces on both materials. The mismatch, which over-predicts SAW speeds on Cu and under-predicts SAW speeds on Al and the PSAW speed on Cu, is likely a result of the potentials used in the MD simulation failing to capture an accurate elastic response on a non-cubic crystal plane. To explore this mismatch further, the set of reduced elastic constants given by the validated MD potentials, as listed in Table 3.1, is used as an input into the calculation of 3\{G_{33}\}. If the set of constants given by these potentials produce SAW and PSAW speeds significantly different from those given by our reference set of constants, it is possible that the TGS simulations are accurately representing the dynamics governed by the MD potentials while disagreeing with experiment and reference calculations. Although the constants given by the Cu potential closely match those of the reference set, the $C_{ij}$ values for the Al potential differ noticeably.
Table 3.2: Calculations and simulations of acoustic wave speed for {001} and {111} orientations on Al and Cu. Speeds from calculations using the reference values for elastic constants (‘ref.’), using the values of elastic constants from MD potentials (‘MD calc.’), and from MD transient grating simulations (‘MD sim.’) are all given in m/s. The ‘% Diff.’ column for each material is the deviation of the ‘MD calc.’ value from the reference value.

Most importantly for the surface direction variation in the acoustic response, the Zener anisotropy ratio for the Al potential ($A = 1.05$) is significantly different from the reference case ($A = 1.22$).

Table 3.2 shows the calculated SAW and PSAW speeds for the primary directions of both orientations and types of crystal investigated using both the reference constants, labeled ‘ref.’, the constants given by the potentials from [94] and [95], labeled ‘MD calc.’, as well as the percent difference of the MD calc. value from the reference value. Additionally, the results found by running the TGS simulation process are listed as ‘MD sim.’ As expected given the values in Table 3.1, the acoustic speeds calculated from the Al potential differ more significantly from the reference case than those for Cu. The values for acoustic wave speeds from calculations using the MD potential elastic constants are, in all cases, closer to the calculated values using the reference constants than the results of the TGS simulations.

3.3.4 Simulation results: materials with defects

Finally, a series of MD simulations along the ⟨100⟩{001} direction in both Al and Cu is carried out with an imposed vacancy fraction $X_v$ ranging from $10^{-4}$ to $10^{-2}$ with initial size $L_x = 42.7$ nm for Al and 47.5 nm for Cu. Simulations of this nature are the first real attempt at validating this type of approach, as it is not possible to make reference calculations of the acoustic response for materials whose elastic constants are not known a priori. The construction process for these simulations proceeds as follows:

- An initial volume of atoms is created with the specified wavelength and orientation.
- A number of atoms necessary to give the desired value of $X_v$ are randomly deleted from the lattice.
- The simulation is allowed to relax at zero pressure in the NPT ensemble.
- The relaxed value of $L_x$, smaller than the initialized value, is recorded.
- The heating and relaxation process proceeds as normal.

Recording the value $L_x$ after $X_v$ is imposed and the lattice relaxed is necessary to accurately calculate the resultant SAW speed from the simulation’s power spectrum. The ⟨100⟩{001} direction is chosen for these simulations because simulations in this direction closely matched both reference calculations and experiments for Cu and Al in perfect crystals. Fig. 3-5 shows the relative change in SAW speed compared to the perfect crystal baseline, as reported in Table 3.2, for both of these cases. For each point on this plot, eight to ten simulations were carried out with different
random configurations of defects, and the speed for each was calculated using the wavelength of the defect-relaxed lattice. The error bars represent one standard deviation between the simulation sets for each $X_v$. An overall reduction in SAW speed as $X_v$ increases is clear for the Cu case, although no statistically significant trend is evident for Al.

### 3.4 Discussion and implications

There are two primary implications of the work presented in this chapter. The major takeaway from the experimental results is that sub-percent relative changes in acoustic wave speed are readily and repeatably detectable using the TGS experiment in its current implementation. Given the scaling in Eq. (3.2), detecting sub-percent changes in the effective elastic modulus is possible. The test problem considered here, the effect of single crystal anisotropy on SAW speed in different directions, is a well-validated physical phenomenon. These benchmark measurements show that TGS can be confidently used as methodology for detecting small changes in elastic properties as a response to different stimuli. In particular, the level of sensitivity shown here (0.1% absolute, < 575ppm relative) is well within the bounds necessary to detect irradiation-induced material responses, such as volumetric void swelling. The detection of drastically increased point defect populations in irradiated materials should also be experimentally possible, and future work will be focused on disentangling the effects of different types of defects on the TGS response.

However, TGS experiments on materials with elevated defect populations cannot be intelligently designed without some tool to predict the variation in response with defect concentration and character. Since the elastic properties of materials with arbitrary, spatially varying, defect populations are not known, the analytical framework appropriate for calculating the acoustic response of pure materials is not an appropriate predictive tool for this use. Therefore, the second major implication of this work is that classical MD can be used to simulate an excitation and detection process very closely resembling experiments. Simulations have been shown to most appropriately capture the dynamics of mesoscale experiment using excitation wavelengths of $L_x \sim 50$ nm with a thickness normal to the surface of $L_z = 2L_x$. 

![Figure 3-5: MD Simulated SAW speed along the (100)(001) direction in Al (red) and Cu (blue), $c$, normalized to the perfect lattice speed, $c_0$, as a function of vacancy fraction, $X_v$, for each material.](image-url)
Simulations with arbitrary crystal orientation and direction can be created and inserted into a general TGS excitation framework, whose parameters have been optimized to provide the most accurate dynamic acoustic response possible with standard EAM potentials.

Throughout this work, the standard MD potentials for Al and Cu have been taken as a given. It is clear that the acoustic response is captured less well on {111} oriented crystals than on {001} oriented crystals and less well for Al than Cu. This, however, is not a failing of the methodology, but rather a weakness of the potentials themselves. We are using these potentials, which have been validated on small-scale parameters such as atomic volume and phonon dispersion, to capture a much larger dynamic process. It is not unexpected, then, that there is some variation between calculated and experimentally measured acoustic responses and those we are able to simulate. It is remarkable, in fact, that mesoscale and even continuum dynamic processes are so well captured by these potentials. One possibility moving forward, given the flexibility of the TGS simulation framework, is to use simulations of these dynamic responses as an additional validation tool for new interatomic potentials, particularly because the TGS process captures more of the non-linear predictions of potentials than simple checks of lattice parameter or elastic constants.

Table 3.2 shows that using elastic constants calculated using the classical MD potentials as inputs in the calculation of $G_{33}$ provides values for SAW and PSAW speeds closer to those calculated from reference constants. This same procedure could be used with uniform defect populations, such as those used in this study, to predict the change in SAW speed with defect concentration. However, the larger-scale excitation technique that is detailed in this work has the advantage of being able to accommodate spatially varying defect populations. The ability to simulate the TGS response of materials with a spatial distribution of defects similar to that induced from radiation damage, both from micro-heterogeneity as well as macro-heterogeneity specific to ion irradiation, will be necessary to use this methodology as a predictive tool moving forward.

The effects of increasing vacancy concentration in simulations gives the first insight into the magnitude of the change in SAW speed that should be expected under irradiation. For these simulations a crystal orientation and direction whose response agrees well with the predicted response for perfect materials is used. In Cu, the reduction in speed is about 3% for a 1% vacancy concentration. However, for Al, the reduction is only about 0.5%. In the limit of small changes in elastic moduli, the scaling in Eq. (3.2), indicates that the change in SAW speed should scale as $\Delta c_R/c_R \approx \Delta E/2E$. Using this simple scaling with previous ultrasonically measured stiffness changes, the expected change in $c_R$ for $X_v = 0.01$ for Cu is 3.5% and for Al is 0.75% [79,80]. Both previous experiments and the new MD simulations show reductions consistent with theory and are within sensitivity limits of experimental TGS detection [74]. In an effort to simulate TGS responses representative of heterogeneous irradiation-induced defect populations, future work includes using MD to simulate damage cascades in materials, evolving these damaged structures using either cluster dynamics or kinetic Monte Carlo methods, and finally simulating the TGS response with the MD methodology described in this work [101–103].

### 3.5 Conclusions

Given the overall sensitivity of transient grating experimental measurements and the ability to simulate the TGS excitation and response using classical MD, this technique is well-poised to be utilized as a mesoscale technique for
identifying radiation-induced changes in material properties. However, much work remains to be able to confidently deconvolve the integral effects of the variety of defects expected as a result of radiation damage. To most robustly validate the technique, initial testing on radiation-affected materials should focus combinations of materials and exposure environments where a single microstructural effect dominates the expected change in properties. In these cases, such as volumetric void swelling in pure metals, multiple effects will likely not need to be deconvolved. Indeed, this case in particular will be addressed next in Chapter 4 as the first demonstration of high-dose radiation effects measured using TGS. The simulation approach detailed here allows the effect of arbitrary defect populations on the dynamic acoustic response to be quantified. This will be an invaluable predictive tool for guiding future TGS experiments on materials with isolated types of defect populations as well as irradiated materials. The work presented in this chapter fulfills the first functionality necessary for this methodology to be successfully implemented as an in situ ion irradiation property diagnostic.
Chapter 4

Detecting self-ion induced void swelling in pure copper

In developing transient grating spectroscopy (TGS) as an in situ irradiation diagnostic, the capability to measure the effects of high-dose irradiation exposure must be demonstrated explicitly prior to the implementation of a true in situ facility. In this chapter, that capability is demonstrated using irradiation-induced void swelling as the target degradation mode of interest. This mode is a particularly useful test-case as it may be induced in simple, pure metallic systems where no effects of chemical segregation or precipitation will be observed under irradiation. Ideally, this simplicity in test material system, along with the extreme volumetric effect which may be induced, will allow for a relatively simple connection to be made between the TGS-observed property changes and microstructure evolution. Here, single crystal copper is chosen as the test system of interest and exposed to high-energy self ions at temperatures close to half of its melting point with the goal of inducing large amounts of void swelling. Property changes resulting from this swelling are detected and measured via changes in surface acoustic wave (SAW) velocities as measured by TGS. Scanning transmission electron microscopy (STEM) links the TGS-observed changes with void swelling-induced microstructural changes. The results of this chapter prove conclusively that TGS has the functionality to detect changes in material properties and microstructure resultant from high-dose irradiation. The work presented in this chapter is primarily sourced from Dennett et al., Acta Mater. 145 (2018) 496–503 [67].

4.1 Introduction

Since its discovery [104], the phenomenon of irradiation-induced void swelling has created numerous problems for both light water reactor (LWR) [105–108] and fast reactor [109–111] operation due to sudden degradation of material properties. Void swelling often requires an incubation period to initiate; materials can spend months or years in reactor operation in a transient regime experiencing little to no swelling before breaking away into rapid steady-state swelling [2]. When designing materials for advanced nuclear systems, it is imperative to be able to both predict this “breakaway dose” to steady-state swelling and develop alloys whose breakaway dose is higher and higher.

However, void swelling is an inherently multiscale phenomenon [112], whose origins span orders of magnitude in length and time [2]. Analytical and computational predictive abilities are rare and advanced codes capable of predicting reactor-relevant conditions have been documented only recently [113–115]. The strong dependencies of breakaway dose on irradiation temperature [116], dose rate [117], helium production or inert gas presence [118,119], prior cold
work [120], and minor alloying elements [121] make it very difficult to predict this transition point in new, otherwise fully characterized alloys. Experimental campaigns to determine this breakaway dose for advanced alloys all require considerable time to irradiate each specimen to one dose at one set of conditions and confirm the presence and distribution of voids using transmission electron microscopy (TEM) [16,122].

Given the difficulties of robustly characterizing the swelling behavior of new materials proposed for lifetime service, the ability to detect this degradation mode will have high impact despite its classification here as a simplified test problem. If a method to detect the onset of void swelling \textit{in situ}, during irradiation were to exist, the time to qualify the swelling resistance of new alloys could be reduced from years to months or even weeks. The ability to watch void nucleation in real time has been demonstrated under electron irradiation during \textit{in situ} TEM experiments [123]. Post-irradiation, traditional contact ultrasonics [124] and advanced non-linear ultrasound techniques [125] have also been used to detect void swelling and other types of radiation-induced microstructure evolution in neutron-irradiated materials. Broadband laser-based resonant ultrasonics have been used to study \textit{in situ} changes in microstructure during the recrystallization of copper, but have not been applied \textit{in situ} during radiation exposure [126]. A mesoscale technique to detect the onset of void swelling during exposure does not yet exist, leaving a gap between nanoscale \textit{in situ} studies and engineering-scale post-irradiated examination.

In this chapter, TGS is used to measure the effect of void swelling through changes in elastic properties in pure, single crystal copper. Although TGS has been used previously to study low-dose effects of ion irradiation in tungsten [65, 66,127], its functionality has yet to be demonstrated on materials with large, radiation-induced defect clusters. In the high-dose study presented here, both the elastic constants and the anisotropy of single crystal copper are found to change as a function of dose. Single crystal copper is chosen for this investigation as it has been shown to readily undergo void swelling under high-temperature self-ion irradiation [128]. Low-dose defect saturation [26] is observed to stiffen the elastic response due to dislocation segment pinning [81,129,130], while at high doses the density and elastic moduli are reduced due to void swelling [82]. Although the ability of TGS to detect void swelling is demonstrated here in the simplest possible case, a pure metallic single crystal, other work using similar acoustic techniques on polycrystalline materials [65,127,131] and iron-based alloys [132] provides confidence that the methodology applied here is readily extendable to more complex materials. The ability of TGS to identify the onset of void swelling \textit{in situ}, during ion irradiation, is proposed based on these results as a way to rapidly screen new materials for resistance to void swelling.

4.2 Experimental methods

Specimens of \{111\} oriented single crystal Cu exposed for this study were purchased from the MTI Corporation. These samples are >99.999% pure, mechanically polished to <3 nm surface roughness, and have surface orientations within $2^\circ$ of the given index. The parameters used for the ion beam irradiations were chosen with the goal of inducing volumetric void swelling. Prior neutron irradiation work on pure copper indicates that at the higher dose rates achieved with self-ion irradiation, significant void swelling should occur at $T = 400^\circ$C (or $T/T_{\text{melt}} = 0.5$) [133]. As TGS relies on a fixed-wavelength surface excitation, only a finite depth into the material will be probed. This penetration depth scales with the wavelength of the imposed excitation, which can be selected in the range of single to tens of microns. Using SRIM calculations to determine ion penetration depths [134], an incident self-ion energy
Table 4.1: Parameters used for copper self-ion irradiation. In practice, the beam current does not remain constant throughout an exposure and ion source depletion was noted during this campaign.

Table 4.2: Self-ion exposure levels for each sample. Stated dose rates are averaged over the length of each exposure.
However, to make any determination of elastic performance, some measure of the change in material density is necessary since the measured surface acoustic wave speed, \(c_R\), scales as

\[
c_R \propto \sqrt{\frac{E'}{\rho}},
\]

where \(E'\) is a directionally-dependent elastic constant and \(\rho\) is the material density [86,137]. Given that both the density and elastic moduli are expected to be reduced as a material swells, it is not immediately intuitive whether the TGS-measured acoustic wave velocity should increase or decrease as a function of volumetric swelling. In the limit of isotropic elasticity and considering matrix porosity distributed in randomly sized spherical pores, Hassleman and Fulrath show that the Young’s modulus should depend on fractional porosity, \(P\), as

\[
E = E_0 (1 - \gamma P)
\]

\[
\gamma = \frac{3(9 + 5\nu_0)(1 - \nu_0)}{2(7 - 5\nu_0)}
\]

(4.2)

where \(E_0\) is the porosity-free Young’s modulus, and \(\nu_0\) is the porosity-free Poisson’s ratio [138]. For copper, and most metals, the value of \(\gamma\) is about 2. Using the wave velocity scaling in Eq. (4.1) and the decrement in density due to porosity, the wave speed of a material with a given amount of porosity normalized by the porosity-free wave speed, \(c_0\), scales as

\[
\frac{c}{c_0} \propto \sqrt{\frac{1 - \gamma P}{P + 1}}.
\]

(4.3)

Notably, for \(P \in [0, 1]\), this function decreases monotonically. This indicates that for increasing levels of induced porosity due to volumetric void swelling, the measured acoustic wave speeds should decrease.

Following TGS measurements, TEM samples are lifted from the center of the ion-irradiated region using a focused ion beam (FEI Helios Nanolab 6000) with a 30 keV Ga\(^+\) ion milling process and a Pt protection layer. Prepared TEM sample thicknesses range from 150–220 nm as measured using electron imaging following liftout. Microstructural changes resultant from the ion beam exposure are imaged using high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) with a beam energy of 200 keV (JEOL 2010F). STEM images are captured using a probe size of 0.2 nm and a camera length of 15 cm. HAADF imaging is chosen to best identify and quantify void size and density at the expense of viewing smaller vacancy clusters such dislocation loops and stacking fault tetrahedra (SFTs).

Calculations of the induced void swelling versus depth are conducted using image analysis on STEM micrographs using two methods: simple areal void fraction and volumetric swelling. For both calculations, images are contrast adjusted and a binary threshold level manually set using ImageJ [139]. Area porosity is calculated by identifying particles whose linear dimensions are both larger than a single pixel in 600 nm bins from the surface of the material to a depth of 6 \(\mu\)m. Areas thresholded to appear as voids with any single-pixel dimension are rejected as image artifacts from the counting process. Large voids, several hundreds of nanometers in diameter, are observed in the most highly irradiated specimens, necessitating the large bin width. The area of the analysis region varies from 16–34 \(\mu\)m\(^2\) and is chosen to be as large as possible for each image based on its quality. To calculate volumetric swelling due to voids
Figure 4-1: Variation in SAW speed as a function of relative angle on the \{111\} single crystal surface for all exposure levels. The two primary surface directions, \langle 11\bar{2} \rangle and \langle 1\bar{1}0 \rangle, are indicated. The largest changes are observed along the \langle 11\bar{2} \rangle direction. Error bars are not shown as they are approximately the size of the markers; the average error for a single measurement is 0.16% and the maximum of any point shown is 0.32%.

only, a spherical, isotropic approximation of the form

\[
\frac{\Delta V}{V} = \frac{2}{\pi} \sum_i d_i^3 - \frac{2}{\pi} \sum_i d_i^3,
\]

(4.4)

is used, where \(d_i = 2(A_i/\pi)^{1/2}\) is the diameter of each of the identified voids where \(A_i\) is the area of each void identified by image analysis, \(A\) is the image area being analyzed, \(\delta\) is the thickness of the TEM lamella, and the sum runs over all voids identified in the specified image area [140,141]. Although other authors have preferred to use the second method, we chose here to calculate the simple areal fraction as well due to the presence of large, faceted voids at high dose. The results of these two methods are compared and found to give comparable results for the most highly-exposed samples.

All raw TGS data, raw and processed images, image analysis parameters, SRIM calculations, and TGS processing scripts can be found on the GitHub repository for the manuscript where this work was originally published [142].

4.3 Results

The acoustic response of single crystal materials depends not only on the surface orientation of the crystal, but also the polarization of the SAW on the crystal surface [88]. For this reason, the acoustic response of both irradiated and unirradiated copper single crystals is characterized using a series of measurements at different SAW polarizations on the surface. In practice, the orientation of the induced acoustic wave is fixed by the optical geometry used for the experiments. The polarization relative to the crystal surface is controlled by mounting the exposed samples on a manual rotation stage and rotating the sample face relative to the projected grating. As the \{111\} plane on face centered cubic crystals has six-fold symmetry, collecting data over an angular range of 60° is sufficient to completely
Figure 4-2: Change in SAW speed along the ⟨11̅2⟩ direction on the {111} surface of pure Cu as a function of the dose level at the damage peak. As data are not sampled uniformly, the values used to calculate this speed change are fit using half-sinusoidal profiles to the experimental data shown in Fig. 4-1.

capture the acoustic response. Surface directions on these crystals are not characterized a priori, necessitating the application of an angular shift to data collected on different samples so the responses may be compared directly. The correction is applied such that for all data, the ⟨11̅2⟩ surface direction (the ‘fast’ direction) appears at 15° and ⟨1̅10⟩ (the ‘slow’ direction) appears at 45°. Data for all samples is collected in 5° increments on a manual rotation stage with 2° gradations. For all samples, the TGS laser spots are placed in the center of the ion beam spot. Some discoloration is visible in the spots exposed to the ion beam, but in all cases the surface finish is of sufficient quality to make TGS measurements.

The variation in measured SAW speed as a function of surface angle for all samples is shown in Fig. 4-1. The unirradiated data presented matches very closely to the expected SAW speeds calculated from elastic theory [72]. At the lowest dose, there is a uniform stiffening in the measured response across all surface angles. At 10 dpa, the response along the slow direction has recovered to the unirradiated case, and the response along the fast direction has softened slightly from the initial case. For the 30 and 50 dpa case there is a continued, small change along the fast direction and no notable change along the slow direction. Finally, at 90 dpa there is a significant reduction in the SAW speed along the fast direction and a small change along the slow direction. At the highest doses, this trend is consistent with the expectations of Eq. (4.3). One feature of note is that, even at the highest doses, the periodicity of the response remains constant, indicating that the crystalline nature of the sample has been retained.

Since measurements are not made at the same absolute values of surface angle on every sample, half-sinusoidal profiles of the form

\[ h(\theta) = A + B \cos(\omega \theta + \phi) \]

are fit to data in the angular range \( \theta \in [0^\circ, 30^\circ] \) to facilitate their comparison, where \( \theta \) is the corrected surface angle in degrees, \( A \) and \( B \) are amplitude constants, \( \phi \) is a phase shift, and \( \omega = \pi/30 \) given the six-fold periodicity of the surface. The maximum value of best fit profile to each set of data can be compared to determine the change in SAW speed as a function of dose along the direction of maximum change. Fig. 4-2 shows this fit speed along ⟨112⟩ as a function of dose and the data is presented in Table 4.3 as well. The trends elucidated here are the same as described
Figure 4-3: a) SRIM calculated dose profile for 35 MeV Cu^{6+} into Cu normalized to 90 dpa at peak with TGS penetration depth indicated. b–f) HAADF STEM cross-sectional images of irradiated copper samples. The crystal matrix is light, while irradiation-induced voids appear dark. A platinum layer is deposited on the sample surface prior to FIB milling to avoid damaging the exposed material. The incident ion beam direction is from the top in all micrographs. The visible contrast bands are due to residue on the lamellae left from sample storage.

above, but are perhaps easier to visualize. The error bars on these points are taken as the error in the measurement of the data point closest to \(\langle 11\bar{2}\rangle\), as the error in the data at different angles varies little.

HAADF STEM micrographs, shown in Fig. 4-3 in addition to the SRIM generated damage profile, confirm the presence of void swelling in all exposed samples. In all cases, the depth profile of the observed voids is non-uniform. At the lowest doses, the swelling region is located away from the damage peak due to the injected interstitial effect [143]. As the amount of swelling increases at higher doses, the depth at which swelling is observed is correspondingly increased as the average density is reduced in the near surface region [144]. In the 5 and 10 dpa samples a sufficient vacancy supersaturation has not been generated in near-surface layer (above the void bands) to nucleate and grow observable swelling. In the 30 dpa sample, this saturation level has clearly been reached in the near-surface region, the dose at 2.4 \(\mu\)m is 6.3 dpa, similar to level at which swelling is initially observed in the 5 dpa sample. For the higher-dose samples, characteristic features such as a void denuded zone near the surface and a decrease in void size near the damage peak are observable. The 50 and 90 dpa samples have large, crystallographic voids with facets aligned with the surface orientation of the single crystal. The swelling profile of the 30 dpa sample is found to be much finer compared to that of other samples. At the exposure temperature used here, prior self-ion irradiation work by Glowinski et al. indicates that reducing the dose rate from the maximum used in this study should promote void nucleation and swelling [145]. Thus the comparatively low dose rate seen by the 30 dpa sample, a factor of 2.2 lower than the 10 dpa sample as shown in Table 4.3, is likely the cause of the qualitative difference in swelling profile. Other higher-order effects such as slight variations in exposure temperature or sample contamination could also affect the difference observed here. Nevertheless, in all cases the damaged region in which the most void formation is observed is within the elastically-excited TGS penetration depth. Diffraction patterns of irradiated samples show no evidence of amorphization, confirming that the crystallinity is retained following irradiation.

STEM micrographs are processed using image analysis to create histograms of swelling versus depth for each sample, both as areal porosity and as volumetric swelling, shown in Fig. 4-4. This analysis shows that, for the high-dose samples, a double-peaked swelling profile is established which is consistent with other pure, self-ion irradiation studies [146]. Fig. 4-4 again shows that the preponderance of the swelling region is captured within the TGS penetration depth. From these profiles an average swelling can be calculated for both methods over the TGS analysis
Figure 4-4: Histograms of areal porosity (solid red) and volumetric swelling (dashed blue) versus depth for all exposed samples calculated in 600 nm bins. Calculated volumetric swelling underestimates the areal porosity for samples with an average void size that much smaller than the lamella thickness.

Table 4.3 shows the swelling calculated in this manner, compared to both the peak and intermediate dose received by each sample. The error in the average swelling values is estimated to be 30% for the 5 dpa sample and 20% for all other samples based on the image resolution of the STEM micrographs and the SEM cross-sections used to determine lamella thickness. At lower exposures, the volumetric swelling method underestimates the total amount of swelling present as the average void diameter is smaller than the thickness of the lamella, particularly for the 5 and 30 dpa samples. At higher doses, despite the spherical approximation used and the faceted voids observed, the two methods return comparable values for the calculated swelling. Given the faceting present, the areal porosity is later used as an estimate of the density change for the 90 dpa sample, which is necessary in the determination of the elastic constants of the exposed material.

4.4 Discussion

Zinkle et al. showed that self-ion irradiation of pure copper up to a level of 40 dpa at peak at temperatures in the range 100–500°C should not induce significant void swelling unless oxygen impurities are present in the copper matrix to stabilize void formation [128]. Despite the high base-metal purity of the samples exposed here (manufacturer specified <1 ppm oxygen), a large amount of void swelling is clearly observed. This behavior is consistent with previous studies of high-purity self-ion irradiated copper which do not specifically out-gas samples prior to exposure [145,147,148]. Furthermore, the faceted voids observed here indicate that even if residual oxygen stabilizes initial void formation, the final voids have little internal gas pressure [2].
Given that observable swelling is present in the lowest-dose sample in the matrix explored here, it is interesting to note that the measured acoustic response at 5 dpa shows stiffening and not softening like higher-dose samples. This response is likely due to the presence of a region near the surface which has experienced much lower dose levels than those at the damage peak. Early work by Friedel explained that an increase in measured elastic modulus of low-dose irradiated metals as measured in ultrasonic experiments can be attributed to a dislocation pinning mechanism [81].

For a material with a given dislocation density, the presence of small defect clusters may decrease the average pinned segment length, decreasing the amount a pinned segment may bow under an elastic load, and thereby increasing the observed elastic modulus. This effect has been observed even in well-annealed, high-purity copper under neutron and electron irradiation [130]. More recently, Li et al. show that in copper self-ion irradiated to low doses, the primary defects formed are stacking fault tetrahedra (SFTs) [26]. In that study, the SFT density was found to saturate at about 1 dpa and change little afterwards. These observations indicate that there is likely a high SFT density in the region between the observed void swelling band and the surface of the 5 dpa sample exposed here, as the dose received at 2.4 µm is 1.1 dpa. Using molecular dynamics simulations, Wirth et al. additionally have shown that SFTs in copper act like hard pins to dislocation motion [149]. Therefore, although earlier work in this area does not seek to identify the defects causing this pinning effect, it seems likely that SFT formation is the root of the saturated stiffening behavior observed here and in previous ultrasonic experiments [129,130].

In these TGS experiments, areas which have experienced different dose levels are being averaged in the measured

<table>
<thead>
<tr>
<th>Peak dose at 4.25 µm (dpa)</th>
<th>Intermediate dose at 2.4 µm (dpa)</th>
<th>Peak dose rate (×10⁻³ dpa/s)</th>
<th>Δc/c₀ along ⟨112⟩ (%)</th>
<th>Areal porosity (%)</th>
<th>Volumetric swelling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>1.1</td>
<td>1.5</td>
<td>+1.24</td>
<td>0.79</td>
<td>0.24</td>
</tr>
<tr>
<td>10</td>
<td>2.1</td>
<td>1.9</td>
<td>-0.89</td>
<td>1.96</td>
<td>1.36</td>
</tr>
<tr>
<td>30</td>
<td>6.3</td>
<td>0.85</td>
<td>-1.31</td>
<td>3.55</td>
<td>1.17</td>
</tr>
<tr>
<td>50</td>
<td>11</td>
<td>1.0</td>
<td>-1.64</td>
<td>8.59</td>
<td>8.82</td>
</tr>
<tr>
<td>90</td>
<td>19</td>
<td>1.7</td>
<td>-4.45</td>
<td>12.8</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Table 4.3: Peak and intermediate doses received by, dose rate at the damage peak for, change in SAW speed along the fast direction of, total areal porosity for, and volumetric swelling for each sample. Swelling is averaged from the surface to a depth of 4.8 µm and increases monotonically with exposure level, with the exception of the 30 dpa volumetric case.

<table>
<thead>
<tr>
<th>Unirradiated</th>
<th>90 dpa</th>
<th>% change</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ (g/cm³)</td>
<td>8.96</td>
<td>7.81</td>
</tr>
<tr>
<td>C₁₁ (GPa)</td>
<td>165.0</td>
<td>142.7</td>
</tr>
<tr>
<td>C₁₂ (GPa)</td>
<td>119.0</td>
<td>102.9</td>
</tr>
<tr>
<td>C₄₄ (GPa)</td>
<td>73.51</td>
<td>52.93</td>
</tr>
<tr>
<td>A (Zener ratio)</td>
<td>3.20</td>
<td>2.66</td>
</tr>
<tr>
<td>Speed along ⟨112⟩ (m/s)</td>
<td>1942</td>
<td>1856</td>
</tr>
<tr>
<td>Speed along ⟨110⟩ (m/s)</td>
<td>1596</td>
<td>1589</td>
</tr>
</tbody>
</table>

Table 4.4: A comparison of best fit elastic constants and anisotropy ratio for unirradiated pure copper starting from constants given in [99] to best fit values for the 90 dpa sample. SAW speeds are experimentally measured using TGS in both cases.
response. In the lowest dose sample, the effect of stiffening due to dislocation pinning above the observed void band dominates over the expected softening due to volumetric swelling [82]. At higher doses, volumetric swelling effects win out and a monotonic softening in the acoustic response is observed. Thinking forward to using TGS as an in situ tool for rapid materials development, this transition in dominant mechanisms can be used as a coarse binary metric to detect the presence of void swelling in the TGS analysis region. Following defect saturation, the transition to a decrease in measured SAW velocity, or the recovery to the pre-exposure value, could be used as a threshold to determine if void swelling has occurred. This general trend should be true for both elastically anisotropic (single crystal) materials as well as isotropic materials (polycrystals). For the single crystal case, as the elastic constants are not changed uniformly, the surface direction expected to experience the largest change, in this case (112), should be aligned with the experimental SAW polarization prior to exposure to ensure ease of detection. That TGS non-linearly averages over regions exposed to different radiation doses is an interesting challenge for correlating property changes to one particular dose. Future work involving comparisons to uniformly damaged microstructures, from neutron irradiations for example, and calculations of the average dose in the TGS analysis region weighted by the mechanical acoustic displacement profile must be carried out to determine the most appropriate single dose to which a TGS measurement may be correlated.

In addition to the ability to give a binary determination about the presence of void swelling in irradiated single crystals, the TGS data collected here, in concert with some determination of the density change resulting from irradiation, can be used to determine the change in a material’s elastic constants. In this case, the calculated areal porosity from STEM imaging has been used to estimate the density change as a result of void swelling. However, future studies could use changes in thermal transport properties as measured through TGS [58,65] to estimate changes in density resulting from void swelling [150,151]. Other authors have constructed optimization technique by which elastic constants can be reconstructed through laser-induced acoustic data similar to those taken here [63,152]. However, as a simple proof-of-principle, a set of cubic elastic constants has been manually optimized to the 90 dpa data through iterative calculations of the SAW response versus acoustic polarization using the method of Every et al. [88]. These calculations are carried out considering a semi-infinite bulk with density and elastic constants specified, and not a layer with irradiation-modified properties atop a pristine substrate. Duncan et al. found that the best-fit values determined using a two-layer approach vary little from a single layer case if the TGS excitation wavelength is equal to or smaller than the ion implantation depth [66].

Materials with cubic symmetry have only three independent elastic constants, $C_{11}$, $C_{12}$, and $C_{44}$. From the acoustic response on the (111) plane of cubic crystals, $C_{11}$ and $C_{12}$ cannot be independently determined, but the value $(C_{11} - C_{12})/2$ may [153]. Therefore, the minimization carried out here modifies $C_{11}$ and $C_{12}$ by the same constant fraction for a given iteration. A useful characterization of the of the anisotropy of the elastic response of a cubic material is given by the Zener anisotropy ratio, $A = 2C_{44}/(C_{11} - C_{12})$ [84]. The SAW response of a material with an anisotropy ratio of $A = 1$ will show no variation with respect to acoustic polarization on any crystal surface. The optimized values for the elastic constants of the 90 dpa sample are given in Table 4.4. Although few direct comparisons exist in the literature, the observed trend of decreasing elastic constants with volumetric swelling is consistent with studies showing a reduction in isotropic elastic constants with increasing porosity in compacted nanocrystalline copper [154]. Of particular note here is the reduction in the anisotropy ratio of the exposed sample, which is to be expected given the non-uniform change in SAW speed along the fast and slow directions on the (111)
surface. This analysis shows that TGS may be used as a tool to determine changes in the elastic performance of highly damaged materials in addition to simply determining the presence of volumetric swelling.

### 4.5 Conclusions and implications

In this chapter, TGS is used to investigate the effects of self-ion irradiation-induced void swelling on the acoustic and elastic properties of pure, single crystal copper. The depth of the imposed damage profile is chosen to closely match the mechanical excitation depth generated using TGS by tuning the implantation energy. HAADF STEM imaging confirms that swelling levels up to 12.8%, as calculated by areal void fraction, are captured in the surface acoustic wave (SAW) response of the irradiated single crystals. At high doses, volumetric swelling has the effect of non-uniformly reducing the cubic elastic constants of copper, reducing the anisotropy ratio. At lower doses, the effect of matrix stiffening via dislocation interactions with SFTs is postulated to be the cause of an increase in the measured SAW speed. The competition between these two mechanisms, stiffening at low doses and softening at high doses, is proposed as a metric to detect the onset of void swelling.

The work presented here demonstrates the second necessary functionality for the TGS experimental methodology. With the foreknowledge that at least one high-dose radiation-induced degradation mode may be detected, if an in situ TGS diagnostic is demonstrated then a whole field of radiation materials questions related to void swelling may be addressed immediately. However, a full extension of this method to highly-exposed engineering alloys must include a careful consideration of effects expected in polycrystalline materials. Particularly, the size of the excitation spot relative to the grain size will be important in interpreting polycrystalline TGS test results. Nevertheless, such a diagnostic, able to detect the onset of irradiation-induced swelling in a single continuous measurement, would be a powerful tool in development of new bulk materials for advanced nuclear applications.

Two implementation functionalities still remain to be demonstrated before TGS can be employed as an in situ diagnostic for ion beam irradiations. First, the measurements made in this chapter are static and use arbitrarily long signal collection times to reduce the noise in the extracted material properties. The capability to transition from static to dynamic TGS measurements is demonstrated in Chapter 5. Second, measurements on the ion irradiated samples in this chapter focused solely on changes in acoustic and elastic properties as a measure of the induced microstructural change. The reason for this lies in the two distinct signal characters which may be extracted from TGS measurements. The signal character which encodes the acoustic response, and therefore the elastic properties, presents a challenge when attempting to extract the thermal diffusivity due to a two-term decay profile. More details and a solution to this challenge are presented in Chapter 6 where a methodology for extracting both thermal and elastic properties from materials simultaneously is detailed.
Chapter 5

Time-resolved, dual heterodyne phase collection TGS

The application of optical heterodyne detection for transient grating spectroscopy (TGS) using a fixed, binary phase mask – as utilized in this thesis – relies on taking the difference between signals captured at multiple heterodyne phases. To date, this has been accomplished by manually controlling the heterodyne phase between sequentially-measured responses with an optical flat. In this chapter, an optical configuration is presented which allows the collection of TGS measurements at two heterodyne phases concurrently through the use of two independently phase controlled interrogation paths. This arrangement allows for complete, heterodyne amplified TGS measurements to be made in a manner not constrained by a mechanical actuation time. Measurements are instead constrained only by the desired signal-to-noise ratio. Between one and ten second temporal resolution is demonstrated here on single crystal metallic samples. This functionality places time-resolved TGS measurements well within the regime necessary to be used as an in situ diagnostic for materials which are dynamically changing due to radiation exposure. The work presented in this chapter is primarily sourced from Dennett and Short, Appl. Phys. Lett. 110 (2017) 211106 [155].

5.1 Introduction and background

For almost two decades, transient grating spectroscopy (TGS), also known as impulse stimulated thermal scattering (ISTS), has been implemented using an optical heterodyne detection technique in an arrangement described in [57]. In this technique, a spatially periodic material excitation is generated by periodic thermal excitation produced by the interference pattern of two crossed pumping laser beams at the material surface. In reflective materials, this excitation manifests itself as surface displacement and/or transient reflectivity change. To interrogate the dynamics of this excitation a third, probing, laser beam is diffracted from the excitation. The first order diffraction of this probe is directed into a photodetector, such that the amplitude of the response oscillates with the frequency of the material excitation. In TGS experiments to date, a fourth laser beam, generated from the same source as the probe, is used as a reference oscillator, allowing the diffracted probe signal to be heterodyne amplified. In this configuration, the measured signal intensity has the form

\[ I_S(t) = I_R + I_D(t) + 2 \sqrt{I_R I_D(t)} \cos \phi, \]  

(5.1)
where $I_R$ is the reference oscillator intensity, $I_D(t)$ is the diffracted signal intensity, and $\phi$ is the heterodyne phase difference between the reference and diffracted beams [57]. As $I_R$ is constant and usually of much greater amplitude than $I_D(t)$, the result is an overall amplification of the time-dependent signal of interest.

To recover large amplitude signals suitable for quantitative analysis of the acoustic and thermal transport properties of materials under investigation, it is common practice to record traces at both $\phi = 0^\circ$ and $\phi = 180^\circ$. These two signals can be subtracted from one another to recover a total signal amplitude

$$I_{\text{tot}}^S(t) = I_0^S(t) - I_{180}^S(t) = 4\sqrt{I_R I_D(t)}.$$ (5.2)

In addition to further amplifying the recorded signal intensity, taking a set of measurements in this manner allows for the removal of any systematic noise, such as the impulse response of the photodetector or other electrical noise present near the experiment, from signals that are used for analysis. In practice, the heterodyne phase is controlled by a manually adjustable, highly parallel optical flat in the path of the probe laser beam. A phase difference between probing and reference beams is generated as a function of the tilt angle of this flat due to small changes in path length [58]. Measurements relying on this type of manual phase control are time-limited by the actuation time between collections at different values of $\phi$, typically in the range of tens of seconds to single minutes. This limitation must be lifted if material systems undergoing dynamic changes are to be studied using TGS. The particular dynamically-evolving systems of interest for this work are those undergoing ion beam irradiation-induced material evolution.

In this chapter, a modification to the optical arrangement for heterodyne amplified TGS experiments is presented which allows for the simultaneous collection of two signals with differing heterodyne phases, hereafter referred to as dual heterodyne TGS (DH-TGS). Throughout this chapter, the material excitation of interest will be a surface displacement response maximized at heterodyne phases denoted $\phi = 0^\circ$ and $\phi = 180^\circ$. For materials which exhibit strong excitations in both displacement and reflectivity under an imposed transient grating, different dynamics can be probed by choosing alternate values of $\phi$ [58]. Here, fixing $\phi$ to $0^\circ$ and $180^\circ$ allows for the collection of a complete TGS measurement of the excitation of interest without the constraint of mechanical actuation. In this chapter, the focus is again solely the acoustic response of the validation materials in question. In Chapter 6, the extraction of multiple properties from signals generated at these choices of heterodyne phase will be explored in detail.

### 5.2 Dual heterodyne optical arrangement

The optical arrangement for a reflective sample is shown in Fig. 5-1(a). The generation of the excitation grating on the sample under investigation is accomplished by passing a short pulsed laser through a volumetric diffraction grating, hereafter referred to as the “phase mask,” which is optimized to diffract most of the light into the \( \pm 1 \) orders. All other orders are spatially filtered and the two pump paths are recombined at the sample using an imaging system of cemented achromatic doublets, L1 and L2. The wavelength of the intensity grating projected onto the sample is given by $\Lambda = M\Lambda_0/2$, where $\Lambda_0$ is the wavelength of the phase mask and $M$ is the magnification ratio between L1 and L2 [57]. In this implementation a matched pair of doublets is used for L1 and L2 such that $M = 1$.

To record two heterodyne phases concurrently, two additional laser paths are added to the standard TGS imple-
1:1 imaging system with cemented achromatic doublets, probing beam from the beam splitter is re-directed such that it laser paths are added to the standard TGS implementation as and

Figure 5-1: (a) Top-view block schematic of the DH-TGS optical geometry showing paths from laser sources to detectors. BS – beam splitter, L1 & L2 – achromatic doublets, ND – neutral density filter, PA1 & PA2 – phase adjustment flats, APD1 & APD2 – silicon avalanche photodiodes. (b) Beam arrangement in the plane of lens L2, just before the sample surface. The positions below the dotted line represent the reflection and diffraction of the reference oscillator and probe beams from the sample surface.

mentation as a probing beam and reference oscillator pair. All of the probing beams are generated from the same continuous wave laser source. Prior to incidence onto the phase mask the probe path is split using a non-polarizing 50:50 beam splitter (BS). The transmitted leg of this probe is focused coincident with the pump source onto the phase mask at an angle \( \theta_1 \) (out of the plane of the page in Fig. 5-1(a)) such that between L1 and L2 there is a vertical separation of the pump and first probing paths. The reflected probing beam from the beam splitter is re-directed such that it, too, is coincident onto the phase mask as the same spot as the pump, but with incoming angle \( \theta_2 > \theta_1 \) such that the vertical separation between the second probe paths and the pump is greater than that of the first pair. For both probes, the ±1 diffraction orders are again retained while transmitted beam and higher orders are blocked. The vertical placement of each of the six beampaths in the plane of L2 is shown in Fig. 5-1(b).

Between L1 and L2 the two reference oscillator beams are passed through a neutral density filter (ND) to avoid saturating the photodetector down-stream. Both probing paths are passed through a first phase adjust flat (PA1) which is used to uniquely control the heterodyne phase of \( I_S^{180}(t) \). The extremal probing path is passed through a vertically separated, second phase adjust flat (PA2), which adds an additional path length difference and uniquely controls the phase of \( I_S^0(t) \). Upon reflection and diffraction from the sample surface, the spatial coincidence of the reference oscillator and the diffracted signal for both probing paths is guaranteed by the optical geometry. In the reflection geometry, both signals pass back through L2. As these paths are now vertically separated below the plane of the pump paths, they can be picked off, separated, and directed into two fast silicon avalanche photodiodes (APD1 and APD2). The path lengths between the sample surface and APD1 and APD2 are managed such that the two
signals are aligned in time when recorded on a digital oscilloscope.

The primary advantage of the optical arrangement described above over previous implementations of the technique is time resolution. The pumping laser in these types of experiments is commonly operated with a repetition rate in the single kHz range. Each measurement, therefore, is taken as an average over hundreds to thousands of laser pulses to reduce noise. Previously, a complete measurement of both heterodyne phases could be time resolution limited either by the signal collection time (in a case where many averages are taken) or by the mechanical action necessary to change the heterodyne phase (in the case where only a few averages are needed). By recording both of these phases independently, the time resolution of the system becomes, in all cases, signal-to-noise ratio limited.

5.3 Experimental performance

DH-TGS experiments using an optical arrangement as described above are carried out using a passively Q-switched, 532 nm, solid-state laser with a pulse length of 300 ps, repetition rate of 1 kHz as a pump laser source with a spot size of 130 μm, and pulse energy at the sample surface of 2.38 μJ. The probe laser source is a 785 nm, CW diode laser modulated to a repetition rate of 1 kHz with a 20% duty cycle, a power at the sample surface of 4.7 mW for both probe/reference oscillator pairs, and a spot size of 105 μm. The probe laser is RF modulated to the frequency of the pump to reduce sample heating. The silicon avalanche photodetectors used have a 3 dB bandwidth of 1.0 GHz and manual external gain adjustment. Their outputs are concurrently recorded on a dual-band 5 GHz bandwidth digital oscilloscope.

In metallic samples investigated using this technique, \( I_{S}^{\text{tot}}(t) \) has two features of interest, a damped acoustic oscillation overlaid on a non-exponential thermal decay curve [89]. A filtered power spectrum of \( I_{S}^{\text{tot}}(t) \) can be used to identify the dominant frequencies of the surface acoustic wave (SAW) oscillation induced by the imposed transient grating. These power spectra can be used as one measure of the quality of the recorded signal. To determine a representative minimum collection time, a series of measurements is carried out on a \{001\} oriented sample of 99.99% pure, single
Figure 5-3: Filtered Fourier transform of DH-TGS measurements collected on {001} oriented single crystal tungsten using $\Lambda = 5.50 \, \mu m$ with collection times varying from 0.550 to 743 seconds. Each spectrum is a representative selection from a series of three measurements at fixed collection time.

crystal tungsten varying the number of traces collected in a single measurement from 10 to 50000. These measurements are carried out using an imposed grating wavelength of $\Lambda = 5.50 \, \mu m$. The time-dependent signals for a 250 trace averaged measurement are shown in Fig. 5-2. The filtered power spectra for each measurement are given in Fig. 5-3. Given the repetition rate of the pump laser, the sampling rate of the oscilloscope, and the communication time between the oscilloscope and the acquisition computer, the total collection time of these measurements ranged from 0.550 seconds to 743 seconds (12.5 minutes). As the collection time is increased, the signal-to-noise ratio of the identifiable acoustic peaks in the spectrum is increased, as is expected.

Table 5.1 shows statistics for each collection time, including the signal-to-noise ratio as well as the 95% confidence interval of the peak position parameter from a Gaussian fit to the spectrum. As there is often a DC component retained in the power spectrum from slow thermal decay, the signal-to-noise ratio is calculated over the noise floor from 0.7 to 1.3 GHz as the DC component is clearly separable from the acoustic peak of interest. The entries in Table 5.1 are the average values given from three measurements of the same record length. For measurements averaging 10 and 25 laser pulses, identifiable peaks in the power spectrum were not always apparent above the noise floor. From this series of measurements, based solely on the consistency of the appearance of peaks in the acoustic spectrum, a minimum temporal resolution of between one and ten seconds is observed.
### Table 5.1: Characteristics of power spectra from $I_{tot}^S(t)$ at varying collection times on single crystal tungsten. The signal-to-noise ratio is calculated as $SNR = 10 \log_{10}(P_s/P_n)$ where $P_s$ is the peak signal power and $P_n$ is the maximum noise power in the range 0.7 to 1.3 GHz. The percent peak position error is the Gaussian fit error divided by the peak position value.

<table>
<thead>
<tr>
<th>Collection Time (sec)</th>
<th>Traces Averaged</th>
<th>Signal-to-Noise Ratio</th>
<th>Peak Position Error ($\times 10^5$ Hz)</th>
<th>% Peak Position Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.550</td>
<td>10</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.770</td>
<td>25</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1.14</td>
<td>50</td>
<td>3.73</td>
<td>5.3</td>
<td>0.109</td>
</tr>
<tr>
<td>1.85</td>
<td>100</td>
<td>6.55</td>
<td>3.7</td>
<td>0.076</td>
</tr>
<tr>
<td>4.19</td>
<td>250</td>
<td>9.97</td>
<td>3.0</td>
<td>0.061</td>
</tr>
<tr>
<td>7.92</td>
<td>500</td>
<td>11.8</td>
<td>2.5</td>
<td>0.051</td>
</tr>
<tr>
<td>15.5</td>
<td>1000</td>
<td>14.1</td>
<td>2.2</td>
<td>0.043</td>
</tr>
<tr>
<td>38.5</td>
<td>2500</td>
<td>15.0</td>
<td>2.1</td>
<td>0.042</td>
</tr>
<tr>
<td>75.7</td>
<td>5000</td>
<td>20.7</td>
<td>1.7</td>
<td>0.035</td>
</tr>
<tr>
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<td>10000</td>
<td>22.9</td>
<td>1.8</td>
<td>0.037</td>
</tr>
<tr>
<td>374</td>
<td>25000</td>
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<td>1.6</td>
<td>0.034</td>
</tr>
<tr>
<td>743</td>
<td>50000</td>
<td>26.3</td>
<td>1.6</td>
<td>0.034</td>
</tr>
</tbody>
</table>

#### 5.4 Discussion

Using this implementation of a TGS experiment, the thermal and acoustic properties of specimens subject to some external driving force can be monitored. Drivers such as temperature, voltage, or irradiation exposure can cause drastic changes in the acoustic and thermal transport properties of materials under investigation. As a simple proof of principle experiment, a series of DH-TGS measurements is carried out on a {111} oriented sample of single crystal aluminum subject to a temperature ramp between 50 and 250°C. Measurements were taken with $\Lambda = 4.78$ µm, using 1000 trace collections on a 20 second interval over a period of about 30 minutes. If acoustic peaks are identified in the power spectrum at dominant frequencies $f_{TG}$, then the surface acoustic wave (SAW) speed for each measurement can be calculated as $c_{TG} = \Lambda f_{TG}$ since the imposed grating wavelength is calibrated before each experiment, as in [72]. Fig. 5-4 shows the variation in SAW speed with temperature as measured on single crystal aluminum. The apparent linear decrease in $c_{TG}$ over this temperature range is consistent with SAW speeds calculated from temperature-dependent elastic constants of aluminum [88,156].

In general, collecting traces of $I_{tot}^S(t)$ of with a signal-to-noise ratio in the time domain sufficiently high enough to accurately fit thermal transport parameters requires a longer collection time than that required to identify the primary excited acoustic oscillations as discussed here. However, the difference in these time scales varies widely between different material systems. For this reason, the discussion thus far has been restricted to the minimum time scale necessary to analyze the acoustic response of the DH-TGS measurement.

A comment is required concerning the difference in the angles $\theta_1$ and $\theta_2$ which control the vertical separation of the two probe paths in Fig. 5-1(b). In practice, these two angles should be set as close as possible to each other while maintaining the ability to independently control the heterodyne phase of each path. The lenses L1 and L2 used in the current iteration of this experiment are achromatically, but not aspherically, corrected doublets. A small spherical aberration present in the lens system causes a focal length shift between the two probing paths, as shown
schematically in Fig. 5-5. The overlap volume of the two pump beams is large enough with the spot sizes used here to allow for simultaneous collection of both $I_0^S(t)$ and $I_{180}^S(t)$ with careful positioning of the sample surface in the beam path direction. Upon initial alignment, the photodetectors must be tuned to compensate for differences in signal amplitude occurring due to lens aberration as well as differences in intrinsic gain. The response amplitudes can be matched by setting the heterodyne phase to $\phi = 0^\circ$ for both probe paths, taking the real-time Fourier transform of the photodetector response on the acquisition oscilloscope, and manually tuning the photodetector gain such that the SAW peak in the transform of each detector has the same power. Future implementations of this technique should utilize both achromatically and aspherically corrected lens systems for L1 and L2 to reduce the sensitivity to this aberration.

The removal of any long-timescale systematic error by subtracting $I_0^S(t)$ and $I_{180}^S(t)$ to find $I_{\text{tot}}^S(t)$ provides several improvements in the analysis of elastic properties through the measured acoustic response. As signal intensity measured on the photodetectors is intrinsically shot-noise limited, the method proposed here relying on the upstream splitting of the same probe laser source to create both probing paths should, in theory, not result in an improvement in the overall acoustic signal intensity compared to a single-phase collection using the same probe laser source. However, as the reference oscillator needs to be attenuated to avoid saturating the photodetector, splitting the probe laser source allows for the ratio of reference oscillator intensity to diffracted signal intensity, $I_R/I_D(t)$, to be increased across two detectors compared to the single detector in traditional TGS experiments. Additionally, the power spectra of short time scale collections with traditional TGS experiments which do not correct the systematic component of $I_{\text{tot}}^S(t)$ may be more complicated to analyze in the low frequency region. This complication becomes detrimental for measurements at long acoustic wavelength or for particularly compliant materials.

### 5.5 Conclusions and implications

Looking forward to this methodology’s full use as an *in situ* multi-property diagnostic, some comment is required on the effect of the experimental implementation changes made in this chapter on the ability to determine thermal
transport properties in addition to acoustic signatures. In contrast to the acoustic analysis, the determination of the thermal diffusivity from $I_{S}^{\text{tot}}(t)$ relies on model fitting, for which the removal of systematic error by subtracting $I_{S}^{0}(t)$ and $I_{S}^{\text{iso}}(t)$ is a necessary step [58,127]. Given this requirement and the presence of a systematic component to the captured signals – which is common – DH-TGS should allow for thermal transport properties to be measured on much shorter time scales than traditional experiments. A full accounting of this final necessary functionality, reliably extracting this property from the signals of interest, is given in the following chapter.

The true advantage using the methodology described in this chapter will be in the ability to near-continuously characterize both the thermal and elastic properties of dynamic material systems undergoing some external forcing. In contrast, traditional TGS experiments have largely been limited to static material systems. This static-to-dynamic shift will allow the transient grating method to be applied in in situ applications which have not yet been practical with single heterodyne phase collection. The particular use case of interest here is, of course, the application of TGS as an in situ multi-property diagnostic during ion beam irradiation. However, the potential utility of the implementation described in this chapter is much broader. Given the necessary optical access, material evolution under a diverse set of conditions such as thermal annealing, cyclic fatigue, or high-voltage switching may all be interrogated non-destructively using this methodology.
Chapter 6

Multi-property determination using phase grating thermal transport analysis

The elastic and thermal transport properties of opaque materials may be measured using transient grating spectroscopy (TGS) by inducing and monitoring periodic excitations in both reflectivity and surface displacement. In these types of measurements, the ‘phase grating’ response encodes both properties of interest, but complicates quantitative analysis by convolving temperature dynamics with surface displacement dynamics. This response has been used in previous chapters for the analysis of elastic properties. Given these convolved dynamics, the alternative ‘amplitude grating’ response is most often used to determine thermal transport characteristics as it can be used to isolate the surface temperature response. However, this signal character requires absolute heterodyne phase calibration and contains no elastic property information. In this chapter, a method is developed by which phase grating TGS measurements may be consistently analyzed to determine thermal diffusivity with no prior knowledge of the expected properties. To demonstrate this ability, the wavelength-dependent 1D effective thermal diffusivity of pure germanium is measured using this type of response and found to be consistent with theoretical predictions made by solving the Boltzmann transport equation. This ability to determine both elastic and acoustic properties from a single set of TGS measurements is the final necessary functionality which must be demonstrated prior to the utilization of this methodology as an in situ diagnostic for dynamic materials evolution during irradiation. The work presented in this chapter is primarily sourced from Dennett and Short, J. Appl. Phys. 123 (2018) 215109 [59].

6.1 Introduction

Optically heterodyne amplified transient grating spectroscopy (TGS) measurements are a powerful tool used in the study of a wide variety of physical phenomenon [58,60–64,68–70,83]. Of particular interest for the validation measurements made in this chapter, TGS has become a powerful tool in exploring short-wavelength, ballistic heat transport in semiconductors [157]. In common implementations, TGS uses two pulsed lasers crossed at the surface of a sample under interrogation to generate a pulsed, spatially periodic intensity pattern on this surface. Laser heating in this periodic pattern induces a periodic material excitation in both temperature and surface displacement, $u(t)$, due to thermal expansion. In most materials, the complex reflectivity, $r^*(t) = r_0[1 + r'(t) + ir''(t)]$, is temperature-dependent, indicating that periodic ‘gratings’ in both reflectivity and surface displacement will be present following
excitation. The dynamics of these gratings are monitored by recording the intensity of the first order diffraction of a quasi-continuous wave probing laser from the surface gratings. In the ‘boxcar’ geometry used for TGS measurements made here [57], the diffracted signal is spatially overlapped with a reference oscillator to heterodyne amplify the recorded signal. Johnson et al. showed that the total optical intensity of heterodyne response for TGS measurements made in the ‘reflection geometry,’ i.e. for opaque materials, is given by

\[ I(t, \phi) = t_r I_0 R_0 [r'(t) \cos \phi - (r''(t) - 2k_p u(t) \cos \beta_p) \sin \phi], \quad (6.1) \]

where \( I_0 \) is the initial intensity of both the reference oscillator and probing beams, \( t_r \) is the attenuation factor of the neutral density filter normally placed in the reference oscillator path, \( R_0 = |r_0|^2 \) is the reflectivity of the sample, \( k_p \) is the optical wave vector, \( \beta_p \) is the angle of incidence of the probe beams onto the sample surface (as shown in Fig. 6-1), and \( \phi \) is the heterodyne phase difference between the reference and probe beams [58].

Eq. (6.1) holds only in the regime where the reference oscillator intensity is much greater than the diffracted signal intensity, which is true in TGS experiments. This form indicates that by setting the heterodyne phase in experiment to \( \phi = 0 \) or \( \phi = \pi \), the real component of the reflectivity change, \( r'(t) \), may be isolated. This selection of phase is referred to as the ‘amplitude grating.’ If the phase is chosen to be \( \phi = \pm \pi/2 \), the ‘phase grating’ may be selected, which is comprised of a combination of the imaginary part of the reflectivity, \( r''(t) \), and the surface displacement, \( u(t) \). Both the gratings in reflectivity and displacement will thermally equilibrate following excitation, with decay rates determined by the thermal diffusivity of the material in question and the wavelength of the imposed excitation, \( \Lambda \). The surface displacement component may contain one or more surface acoustic oscillations depending on the surface structure and composition of the material in question. It is these acoustic modes which may be analyzed to determine information like elastic properties and surface layering structure [83,158].

Given the ability to isolate the reflectivity dynamics in the amplitude grating response, most authors choose this signal character when measuring thermal performance using TGS [58,157]. However, amplitude grating measurements require absolute heterodyne phase calibration and only contain information regarding thermal transport characteristics. The phase grating response, in contrast, allows for simultaneous determination of both thermal and acoustic properties. As the goal of this work is to develop a multi-property \emph{in situ} diagnostic, the phase grating response is, by necessity, the signal character of interest. Measurements made in this manner also have the advantage of being insensitive to deviations in the heterodyne phase at which data is collected, rendering experimental measurement of thermal transport easier to implement in practice. In this chapter, a method is constructed by which a determination of thermal performance may be made using phase grating measurements. The method proposed here is benchmarked by measuring the grating-wavelength-dependent thermal diffusivity of pure Ge from \( \Lambda = 3.6 \) to 9.8 \( \mu \)m. Measured values of thermal diffusivity are compared to the expected thermal diffusivity at these wavelengths as computed using a variational solution to the Boltzmann transport equation and found in good agreement. Using this analysis, best practices are recommended for phase grating thermal transport determination in future studies.
6.2 Methods

To investigate the thermal performance characterization using phase grating TGS, a series of measurements are carried out on pure, undoped, germanium single crystals purchased from the MTI corporation. Three single crystals with surface orientations \{001\}, \{011\}, and \{111\}, each polished to a surface roughness of <8 Å are used. TGS measurements are carried out along primary surface directions \langle100\rangle\{001\}, \langle11\rangle\{011\}, and \langle12\rangle\{111\} by fixing the rotation of the sample with respect to the optical arrangement. These directions are indicated by the manufacturer and confirmed by comparing the measured surface acoustic wave (SAW) velocities to values computed for these surface directions using elastic theory [85,152]. In materials with phonon-dominated thermal transport, several authors have shown that thermal diffusivities measured using short-wavelength excitations, like those used in TGS, will be smaller than bulk diffusivities [61,157]. In brief, this reduction occurs due to the exclusion of long-wavelength phonons from the heat transport process. For SiGe alloys, Huberman et al. have implemented a variational approach to solving the Boltzmann transport equation (BTE) for short-wavelength, 1D periodic excitations [157]. That method allows for the calculation of the expected value of the effective thermal diffusivity in pure Ge comfortably including the normal operating range of TGS test wavelengths of \(\Lambda = 1 - 10 \, \mu m\). Using these calculated values as a benchmark, phase grating thermal transport measurements may be quantified by collecting data at a variety of TGS wavelengths on only a small number of samples.

Experimental TGS measurements are made using a dual heterodyne phase collection (DH-TGS) optical geometry [155]. A schematic of the optical arrangement used for these experiments is shown in Fig. 6-1. Excitations are generated using a passively Q-switched, 532 nm, solid state laser with a pulse length of 300 ps, and a repetition rate of 1 kHz as a pump laser (TEEM Photonics STG-03E-120). At the sample surface, the laser spot size is 140 \(\mu m\). The probing laser source is a 785 nm, CW diode laser (Thorlabs LD785-SEV300 with controller LTC100-B) modulated to a repetition rate of 1 kHz with a 25% duty cycle using an optical chopper wheel and a spot size at the sample surface of 105 \(\mu m\). The probe laser is RF modulated in this way to reduce sample heating while matching the repetition rate of the pump laser. Silicon avalanche photodiodes (Hamamatsu C5658) with a 50 kHz–1 GHz bandwidth are used to detect the heterodyne-amplified probe signal. Their outputs are concurrently recorded on a dual-band 5 GHz digital oscilloscope. Each measurement is taken as the average of 10000 laser shots to reduce noise. All measurements are made in rough vacuum (< 15 mTorr) to remove the possibility of exiting acoustic oscillations in air near the sample surface.

A variety of TGS test wavelengths may be chosen in experiment using a custom volumetric diffraction optic with many etched patterns. Each pattern, in conjunction with the optical geometry, fixes the nominal wavelength, \(\Lambda_0\), at which the periodic excitation is projected [57]. However, as minor misalignments may affect this projected grating spacing, the actual projected grating is calibrated before experiments at each wavelength using a tungsten reference sample with a known SAW speed. Here, six grating spacings are used ranging from 3.6 to 9.8 \(\mu m\) and the maximum deviation of any of the calibrated grating spacings from the nominal grating spacings is measured at 0.28\%. Measurements will be referred to in the text by their nominal grating spacings, though for each fit the calibrated spacing is used as a fixed parameter. At 3.6, 4.8, and 6.4 \(\mu m\), 10 measurements are made on each of the three single crystal orientations for a total of 30 points per grating spacing. Each measurement point is mechanically translated across the sample surface to provide a spatial average. Analysis of these measurements shows no statistical difference between values
Figure 6-1: Top-view schematic diagram of DH-TGS arrangement used in this work. Following the beam splitter in the probe path, the two vertically separated probe beams are not rendered. The angle of incidence of the probe beams, $\beta_p$, onto the sample surface is indicated. More details on the optical arrangement can be found in [155].

6.3 Grating thermal transport

In order to extract thermal property information from TGS measurements, the temperature and displacement dynamics resulting from an infinite 1D periodic excitation have been analytically investigated. Käding, et al. showed that in the limit of surface energy absorption and isotropic thermal diffusivity the surface temperature dynamics, and therefore the reflectivity dynamics, of a grating excited by a delta function laser impulse should follow

$$\{r'(t), r''(t)\} \propto \frac{1}{\sqrt{\tau}} \exp \left( -q^2 \alpha t \right) ,$$  \hspace{1cm} (6.2)

where $\alpha$ is the isotropic thermal diffusivity and $q = 2\pi/\Lambda$ is the imposed grating wave vector [89]. In the same limits, the surface displacement profile takes the form

$$u(t) \propto \text{erfc} \left( q\sqrt{\alpha t} \right) ,$$  \hspace{1cm} (6.3)

where erfc(·) is the complimentary error function. As the penetration depth of the 532 nm laser excitation is about 9 nm in Ge, this surface excitation approximation is good for the material system considered here [161]. Similarly, the isotropic diffusivity approximation is appropriate for bulk materials with cubic symmetry, but may fail for systems with hexagonal symmetry or heterostructures. These forms have both been used with success to determine thermal diffusivities from TGS experiments [58,61,127]. In practice, TGS measurements often make use of the heterodyne...
phase dependence in Eq. (6.1) to construct a composite trace which is the difference of two measurements made at complimentary heterodyne phases such that

\[ I_{\text{tot}}(t) = I(t, \phi_1) - I(t, \phi_2) \]

\[ \propto [r'(t) \cos \phi_1 - r'(t) - 2k_p u(t) \cos \beta_p] (\sin \phi_1 - \sin \phi_2) \]

(6.4)

In this manner, systematic background noise may be removed from the composite measurement without changing the dynamics of the response.

### 6.3.1 The amplitude grating

Using the construction of Eq. (6.4), complete amplitude grating measurements may therefore be collected by making two measurements at \( \phi_1 = 0 \) and \( \phi_2 = \pi \) either sequentially or concurrently using the dual heterodyne phase collection geometry [155]. Since the grating wave vector, \( q \), is fixed by the experiment, this composite trace may be fit using non-linear least squares optimization to the form

\[ I_A(t) = A \sqrt{t} \exp(-q^2 \alpha t) + B, \]

(6.5)

where \( A \) and \( B \) are constants, to uniquely determine the thermal diffusivity of the sample in question. This method has been used to study thermal transport in a variety of systems including thick PbTe films [58], bulk SiGe alloys [157], and bulk GaAs [162]. However, as mentioned above, measurements of this type do not retain any information related to acoustic properties as those properties are uniquely contained in \( u(t) \). In addition, measurements made in this manner rely on an absolute calibration of the heterodyne phase used in experiment, which is practice is quite difficult. If measurements are collected at heterodyne phases off from 0 or \( \pi \), some contribution to the signal intensity will be made by the displacement response and fitting to Eq. (6.5) will not return the correct value for thermal diffusivity. Johnson et al. note this strict phase requirement and recommend the use of a reference sample for phase calibration [58]. Absolute optical measurements of heterodyne phase without the use of a reference sample are possible, but implementing these methods may not be practical for all applications [163].

### 6.3.2 The phase grating

In comparison, making a complete phase grating measurement requires taking the difference of two measurements made at \( \phi_1 = \pi/2 \) and \( \phi_2 = -\pi/2 \). Excluding the contribution of \( u(t) \) due to acoustic oscillation, the complete phase grating signal is given by

\[ I_P(t) = A \left[ \text{erfc} \left( \frac{q \sqrt{at}}{\sqrt{t}} \right) - \frac{\beta}{\sqrt{t}} \exp \left( -q^2 \alpha t \right) \right] + B, \]

(6.6)

where \( \beta \) is a constant describing the ratio of displacement and reflectivity contributions and \( A \) and \( B \) are again amplitude constants. Fig. 6-2 shows the displacement, reflectivity, and complete phase grating response calculated based on Eq. (6.6) for best-fit parameters from a measurement at 6.39 \( \mu m \) on Ge and Fig. 6-3 shows measured amplitude and phase grating data for an excitation wavelength of 4.8 \( \mu m \).

Unlike amplitude grating measurements, Eq. (6.6) is robust against small changes in heterodyne phase. A phase
Figure 6-2: Components of the phase grating thermal transport model calculated using Eq. (6.6). Parameters are extracted from one measurement point on a \{111\} Ge sample as $\Lambda = 6.39 \text{ um}$, $\alpha = 0.267 \text{ cm}^2/\text{s}$, and $\beta = 2.25 \times 10^{-5} \text{ s}^{1/2}$.

A grating measurement made at $\phi_1 = \pi/2 + \delta_1$ and $\phi_2 = -\pi/2 + \delta_2$ for $\delta_i \ll \pi/2$ will, by Taylor expansion, follow

$$I_{\text{tot}} = A \left[ u(t) + cr'(t)(\delta_1 + \delta_2) - dr''(t) \right] + B$$

$$= A \left[ \text{erfc} \left( q\sqrt{\alpha t} \right) + \frac{c(\delta_1 + \delta_2) - d}{\sqrt{t}} \exp \left( -q^2 \alpha t \right) \right] + B$$

$$= A \left[ \text{erfc} \left( q\sqrt{\alpha t} \right) - \frac{\beta}{\sqrt{t}} \exp \left( -q^2 \alpha t \right) \right] + B$$

(6.7)

where $c$ and $d$ above are constants which may be combined with the phase offsets $\delta_i$ to give the fitting constant $\beta$. This expression is, of course, the same form as Eq. (6.6). Therefore, in practice, phase grating measurements need be made only by roughly optimizing the heterodyne phase to the correct value and thermal parameters may still be extracted.

This approximate optimization may be conducted by making use of the acoustic component of $u(t)$. These oscillations are evident in Fig. 6-3, and the inset shows the Fourier transform of the response, by which the dominant frequencies may be easily identified. By adjusting $\phi$ to $\pm \pi/2$, the amplitude of these acoustic oscillations will be maximized. By using the real-time Fourier transform capability of any modern digital oscilloscope, $\phi$ may be set and manually optimized to very close to this value by maximizing the intensity of the peak due to acoustic oscillations. Phase grating responses optimized in this manner do not require absolute phase calibration and thermal diffusivities fit to such profiles are insensitive to small deviations in heterodyne phase. All phase grating measurements carried out here use this method of optimization.
Figure 6-3: Experimental amplitude and phase grating data for $\Lambda_0 = 4.8$ µm on a \{011\} Ge crystal. The inset shows the filtered Fourier transform of both amplitude and phase grating responses. The retention of a small peak in the Fourier transform of the amplitude grating data indicates either a slight offset in the heterodyne phase or a small pump/probe spatial mismatch.

### 6.3.3 Parameter estimation

Two major difficulties arise in naively using a standard non-linear least squares optimization algorithm with Eq. (6.6) to extract thermal diffusivity values from TGS measurements. The presence of the imposed acoustic oscillation from $u(t)$ is not taken into account in Eq. (6.6) and complicates finding robust optimal values for $\alpha$. This detail is discussed at length in Section 6.4. Additionally, for some values of $\alpha$ and $\beta$ a naïve fit will tend to ignore the maximum in the thermal response profile seen at $t_0$ in Fig. 6-2. In these cases, the value of $\beta$ is underestimated; the fit parameters represent a local minimum and will not return an accurate value for $\alpha$. This tendency can be overcome by providing a good initial guess for both $\alpha$ and $\beta$, which is often possible when measuring materials with known or expected properties.

However, for materials with unknown properties, providing these initial estimations may be problematic. In these cases, it is possible to pre-compute initial guesses for $\alpha$ and $\beta$. For profiles with a maximum present, the location of $t_0$ can be found analytically by solving

$$\left. \frac{\partial I_P(t)}{\partial t} \right|_{t_0} = 0,$$

which yields the following expression for $t_0$:

$$t_0 = \frac{\beta}{2} \left[ \frac{q\sqrt{\alpha}}{\sqrt{\pi}} - \beta q^2 \alpha \right]^{-1}.$$

By noting that this expression is only physically meaningful if $t_0 > 0$, the maximum value of $\beta$ possible for this feature to appear is

$$\beta_{\text{max}} = \frac{1}{q\sqrt{\pi\alpha}},$$

for a measurement conducted with a given value of $q$ on a material with a thermal diffusivity $\alpha$. This expression
becomes of use when noting that simple maxima may be easily identified using standard data processing tools. Therefore, when attempting to extract values for thermal diffusivity from TGS measurements with no prior knowledge of the expected value (like the phase grating measurement in Fig. 6-3), we may pre-compute guesses for $\alpha$ and $\beta$ using a simple algorithm and by noting that Eq. (6.9) may be inverted to read

$$
\beta = \frac{q\sqrt{\alpha}}{\sqrt{\pi}} \left[ q^2 \alpha + \frac{1}{2t_0} \right]^{-1}.
$$

(6.11)

The pre-computation algorithm then proceeds by the following steps:

1. Find $t_0$ from the measured response by taking the location of the absolute maximum of the profile.
2. Perform an initial fit to the measured data using solely an erfc($\cdot$) to describe the thermal decay. This provides an initial estimation for $\alpha$.
3. Calculate an initial estimate of $\beta$ using Eq. (6.11), $t_0$, and the initial estimate of $\alpha$.
4. Re-fit the measured response to the form of Eq. (6.6) by fixing $\beta$ to the calculated value and varying only $\alpha$.
5. From the new value of $\alpha$, re-compute $\beta$ using Eq. (6.11) and $t_0$.
6. Iterate steps 4 and 5 until the values of $\alpha$ and $\beta$ converge.

For an idealized thermal decay which includes no acoustic oscillation, this procedure should converge to the true value of $\alpha$ and $\beta$. However, the acoustic oscillation normally included in $u(t)$ most often causes a value of $t_0$ to be found which is close to, but not the true value of $t_0$ as determined by Eq. (6.9). However, these values may be taken as initial guesses in a full fit of Eq. (6.6), allowing all four parameters ($A$, $B$, $\alpha$, and $\beta$) to vary. It is the output of this final fit which is indicative of the true value of thermal diffusivity for a given TGS measurement. All analysis carried out here uses this pre-computation method with a fixed number of iterations (10, in this case) to supply starting points for the optimization of $\alpha$ for each profile.

### 6.3.4 Acoustic oscillations

Previously, Hofmann et al. have used phase grating TGS measurements to determine changes in the thermal performance of ion irradiated tungsten [127]. In their case, phase grating measurements were necessary due to the lack of a discernible amplitude grating response. Physically, this indicates that there is very little change in the reflectivity of tungsten as a function of temperature. This allowed them to fit phase grating measurements to a form of Eq. (6.3) only, without needing to include the second term present in Eq. (6.6). They noted that the best fit value of $\alpha$ from their procedure seemed to depend on the starting point at which the profile was fit with respect to the observed acoustic oscillation. However, by fitting their data to Eq. (6.3) with the addition of a decaying sinusoidal oscillation, the variation in the best-fit value of $\alpha$ at different fit start times was reduced.

This variation in best-fit value with fit starting time is also observed in the data collected here, which includes a non-negligible contribution in reflectivity change in the phase grating response. Therefore, like Hofmann et al., data here are also fit with the addition of a decaying sinusoidal contribution to account for acoustic oscillations. Following parameter pre-computation, the final fit to experimental data is of the form

$$
I_P(t) = A \left[ \text{erfc} \left( \frac{q\sqrt{\alpha}t}{\sqrt{\pi}} \right) - \frac{\beta}{\sqrt{t}} \exp \left( -q^2 \alpha t \right) \right] + B \sin (2\pi ft + \theta) \exp (-t/\tau) + C,
$$

(6.12)
where \( A, B, \) and \( C \) are amplitude constants, \( f \) is the frequency of the acoustic oscillation, \( \theta \) is the acoustic phase, and \( \tau \) is the acoustic decay constant. In this fit the free parameters are \( A, B, C, \alpha, \beta, \theta, \) and \( \tau \). The acoustic frequency \( f \) is not taken as a free parameter, unlike the procedure followed by Hofmann et al., as that frequency is easily identifiable by analyzing the power spectrum of the measured response (see Fig. 6-3). For each fit, that frequency and the grating wave vector, \( q \), are provided as fixed parameters.

Similar to the estimation steps taken for the parameters \( \alpha \) and \( \beta \) prior to complete non-linear optimization, the acoustic decay parameter \( \tau \) may be estimated by one of several methods and provided as a start point for the fit to Eq. (6.12). First, this decay time may be estimated from the Q-factor of the power spectrum of each measurement. The Q factor is computed by fitting the peak in the power spectrum to a Lorentzian to extract the full-width at half maximum, \( \Delta f \), and peak frequency \( f_0 \). As \( Q = f_0 / \Delta f \) the decay time is then computed as

\[
\tau = \frac{Q}{\pi f_0} = \frac{1}{\pi \Delta f}. \tag{6.13}
\]

However, for measurements made on materials with non-lossy acoustic modes, such as the pure SAW modes measured here, the acoustic decay should be dominated by the ‘walk-off’ effect. Namely, as the two counter-propagating acoustic waves which comprise the standing surface acoustic wave under investigation propagate out of the excitation area, that standing wave intensity decays [164]. If the beam spot size in the wave propagation dimension is given by \( 2a \), then the walk-off time will be \( \tau \approx a / v_g \), where \( v_g \) is the group velocity of the acoustic mode in question. For the measurements conducted here on single crystal Ge, the SAW modes should be nearly dispersionless, meaning that we have the ability to estimate the walk-off time from the phase velocity, \( v_p \), measured directly in experiment as

\[
\tau = \frac{a}{v_p} = \frac{a}{f_0 \Lambda}. \tag{6.14}
\]

Fits using either of these estimations as starting points for the final optimization may be used, and either may perform better depending on the conditions of the experiment and the character of the acoustic modes present. For this work, a constant fixed starting value, the walk-off estimation, and the Lorentzian fit estimation for \( \tau \) were found to produce identical final results. The walk-off and Lorentzian fit estimations for \( \tau \) were both found to slightly under-predict the final optimized value with the walk-off estimate on average being closer. For the data presented below, we have used the walk-off estimation method for all analysis to further remove arbitrarily-chosen fitting parameters.

### 6.4 Results and discussion

In the analysis of phase grating thermal transport measurements, the primary challenge arises from the necessity of choosing a time at which to begin the fit of either Eq. (6.6) or Eq. (6.12) to experimental data. In previous studies using amplitude grating measurements to determine thermal diffusivity, the choice of fit start time is not complicated by the presence of an acoustic oscillation. The choice is determined, rather, by noting that the \( t^{-1/2} \) dependence in Eq. (6.2) arises due to a contribution from cross-plane diffusivity into the bulk of the material and not from the in-plane diffusion of heat from grating peak to trough. In these cases, good fits to experimental data may be found simply by starting the fit late enough to not be influenced by the divergence in Eq. (6.2) at \( t = 0 \), and therefore a fixed starting point may be chosen which is appropriate for a wide range of measurements.
Figure 6-4: Variation in best fit value of $\alpha$ with changing fit start time for measurement at 6.4 $\mu$m grating spacing on \{111\} oriented Ge. The solid line is the best-fit value using Eq. (6.6) and the dashed line is the best-fit value using Eq. (6.12). An initial saturation period followed by oscillation in $\alpha$ at the acoustic frequency are characteristic features observed for all measurements. The vertical line denotes the final null-point start time chosen for this measurement.

This singular choice of fitting start time it not appropriate when fitting phase grating TGS measurements. Fig. 6-4 shows the variation in the final best-fit value of effective thermal diffusivity found using both Eq. (6.6) and Eq. (6.12) as a function of the fit start point on the \{111\} Ge sample, measured at 6.4 $\mu$m. The point $t = 0$ is calibrated as the time of laser impulse, determined in this case by location of the peak intensity in amplitude grating measurements made in this geometry, as in Fig. 6-3. This point is determined by experimental optical geometry and electronic settings and may reasonably be characterized once for a series of measurements. For fits conducted both with and without a sinusoidal variation, the best-fit value of $\alpha$ is initially underestimated at very short time scales. Following the rapid increase in best-fit value, the fit values saturate and then oscillate fairly consistently. In both cases, these oscillations in diffusivity value occur at the same period as the acoustic oscillation present, in this case at 2.28 ns.

For fits to Eq. (6.6), oscillations in $\alpha$ are out-of-phase with the acoustic oscillation, i.e. maxima in the fit value of the effective diffusivity do not correspond to maxima in the recorded signal. In contrast, fits to Eq. (6.12) show smaller amplitude oscillations which are in-phase with the acoustic oscillations in the recorded signal.

After the initial saturation period, for the example trace in Fig. 6-4 the deviation in the best-fit value for $\alpha$ over one acoustic period is $\Delta \alpha/\alpha = 9.3\%$ when fitting to Eq. (6.6). When fitting to Eq. (6.12), this deviation over one period is reduced to $\Delta \alpha/\alpha = 3.5\%$. This trend of a reduction in deviation with the inclusion of a decaying sinusoidal term is consistent across phase grating data at different grating spacings. It is also consistent with the work of Hofmann et al., who noted a reduction in this deviation from 6% to 1% when including the same oscillatory term [127]. The poorer performance in the case presented here is likely due to the added complexity of the non-negligible reflectivity component in the phase grating response. Nevertheless, the reduction in deviation using Eq. (6.12) strongly motivates the use of this form to fit phase grating data of this type.

The total uncertainty on thermal diffusivity values measured using amplitude gratings is reported by Johnson et al.
to be in the range of 2-3% [58], making the performance variation shown in Fig. 6-4 less than ideal. One method of combating this variation would be, for every measurement analyzed, to perform a series of fits to the data using sequential start times over one acoustic oscillation period following the saturation period. The average of these sequential fits could then be used as the ‘best-fit’ value for the measurement. This procedure is potentially quite computationally expensive, especially for measurements with low frequency acoustic oscillations.

Instead, a fixed null-point start time selection criterion may be established to provide results that are consistent with averages made over an entire acoustic period. Fig. 6-5 describes these null points by showing both a complete measurement made at 5.5 μm on a {001} Ge sample in addition to an insert showing the first 5 ns of the same trace after shifting $t = 0$ to the laser impulse time. The null-points in the inset are computed as mid-points of sequential maxima and minima in the recorded measurements. Since the oscillations in best-fit values of $\alpha$ are found to be in phase with recorded acoustic oscillations, these null-points are good indications of the mean value of the oscillation shown in Fig. 6-4. Therefore, by picking one of these null-points as the start position of the fits to Eq. (6.12) a self-consistent best choice fit start point may be selected individually for each measurement analyzed.

The performance of each null-point start may be evaluated, in this case, by direct comparison of the extracted effective thermal diffusivity to that calculated using the method of Huberman et al. This comparison indicates that the choice of null-point 2, as indicated in Fig. 6-5, is the most consistently appropriate choice for start times for fits to this type of phase grating data. For the example measurement analyzed in Fig. 6-4, this null-point start time is $t_2 = 2.00$ ns, and is indicated by the dashed vertical line on that plot. For that trace, the best-fit effective thermal diffusivity is $\alpha = 0.252 \pm 0.003$ cm$^2$/s, where the uncertainty is the 1σ confidence interval on the fit value. In comparison, the average value of the effective thermal diffusivity fit using Eq. (6.12), taken over one acoustic period using $t_2$ as the
Table 6.1: Average fit start times used for TGS measurement at each grating spacing used on pure Ge. All measurements use a null-point 2 start except for one third of the measurements made at 3.6 µm which use a null-point 3 start, leading to the relatively large variation.

<table>
<thead>
<tr>
<th>Grating spacing [µm]</th>
<th>Final fit start time [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6</td>
<td>1.11 ± 0.35</td>
</tr>
<tr>
<td>4.8</td>
<td>1.36 ± 0.05</td>
</tr>
<tr>
<td>5.5</td>
<td>1.48 ± 0.03</td>
</tr>
<tr>
<td>6.4</td>
<td>2.01 ± 0.05</td>
</tr>
<tr>
<td>8.5</td>
<td>2.79 ± 0.02</td>
</tr>
<tr>
<td>9.8</td>
<td>3.21 ± 0.02</td>
</tr>
</tbody>
</table>

center point, is $\alpha = 0.248 \pm 0.009$ cm$^2$/s, indicating that the null-point 2 start does in fact capture the behavior of the period-averaged effective thermal diffusivity accurately.

Null-point 2, therefore, is taken as the start point of choice and each TGS measurement is analyzed using a fit to Eq. (6.12) following parameter pre-computation as described in Section 6.3.3. The exception to this proscription is the data collected at $\Lambda_0 = 3.6$ µm on the {111} oriented sample. That series of measurements includes an intensity spike which is large compared to the oscillation intensity at the time of the pump laser impulse. This feature interferes with optimization to Eq. (6.12) at short times. As a consequence, those ten measurements are fit using a null-point 3 start instead of null-point 2. The average and standard deviation in fit start times for each grating spacing are given in Table 6.1. The deviation in start times for 4.8 and 6.4 µm measurement are relatively greater than those for the 5.5, 8.5, and 9.8 µm measurements as the location of the null-points depends on the principle acoustic frequency of each measurement, and this frequency will change as a function of crystal surface and direction. For measurements made at 3.6 µm, the large variation in start time is due to the third of the data set using null-point 3 as opposed to null-point 2. Nevertheless, this start time is extremely consistent across measurements at a given grating spacing and null-point; the deviation at each applied grating spacing at a fixed null-point is less than or equal to the oscilloscope time step of 0.05 ns.

Using this framework, the best-fit effective thermal diffusivity, taken as the average of 30 measurements at each grating spacing, is shown in Fig. 6-6 plotted versus the calculated value for 1D thermal transport at each wavelength. Here, averages which are taken over three Ge crystal orientations, ⟨100⟩{001}, ⟨111⟩{011}, and ⟨112⟩{111}, are indicated by diamond symbols and averages of measurements made only on the {001} oriented sample are indicated with circles. Calculations of the 1D effective thermal conductivity from the BTE are converted to thermal diffusivity using standard values for Ge density and heat capacity at room temperature [165]. These experimentally determined values for effective thermal diffusivity agree well with those predicted by the model. Error bars are given as the standard deviation of the spatially averaged data points at each grating spacing. Calculated in this way, errors range from a maximum of $\Delta \alpha/\alpha = 7.2\%$ for measurement at 6.4 µm to a minimum of 1.7% at 8.5 µm. Averages which are taken over multiple samples consistently show larger deviations, which is to be expected.

In addition to the final best-fit values for thermal diffusivity, it is also instructive to inspect the best-fit profiles to each measurement. Example experimental traces with two forms of the best-fit profile are shown for each grating spacing in Fig. 6-7. These plots show both the final fit for the data using Eq. (6.12) as well as profiles generated using all the
Effective Thermal Diffusivity [cm\(^2\)/s]

Figure 6-6: Average best-fit effective thermal diffusivity versus applied grating wavelength, \(\Lambda\). Diamond symbols indicate measurements taken on three Ge crystals at different orientations and circles indicate measurements taken only on the \{001\} Ge crystal. The solid line indicates the expected thermal diffusivity at these wavelength calculated using a variational solution to the BTE.

The same best-fit parameters, except for setting the sinusoidal decay constant to \(\tau = 0\). This has the effect of generating a profile that appears to trace the centroid of the acoustic oscillation. It is perhaps easier to qualitatively judge the performance of the fit profile in this manner. Fits reproduce the measured behavior quite well in general. The one parameter that visually does not fit as well is the acoustic decay parameter, \(\tau\). The exponentially decaying term in Eq. (6.12) is currently a phenomenological model. Deviations from that behavior in particular are not considered physically significant in this analysis and further investigation into the governing mechanisms of that decay may yield more appropriate models.

The optimization methods developed here have only considered TGS phase grating responses containing one dominant acoustic mode. However, responses with multiple acoustic modes are often seen in practice, for example Lamb modes in thin films or pseudo-surface acoustic modes in anisotropic crystals [83,88]. For multi-mode propagation, appropriate terms would need to be added to Eq. (6.12) for each mode, and a systematic study conducted to determine a generalized n-mode null-point start criterion.

6.5 Conclusions

This chapter has explored the use of phase grating TGS measurements in determining thermal transport properties of opaque materials. Major takeaways from the analytical and experimental work carried out here include:

- Phase grating TGS measurements have thermal responses characteristics which are insensitive to small changes in heterodyne phase. This allows for characterization without careful control of the absolute heterodyne phase, easing previous practical experimental constraints.

- Best-fit profiles to phase grating data should use the form of Eq. (6.12) to minimize the effect of acoustic
oscillations on the final value of $\alpha$.

- Using the characteristic maximum at $t_0$, model parameters may be estimated in the case that prior information regarding the thermal performance of materials under study is unavailable.

- A fixed null-point start time method allows for self-consistent fitting to measurements made with different acoustic periods without the need for performing many fits over an entire acoustic period.

- Thermal characterization carried out using these best practices can capture wavelength-dependent thermal transport in germanium with spatially averaged errors on the order of a factor of two greater than amplitude grating TGS characterization.

It is important to recall that the motivation for using the phase grating response is the presence of the acoustic component of the surface displacement which it contains. By using the best practices delineated here, both acoustic (and therefore elastic) property determination and thermal transport determination may be carried out concurrently on a wide variety of materials. This ability is a particularly powerful tool when coupled to experimental TGS implementations designed as time-resolved diagnostics for dynamically changing materials systems. Given the non-contact and non-destructive nature of TGS interrogation, the possibilities for future study using these methods are extremely broad.

With the results of this chapter in hand, all four of the necessary functionalities of TGS delineated at the end of Chapter 2 have now been demonstrated. To recap: in Chapter 3, theoretical sensitivity to radiation effects was shown through a series of sensitivity experiments and coordinated MD modeling; in Chapter 4, high-dose radiation effects in the form of self-ion induced void swelling were measured in single crystal copper; in Chapter 5, a new optical
geometry was implemented which allows for phase grating TGS measurements to be made with a temporal resolution on the order of 10 seconds; and finally, the analytical techniques developed in this chapter show that phase grating measurements may be analyzed reliably to extract both thermal and elastic material properties simultaneous. Given the success of the experiments described in Chapter 4, the Ion Beam Laboratory at Sandia National Laboratories was chosen as the location to construct a first-of-a-kind in situ TGS ion irradiation facility as the primary goal of this thesis.
Chapter 7

Real-time property monitoring during ion beam irradiation using \textit{in situ} TGS

This chapter describes a facility for continuously monitoring the thermal and elastic performance of materials under exposure to ion beam irradiation which has been designed and commissioned as the primary goal of this thesis. By coupling a transient grating spectroscopy (TGS) optical diagnostic to a 6 MV tandem ion accelerator, bulk material properties may be measured at high fidelity as a function of irradiation exposure and temperature. Ion beam energies and optical parameters may be tuned to ensure that only the properties of the ion-implanted surface layer are interrogated. This facility provides complementary capabilities to the set of facilities worldwide which have the ability to study the evolution of microstructure \textit{in situ} during radiation exposure, but lack the ability to measure bulk-like properties. Here, the measurement physics of TGS, design of the experimental facility, and initial results using both light and heavy ion exposures are described. Finally, several short- and long-term upgrades are discussed which will further increase the capabilities of this diagnostic. The work presented in this chapter is primarily sourced from Dennett et al., \textit{Nucl. Instrum. Meth. Phys. Res. B} \textbf{440} (2019) 126–138 [166].

7.1 Introduction

One major challenge in developing new materials for radiation environments is the timescale on which exposure and post-irradiation examination (PIE) is normally carried out. Due to physical and radiological constraints, improving the standard “cook and look” test cycle is difficult for high-dose neutron exposures. However, ion beam irradiation is increasingly being used to emulate neutron environments seen in practice [14,15] and for the study of fundamental properties of radiation-solid interactions, in general [167]. Extracting thermal and mechanical performance information – which determine a suitability for service – from ion irradiated samples is challenging, requiring specialized nanomechanical PIE methods to extract property information from the small damaged volume [168,169]. Here, transient grating spectroscopy (TGS) has been identified as a methodology with the ability to extract bulk thermal and mechanical properties from ion-exposed samples continuously, as irradiation is ongoing. The ability to observe changes in performance properties in real time with \textit{in situ} TGS, at the appropriate length scale, would allow for high-resolution mapping of dose-property relationships at a fidelity and speed not previously possible. In addition, such a tool could be used for detecting emergent irradiation-induced microstructural evolution such as the transition
From incubation to steady-state void swelling [9,16]. Together these capabilities would make in situ TGS an extremely powerful tool in the design of new materials being placed in service in extreme conditions including radiation.

With the demonstrated functionalities of the previous four chapters of this thesis in hand, an in situ ion irradiation TGS (I³TGS) experiment has been designed, constructed, and tested on a 6 MV tandem accelerator at the Sandia Ion Beam Laboratory (IBL). This facility is the most recent addition to the suite of in situ irradiation facilities at the IBL, which include a transmission electron microscope (I³TEM) [18] and a scanning electron microscope (I³SEM), both of which include ion beams from the same 6 MV tandem. Given the relative novelty of TGS as a method for monitoring irradiation-induced microstructural evolution, a short physical process description will be given before the I³TGS facility is described in detail. Prior to installation onto the ion beamline, the optical system comprising the core of the facility was constructed and tested on the bench top. These tests are described to confirm normal performance. Following beamline installation, a static, high-temperature test is conducted to ensure stability up to a sample temperature of 600°C. Two in situ experimental tests are described which demonstrate the capabilities of the I³TGS facility to monitor acoustic wave speeds and thermal diffusivity under both light and heavy ion irradiation. In particular, parameters for the heavy ion irradiation case are chosen such that volumetric void swelling, the canonical degradation mode of interest in this thesis, is induced. Finally, several areas for improvement are discussed and current development steps described. All original data files generated during the course of this work and code used for analysis/processing can be found in the permanent GitHub repository for the manuscript where this work was originally published [170].

7.2 In situ TGS ion beamline facility

7.2.1 Transient grating spectroscopy

The details of the physical processes utilized for excitation and detection in transient grating spectroscopy (TGS) have been described in already in this thesis. In particular, Chapter 3, Chapter 5, and Chapter 6 each describe the theory behind the methodology, the particular optical implementation which will be used in this new facility, and the steps necessary to extract multi-property information, respectively. An example recorded TGS measurement made using the facility which will be described in this chapter is shown in Fig. 7-1 including the results of the model fitting procedure used to extract in-plane thermal diffusivity. As a reminder, acoustic wave speeds – and therefore elastic properties – and thermal transport information are recorded over different effective length scales for a single TGS experiment. The penetration depth of the mechanical actuation is taken as the excitation wavelength, Λ, as both the stress and displacement profiles have exponentially decayed to 1/e of their maximum values by that depth [137,171]. Therefore, by tuning the ion energy and excitation wavelength, the elastic properties of only the ion-damaged region near the surface may be probed by monitoring the acoustic wave speed [66,67,127]. The thermal depth sensitivity is Λ/π such that only the thermal transport properties of an even nearer-surface region are probed for a fixed Λ [58,65]. This thermal penetration depth is determined as the thermal diffusion depth over the characteristic time scale of the thermal decay, τ = (Λ/2π)²/α, where α is the in-plane thermal diffusivity [89]. The ion energy chosen for exposure may be chosen to match this thermal penetration depth rather than the mechanical actuation depth if changes in thermal performance are expected in a particular material. Ferry and coworkers demonstrated just this capability for
Figure 7-1: Example TGS measurement from the 31 MeV Ni$^{5+}$ in {001} Ni in situ measurement described in this work. (a) includes the entire recorded TGS trace averaged over 1000 laser shots and the inset shows the filtered Fourier transform of the response. (b) shows the first 120 ns of the recorded response fit to a model to extract the thermal diffusivity [59].

low-dose ion irradiation of refractory metals [172,173]. For the demonstration tests shown in this chapter a damage length scale is chosen which is appropriate for elastic properties.

7.2.2 İTGS facility components

A schematic of the initial configuration of the İTGS facility is shown in Fig. 7-2 and photographs are shown in Fig. 7-3. The facility target chamber is designed such that samples may be placed at the coincidence point of an ion beam from the 6 MV EN Tandem Van de Graaff-Pelletron accelerator and the six laser beam paths used for TGS excitation and detection. A wide variety of ion beams may be generated in this machine ranging in mass from H to Au with a lower energy limit of 800 keV and an upper beam energy limited by various effects including neutron hazards and charge state selection. For example, beams as energetic as 4.5 MeV H and 100 MeV Au have been generated. Fig. 7-2(a) shows the overall layout of the target chamber with approximations of the ion and laser beam paths shown. Samples are placed roughly normal to the incident ion beam and with a surface angle of roughly 45° to the incident laser beam paths. Deviations from normal and 45° are significant and will be described in detail shortly. Each sub-component of the facility is placed with a representative geometry and labeled in this overview schematic. During the development of this facility, benchtop optical optimization and beamline vacuum system construction occurred in parallel. This division is made possible by mechanically decoupling the vacuum and optics systems. Therefore, all optical enclosures may be removed from their placement around the target chamber for major realignment, if ever necessary.

The optical arrangement of the launch side of the TGS system is shown in Fig. 7-2(b). Excitation is accomplished using a 532 nm, Q-switched pump laser with a pulse length of 400 ps, an average pulse energy of 23 µJ, and a repetition rate of 1 kHz (TEEM Photonics PNG-M02010-130). Probing is carried out using a 785 nm, narrow linewidth, CW laser system comprised of a solid state seed laser (Newport SWL-7513-P) fiber coupled into a semiconductor taper amplifier (Newport TA-7613-H) with a maximum output of 2 W. To reduce the total laser power incident on the sample, the probing laser is modulated to a 25% duty cycle with an optical chopper wheel locked at 1 kHz to the pulse train of the pump laser (digital pulse generator Directed Energy, Inc. PDG-2520). During normal operation
Figure 7-2: Schematic of the T3TGS facility. An overview of the experimental target chamber is shown in (a) and the spatial locations of each of the other sub-figures are indicated. The top-down view of the launch-side optical components which form the core of the TGS facility are shown in (b) and the collection side optics and electronics are shown in (c). A front view of the spatial location of all six laser beam paths entering the target chamber in the plane of the launch-side vacuum window is shown in (d). Ion beam optics and diagnostics immediately upstream of the target chamber are shown in (e).
Figure 7-3: Photographs of the I³TGS facility (a) from above the beamline and optical boxes, (b) of the laser launch side including laser control rack, and (c) of the detection side including control and data acquisition (DAQ) computer. The screen image in (c) shows the TGS DAQ during an in situ experiment.
neither pump nor probe lasers are operated at their full power output as those power levels have been seen to
damage, via melting or ablation, material surfaces in low vacuum or ambient conditions. Power from the pump laser
is controlled using a manually adjustable, variable optical density (OD), reflective neutral density filter placed at
an angle immediately following the laser output such that the reflected intensity is not directed back into the laser
cavity. Probing output power is managed through the digital power supply for the probe tapered amplifier. Normal
operational parameters are an OD 0.3 filter placed in the pump laser path leading to a power immediately prior to the
phase mask of 11.5 mW and a power on the sample surface of 5.2 mW, which indicates the surface is being pumped
at 5.2 µJ per pulse. Tapered amplifier output is normally set to 30% of the maximum, with a measured output
power immediately prior to the phase mask of 121 mW and a power on the sample surface of 13.5 mW. The phase
mask is custom designed to provide highly efficient diffraction of 532 nm light into the ±1 diffraction orders and to
include many areas patterned at different wavelengths (manufactured by Nanopteron Inc.) At normal incidence prior
to installation on the beamline, the spot size of the pump and probe at the sample position are measured (horizontally
× vertically) at $170 \times 200 \mu m^2$ and $100 \times 90 \mu m^2$, respectively with an estimated error in each dimension of ±10 µm.

As seen in Fig. 7-3, both laser launch and detection stages are housed in light-tight enclosures, whose only opening
mechanisms are interlocked to both pump and probe lasers. Additionally, custom 3D printed optical couplers allow
a sliding light-tight seal to be made between the lens tube on the outside of each containment box and the vacuum
window. Therefore, despite potentially operating as a Class 4 laser experiment when uncontrolled, during beamline
experiments the entire facility is a self-contained Class 1 system, which may be operated with no personnel controls
in place in the IBL tandem experimental hall. Both input and output vacuum windows are high-parallelism widows
with a 1.13” clear aperture, anti-reflection coated for the probe laser wavelength (Thorlabs VPCH42-B). This clear
aperture, along with the clear aperture of the two achromatic lenses that comprise the grating imaging system, will
become important in a discussion of several current limiting experimental factors to follow.

From the final recombination achromatic lens in the launch side optical enclosure, the working distance to the sample
surface inside the target chamber is 180 mm. Since the geometric crossing point of the ion beam and laser windows
is fixed by the port geometry on the target chamber, an extra positioning degree of freedom in line with the laser
propagation direction is needed to ensure that samples will be able to be placed at the correct working distance.
To accomplish this, the entire laser launch side enclosure, as diagrammed in Fig. 7-2(b), is affixed to a 200 mm
linear translation stage with 5 µm positioning resolution (Newport ILS200CC using a SMC100CC controller). This
arrangement is visible in Fig. 7-3(b), where the launch enclosure can be seen affixed via the translation stage to the
support frame. Once the working distance is optimized for laser and ion beam alignment, it should not need to be
modified for each experiment. This set point distance has been optimized at +17.0 mm on the linear staging; all
experiments described here are carried out at this fixed position.

The detection optics and electronics are shown in Fig. 7-2(c). To accomplish repeatable sample alignment, the signal
beampath is centered on the output optical window and passed through a fixed iris in the detection box. It is
important to note that the input and output vacuum windows are both centered 45° from the ion beam pipe by
the physical geometry of the chamber. Output signal centering is accomplished by tilting the sample off-normal
with respect to the ion beam. In this enclosure, the two independent probing channels are separated and directed
into matching Si avalanche photodiodes (APD, Hamamatsu Photonics C5658). Both APD modules are placed in
light-tight enclosures with the optical access only through a narrow width laser line filter. The filters ensure that no scattered light is detected on the 1 mm square APD active area. These modules have a frequency range from 50 kHz–1 GHz ensuring that both acoustic oscillations in the 100s of MHz range and the slow thermal decay of induced grating will be captured. As thermal transport properties will be extracted using model fitting, it is important that the lower frequency cutoff is low enough to ensure that the shape of the decay curve is not affected. The APD output signals are recorded concurrently on a 5 GHz (20 GS/sec), dual band digital oscilloscope (Lecroy Wavemaster 8500A). One APD module is placed on a manual delay stage, such that the distance from sample surface to detection can be very carefully equilibrated between the two channels. This equilibration in concert with the use of matched RF transfer cables, ensures that laser impulses are always recorded at the same timestep on the oscilloscope. Fig. 7-2(d) shows the arrangement of all six laser paths in the plane of the vacuum window between the launch side and the target chamber. The vertical separation of these beam paths is necessary as the individual beams must be picked off and directed into separate APD modules.

Fig. 7-2(e) shows the ion beamline components immediately upstream of the TGS target chamber. Prior to opening the target chamber to the high vacuum beamline, the chamber is pumped to better than $10^{-3}$ Torr using two stages of cryogenic sorption pumping, seen in Fig. 7-3(c). Experiments are routinely allowed to pump overnight on the beamline ion pump such that vacuum levels in the target chamber are approximately $5 \times 10^{-6}$ Torr during exposure. Two dimensions of steering magnets, a focusing quadrupole, and two dimensions of beam slits are used to control the ion beam shape and position on the target. Ion beam current is continuously recorded during exposure by collecting charge from the spinning wire beam profile monitor (BPM). This collected charge is converted to current on-target by manually recording beam current on the Faraday cup downstream of the BPM. The timestep for this charge collection is currently fixed by the 20 nC charge limit on the charge collector. Due to the lack of electron suppression in the current BPM configuration, a sharp jump is consistently noted in the current record when the position of the downstream Faraday cup changes. Therefore, an additional calibration step is taken by equilibrating the average current recorded in the minute prior to cup position change to that in the minute following cup position change. Taken together, these two steps allow for the on-target beam current to be recreated smoothly during the length of the exposure.

The final important beamline component shown in Fig. 7-2(e) is the forward imaging system. As shown, this sub-system consists of a monochrome CCD camera (Watec 902H2 Ultimate camera with Edmund Optics fixed focal length lens #59-871) and a mirror placed on a linear actuator which are connected onto the beamline with a vertical 4-way cross. This mirror is affixed at an angle slightly greater than 45° from vertical and placed just above the centerline of the beam tube, allowing the ion beam to pass clearly underneath. By pointing the CCD camera up at this mirror from below, the surface of the sample inside the target chamber may be imaged at nearly-normal incidence. This forward imaging allows for beam characteristics such as spot size and shape to be measured directly on graded quartz using ion beam luminescence. It also allows for ion beam and laser coincidence imaging to be carried out to ensure that the laser measurement spot is being placed within the exposed area on the sample surface.

Finally, the sample stage is shown in Fig. 7-4. The stage is hung vertically into the target chamber and positioning is controlled by a 4-axis manual stage, these four axes are shown schematically in Fig. 7-4(a). The stage consists of a primary and secondary position. The primary position, Fig. 7-4(b) and (c), consists of a 1/2" diameter high
temperature resistive button heater held in a refractory metal heat shield (Heatwave Labs 101137). The heating

element is rated up to 1200°C by the manufacturer but has been tested only to 600°C (Section 7.4.1). Samples

are held in contact with the surface of this heater using up to three sample clips. One of the sample clips has a

0.01” diameter, type K thermocouple spot-welded to the tip, which is placed in physical contact with the sample

surface. This surface thermocouple is used for temperature monitoring and control in concert with a phase angle

drilled power supply rated up to 16 V and 94 A (Heatwave Labs 101303). The power supply is operated using a

custom-built LabVIEW controller to both set and record sample temperature. The secondary position consists of a

simple aluminum plate which has been adjusted to the same height, relative to the stage rod, as the surface of the

button heater. This height tuning is necessary to ensure that as the stage is translated in \( \hat{z} \) between the primary

and secondary positions, the location of the ion and laser beams relative to the surface do not change. The most

common use for the secondary stage, as shown in Fig. 7-4(b), is for a piece of quartz or slide glass with a lined backing

to be placed there and used for imaging of the ion beam size and shape at the sample position prior to exposure.

The backing, in most cases lined 5 mm squares, allow for image sizes from the CCD camera to be calibrated to real
dimensions. The magnification factor (CCD screen):(real space) is 4.3:1 in the current configuration.

For \textit{in situ} testing, coincidence alignment proceeds as follows. With the upstream Faraday cup closed, the stage is

set to the primary position and TGS alignment carried out to generate the optimized dual-channel response. The

position of the laser spot on the sample surface is marked on the CCD camera screen. Next, the lasers are blanked

and the stage translated in \( \hat{z} \) to the secondary position. The Faraday cup is opened, and the ion beam position

visualized using the quartz. Ion beam position and shaping is controlled with the steering magnets, focusing magnet,

and slits until the desired beam shape is co-located on the mark corresponding to the laser location on the CCD

camera. The Faraday cup is then re-inserted and the stage translated back to the primary position. At this point

both temperature and current monitoring, which will remain on continuously throughout the exposure, are started.

The sample is brought up to the desired temperature for exposure and adjustments made to the positioning due to

thermal shifting, if necessary. The TGS monitoring is started prior to opening the Faraday cup to provide baseline,

at-temperature data. Finally, the Faraday cup is opened and the ion beam allowed to impinge on the sample surface

coincident with the TGS laser spot and exposure commences with \textit{in situ} monitoring.
7.2.3 Geometric beam/sample configuration

A schematic of the off-axis sample tilt geometry is shown in Fig. 7-5 for a single pair of probing laser beams. Most TGS experiments utilize a geometry where the sample is placed normal to the incoming laser beam paths. In that case, the projected grating spacing on the surface is uniquely determined by the line spacing of the phase mask and magnification ratio of the two-lens imaging system [57]. That spacing can be described by

$$\Lambda = \frac{\lambda_e}{2 \sin \phi}, \quad (7.1)$$

where $\lambda_e$ is the wavelength of the laser used and $\phi$ is the half angle between the incoming laser paths. In the $\text{I}^3$TGS geometry, that line spacing is increased by a geometric factor as it is being projected at an angle onto the surface under interrogation. If the sample were placed normal to the ion beam path, then that projection angle would be $45^\circ$. But, given the arrangement where the signal is centered in the output window, the sample must be rotated towards the incoming laser beams, therefore reducing the angle at which the grating is being projected. Given that the optical arrangement uses a 1:1 imaging system, Eq. (7.1) may be inverted to say,

$$\phi = \arcsin \left( \frac{\lambda_e}{2 \Lambda} \right), \quad (7.2)$$

as a function of nominal grating spacings known from the phase mask. This angle $\phi$, then, is the amount the sample must be rotated away from normal to the ion beam to achieve the desired centering. Therefore, the actual projected grating spacing on the sample surface in this configuration may be written as

$$\Lambda' = \frac{\Lambda}{\cos \left( \frac{\pi}{4} - \arcsin \left( \frac{\lambda_e}{2 \Lambda} \right) \right)}, \quad (7.3)$$

Figure 7-5: Top-down schematic of sample geometric arrangement with respect to incident probe laser beams and ion beam. All beam paths drawn not labeled “ion beam” are 785 nm probe laser paths, differences in color are for clarity only. The angle $\phi$ is described in Eq. (7.2).
where again $\Lambda$ is the nominal grating spacing provided as a specification from the manufacturer of the phase mask. For example, the shortest wavelength currently usable on the I$^3$TGS facility is $3.7 \, \mu m$ on the phase mask. In this case Eq. (7.2) and Eq. (7.3) indicate that the sample will need to be rotated $6.1^\circ$ off of the ion beam normal which produces a projected grating spacing of $\Lambda' = 4.76 \, \mu m$.

In practice, $\Lambda'$ is calibrated with the use of a reference sample for each in situ exposure (or set of exposures if several similar tests are carried out sequentially). This is normally accomplished using a reference sample of $\{001\}$ single crystal tungsten. Tungsten is the most elastically isotropic pure metal and the acoustic wave speed expected on the $\{001\}$ surface can be calculated using aggregate values of elastic constants from the literature [90–92] and elastic theory using the method of Du and Zhao [152]. These calculations indicate that at room temperature, the surface acoustic wave velocity on $\{001\}$ tungsten varies by only $0.009\%$ across all surface angles around the mean value of $c_W = 2668.0 \, m/s$, indicating that the calibration sample may be effectively positioned at any orientation. From this value, the calibration is carried out by measuring several spots on the W single crystal surface, extracting the mean peak acoustic frequency from the TGS signals as $f_W$, and calculating $\Lambda'$ as

$$\Lambda' = \frac{c_W}{f_W}. \quad (7.4)$$

Using the nominal $3.7 \, \mu m$ phase mask setting, the calibrated grating spacing for the in situ experiments described later is $\Lambda' = 4.54 \, \mu m$. This value is about $4\%$ smaller than expected based on the formulation of Eq. (7.3) and indicates that the sample surface is rotated to $9.5^\circ$ from normal to the ion beam. This likely occurs due to a combination of imperfect centering of the laser paths in both the launch and detection side vacuum windows and motivates the calibration of the actual applied grating spacing as frequently as possible using this calibration sample. Nevertheless, Eq. (7.3) provides a good initial estimation for setting the experimental grating spacing in this geometric configuration using only the nominal phase mask position. The incidence angle of the ion beam onto the sample surface is also important when calculating the implanted ion and imposed damage profiles. An accurate measure of $\Lambda'$ is critical in determining material properties from TGS measurements as it is used as a fixed parameter in both the calculation of acoustic wave speeds from measured frequencies and in the optimization model for extracting thermal diffusivity [59].

Using the calibrated angle of $9.5^\circ$ from ion beam normal, the projected size of the pump and probe beam spots on the sample surface can be calculated as $210 \times 200 \, \mu m^2$ and $120 \times 90 \, \mu m^2$, respectively.

### 7.3 Benchtop facility performance

Prior to installation on the dedicated I$^3$TGS beaming, the optical components of the system are constructed and optimized on the benchtop to calibrate performance. Specifically, by measuring the surface acoustic response of a well-characterized metallic single crystal, normal operation of the optical system can be confirmed. Practically, conducting the geometric optical alignment in a controlled location is much easier than attempting the alignment in place. In this initial alignment, samples are placed at normal incidence to the incoming laser path such that the projected grating spacing should only be a function of the nominal spacing selected on the phase mask and the magnification ratio of the two-lens imaging system. A series of measurements on a $\{001\}$ oriented Ni single crystal
are conducted to measure the magnification ratio of the as-constructed optical system. Due to the elastic anisotropy of pure Ni \((A = 2.5)\) pure surface acoustic wave (SAW) modes will only exist at certain directions on the sample surface \([88]\). In other directions, pseudo, or ‘leaky,’ surface acoustic wave (PSAW) modes will propagate. These modes typically have higher frequencies and different excitation vs. depth profiles than pure SAW modes as energy is radiated away into the bulk of the material. On the \{001\} surface of Ni, pure SAW modes exist out to about 25° away from the \(\langle 100 \rangle\) surface direction.

For these calibration experiments, TGS measurements are taken at two nominal grating spacings, 5.2 µm and 3.4 µm, primarily over the SAW range, as SAW modes will be those targeted during in situ experiments. Using the calculated elastic response of \{001\} Ni based on single crystal elastic constants from Epstein and Carlson \([174]\), a multi-point calibration is carried out to determine the actual grating spacing, \(\Lambda'\), projected onto the sample. Measurements are made in 5° increments on a manual rotation stage with positioning resolution of 1° over a total range of 35° degrees for each measurement. Surface angles on the Ni samples are not determined prior to measurement; rather, the actual surface angle at which each measurement is carried out is calibrated post-measurement by adding an angular offset and optimized by minimizing the standard deviation of the grating spacing calculated at each point. The results of this process can be seen in Fig. 7-6, where measurements made at both nominal grating spacings are presented. The final multi-point calibration indicates that the actual projected gratings are \(5.22 \pm 0.02\) µm and \(3.40 \pm 0.01\) µm. These values indicate that within experimental error, the imaging system is indeed 1:1, as intended. Thus, relatively good assumptions for available choices of \(\Lambda'\) may be made based on nominal phase mask parameters and Eq. (7.3). These available options are important design points when choosing parameters for in situ testing.

Additionally, the temporal resolution of the measurement system may be tested prior to beamline installation. Each TGS measurement is taken as the average of many individual grating excitations that occur at the pump laser repetition rate of 1 kHz. The number of laser shots over which a desired signal must be averaged is a competition between two effects. As the number of shots averaged increases, the signal-to-noise-ratio of the TGS response, and therefore the certainty of material properties extracted from those responses, increases \([155]\). However, that averaging time should ideally be shorter than some dynamic evolution timescale to ensure that all of the property changes being
Table 7.1: TGS data collection time as a function of laser shots averaged. This performance is linear, with a slope of 0.033 sec/shot and an intercept of 1.7 sec.

<table>
<thead>
<tr>
<th>Number of laser shots</th>
<th>Collection time [sec]</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>250</td>
<td>9.63</td>
</tr>
<tr>
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<td>1250</td>
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<td>1500</td>
<td>50.6</td>
</tr>
<tr>
<td>1750</td>
<td>59.6</td>
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<td>2000</td>
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<tr>
<td>5000</td>
<td>167</td>
</tr>
<tr>
<td>7500</td>
<td>249</td>
</tr>
<tr>
<td>10000</td>
<td>331</td>
</tr>
</tbody>
</table>

induced are captured. This timescale will change for each material system and set of exposure conditions. Table 7.1 shows the signal collection time, in dual-channel operation, as a function of the number of laser shots being averaged. These data are useful reference points for determining what parameters to set for in situ experiments. Note that the measured collection time is dominated by electronic signal collection and processing time; the realized collection time for a 1000 laser shot average is 35 sec and not the 1 sec which may be intuitive given the laser repetition rates. This electronic processing and communication time precludes continuous recording of each laser shot and makes the averaging method described above the most efficient method for recording data. Assuming a fixed signal quality based on number of shots averaged, the overall time resolution of the system could be greatly improved by upgraded collection electronics, primarily the dual-channel scope.

7.4 *In situ* performance

Following optical optimization, the launch and detection side enclosures are set in place on the I³TGS facility as described previously. A series of tests are then performed to demonstrate this facility’s capabilities. Three of these tests are described in detail here. The first is a static high temperature test, with no incident ion beam, to ensure that the staging and vacuum systems are stable and able to operate at high temperatures. Second, to demonstrate performance using light ion beams, a single crystal tungsten sample is exposed to a 3.7 MeV He⁺ beam and monitored using TGS for approximately 10 hours at room temperature. Finally, to demonstrate performance using heavy ion beams, a single crystal nickel sample is exposed to a 31 MeV Ni⁵⁺ beam at 550°C and monitored for approximately 8 hours. Although only two beam types are explicitly demonstrated here, the tandem accelerator has the ability to generate a wide range of ion species and energies. Some of these beams have recently been described in the work by Hattar et al. [18].
Before describing the light and heavy ion tests in detail, a note is required about the nominal dose that each sample will be receiving through its exposure. To calculate the dose in displacements per atom (dpa) that each sample receives, SRIM calculations are carried out using the quick Kinchin-Pease mode [134,135] with a displacement energies specified in the ASTM standard for metals [136]. For each calculation, the ion incidence energy is set to that used in experiment, the incidence angle set to 9.5° to match that determined by the grating calibration, and, if the sample is being exposed at elevated temperature, the density reduced accordingly. As beam spot sizes will routinely be a factor of 10 or more greater than the TGS analysis area, edge effects due to the non-normal beam incidence are not considered. From these SRIM calculations, the dose profiles may be calculated in dpa by using the imaged beam spot size assuming a uniform 2D beam profile and the ion beam current, either monitored continuously or at points throughout the exposure. The results of these calculations for 3.7 MeV He⁺ into W at room temperature and 31 MeV Ni⁵⁺ into Ni at 550°C are shown in Fig. 7-7. The total doses are scaled to the final doses that each sample received at the end of the in situ experiments. Also included are the thermal and acoustic penetration depths for the measured test wavelength of \( \Lambda' = 4.54 \mu\text{m} \). For acoustic properties extracted from TGS measurements, the dose reported for each measurement is the dose linearly averaged over the SRIM profile up to the acoustic penetration depth, \( \Lambda' \).

Similarly, for thermal diffusivity, the dose reported will be averaged over the profile to the thermal diffusion depth of \( \Lambda'/\pi \). Further comments on correlating the measured material response to a particular dose, given the non-linear damage profile incurred under ion bombardment, are provided in the discussion.

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1Following the work presented in this chapter, it was discovered that electron suppression on the beamline Faraday cup used to calibrate ion beam current measurements was not active during the experiments presented here and in Chapter 8. As such, the reported doses in all following experimental results are likely off by a factor of order unity. Exactly how much active electron suppression affects the measured beam current depends on particular parameters of positioning and shaping which vary for each condition tested. Therefore, although all of the major conclusions from the following data remain valid, the doses at which particular features appear should not be considered meaningful.
7.4.1 Static high temperature test

Static high temperature testing is carried out on a \{001\} Ni single crystal whose orientation was confirmed previously during benchtop testing. This material is sourced from a previous study conducted by Zhao and coworkers [175]. Based on previous acoustic measurements, the sample is mounted with the (100) surface direction approximately aligned with the optically-fixed grating polarization. Following sample mounting, the \( I^3 \)TGS target chamber is allowed to pump to \( 4.4 \times 10^{-6} \) Torr at room temperature prior to TGS measurement. Each TGS measurement is taken as the average of 10000 laser shots. Prior to heating, three measurements are taken at room temperature (measured as 23\(^\circ\)C), such that the actual surface angle of the sample may be calibrated from room temperature measurements. The calibrated grating spacing for this measurement is measured as \( \Lambda' = 4.53 \mu \text{m} \), and the measured room temperature speed of \( c_{RT} = 2759.8 \text{ m/s} \) indicates the sample is oriented \( 8 \pm 1^\circ \) from the (100) direction on the \{001\} surface. The orientation determination is again based on the room temperature elastic constants of pure Ni from Epstein and Carlson [174].

However, to facilitate comparison with high-temperature data, the elastic constants and density of Ni are also needed as a function of temperature and Epstein and Carlson do not provide this data. However, they are provided by Alers et al. [176]. Unfortunately, the reference data from Alers is not consistent at room temperature with the variation in SAW speed as a function of surface angle as measured during benchtop testing. Therefore, the temperature dependent elastic constants used for comparison to experimental data, \( C_{ij}(T) \), are taken as

\[
C_{ij}(T) = \left[ C_{ij}^A(T) \right] C_{ij}^E(298 \text{ K}),
\]

where \( C_{ij}^A(T) \) are the temperature dependent fourth-order elastic constants taken from Alers and coworkers, and \( C_{ij}^E(298 \text{ K}) \) are the set of room temperature constants given by Epstein and Carlson. In this way, the functional temperature dependence of the constants can be implemented from the source from which it is available, scaled to the room temperature elastic constants that agree with the surface-angle-dependent acoustic response measured in experiment. The function \( C_{ij}^A(T) \) is constructed as a linear fit to the data from Alers in the range 300 K to 760 K. Lower temperature constant data is excluded in this simple linear fit as the fourth-order constants all approach 0 K with zero slope [176]. However, in the room temperature and above range of interest for this test, a linear model captures the temperature dependent behavior quite well. In addition to the elastic constants, the density of pure Ni as a function of temperature is a necessary input in the calculation of the SAW velocity. Temperature dependent density is determined by scaling the standard value for room temperature density, 8.908 g/cm\(^3\), based on temperature dependent x-ray analysis of the lattice parameter of pure Ni. Lattice parameter data from Suh et al. is fit to a second-order polynomial and used for this purpose [177].

Following angular calibration, the sample is taken from 23\(^\circ\)C to 50\(^\circ\)C and subsequently in steps of 25\(^\circ\)C up to 600\(^\circ\)C. This temperature limit is chosen as it is roughly 50\% of the melting temperature of pure Ni and since most immediate-term testing is planned at this temperature or lower. Each step comprises a temperature rise followed by TGS measurement and takes on average 9 minutes for a total test time of about 3.5 hours. The SAW velocity measured at each temperature step is shown in Fig. 7-8(a), and the whole test temperature profile is shown in Fig. 7-8(b). During heating, the pressure in the chamber increased to a maximum of \( 7.8 \times 10^{-6} \) Torr at a sample
temperature of 600°C. The dashed line in Fig. 7-8(a) denotes the expected SAW velocity at 8° from ⟨100⟩ on pure Ni as a function of temperature. This profile is generated using the temperature-dependent materials properties as inputs to the method of Du and Zhao set to calculate the SAW velocity at the prescribed angle [152].

This test indicates that all components of the end station are temperature-stable up to the currently tested limit, and that the material response measured is consistent with what is expected from literature values of temperature dependent material properties. Should future in situ tests operate at a temperature set point closer to the manufacturer limit specified for the heating element, further calibration testing should be carried out to ensure facility stability. This test has here been referred to as a ‘static’ temperature test as each temperature increase is applied slowly in a controlled manner with no ion beam. Even here, slight positioning adjustments need to be made as the temperature increases due to thermal shifting. For faster ramps carried out prior to high-temperature implantation, it is likely that the sample position and laser pointing in the detection enclosure will need to be optimized once the set point temperature is reached.

### 7.4.2 Light ion exposure

As the inaugural demonstration of the I3TGS facility’s capabilities, a {001} oriented single crystal tungsten sample was exposed to 3.7 MeV He⁺ ions. This test was motivated by the interest in tungsten in the nuclear materials community, especially as a material for plasma-facing and high-heat flux components in future fusion energy devices [65,127,178–181]. A 99.99% pure tungsten single crystal was purchased from the Goodfellow Corporation specified to ±3° of the given index. The sample was procured with a 1 μm mechanical surface polish and further finished using a 0.3 μm alumina slurry prior to exposure. The He ion energy is chosen to provide a relatively flat dose profile and to avoid a high concentration of He in the analysis region. This exposure was conducted prior to installation of online beam current monitoring, so the beam current is measured at 2 hour intervals during the exposure by inserting the upstream Faraday cup and cutting off the beam from the sample surface. Using this method, the average ion beam current on the sample is 60 nA (limited by the ion source) over a 5 mm diameter beam spot size. The total ion fluence
Figure 7-9: SAW speed and temperature measured during W exposure to 3.7 MeV He⁺ ion beam as a function of dose linearly averaged over the acoustic excitation depth. The dose for these measurements is calculated using the average ion beam current measured at 2 hour intervals during the exposure. The timing of these current measurements is indicated by the dips in the temperature record as the beam is blanked from the surface. A fault in the TGS data acquisition system caused 30 minutes of data to be lost around six hours into the exposure. Beam heating is evident during the first several hours of the experiment.

at the conclusion of the exposure is $6.7 \times 10^{16}$ ions/cm². TGS measurements are taken continuously throughout the exposure in 1000 laser shot batches, for an average time between points of 35 sec at $\Lambda' = 4.54$ µm. In total, 934 individual TGS measurements are made sequentially throughout the exposure. Sample temperature is recorded continuously on the surface-contact thermocouple throughout the exposure in 2 second intervals.

Fig. 7-9 shows both the measured acoustic wave velocity as a function of dose and the sample temperature measured during the duration of the in situ experiment. The slow temperature rise during the first three hours of the experiment is due to ion beam heating. At around six hours into the exposure, the TGS data acquisition system faulted, stopping collection for about thirty minutes. During this time, the ion beam remained incident on the sample surface and the record was started again as soon as the fault was noticed and cleared. The periodic dips in the temperature profile correspond to the instances where the upstream Faraday cup was closed to record the ion beam current. Linearly averaged over the acoustic penetration depth, the sample received a total of 0.031 dpa in the analysis region during the course of the experiment. He concentration has been found to be an important factor in the degradation of W material properties; however by aiming to analyze a uniform damage and concentration profile, the average implanted helium concentration is calculated to be only 47 appm in the acoustic analysis region at the end of the exposure. The measured thermal diffusivity as a function of dose averaged over the thermal analysis region is given in Fig. 7-10.

The temperature and dose histories for thermal diffusivity measurements are the same as in Fig. 7-9 as a function of
Figure 7-10: Thermal diffusivity measured during W exposure to He\textsuperscript{+} ion beam as a function of dose linearly averaged over the thermal diffusion depth. The temperature profile as a function of time for this plot is the same as in Fig. 7-9.

time, but are not reproduced in Fig. 7-10. The highest dose achieved in this region is 0.018 dpa with a corresponding He concentration of 3 appm.

Neither Fig. 7-9 or Fig. 7-10 show clearly discernible trends as a function of He ion exposure. The SAW data presented in Fig. 7-9 possibly seem to indicate an initial increase in acoustic velocity as exposure begins, however this time region also corresponds to the duration of greatest temperature change as beam heating occurs. The dip in SAW speed around 2 hours into the exposure corresponds to first closure of the Faraday cup for beam current measurement, after which the speed changes little during the rest of the exposure. Similarly, little change is observed in the thermal diffusivity over the duration of the experiment. Previous work on He implanted tungsten has shown that the implanted He gas has a more dramatic effect on bubble formation and stabilization than displacement damage alone [65,179–181]. Post-irradiation mechanical testing [65,179,180] and \textit{in situ} TEM analysis [181], have shown that helium bubble formation, or He-vacancy complexes, should form at around 300-3000 appm. As our average implanted He level in the acoustic analysis region is several times lower (and several orders lower in the thermal analysis region) than those limits, it is within reason that no large trend is observed in either property during this experiment.

### 7.4.3 Heavy ion exposure

To test the heavy ion and high temperature performance of the facility, an \textit{in situ} exposure is conducted using 31 MeV Ni\textsuperscript{5+} self-ions into the \{001\} oriented single crystal Ni sample which has previously been used for static high temperature testing. In addition to being an important constituent in many engineering alloys, pure Ni has been shown to undergo volumetric void swelling under high temperature self-ion irradiation [182]. Void swelling is one of the radiation-induced effects that this facility is designed to detect, so this initial test on a simple material system serves as a useful baseline. Westmoreland and coworkers provide some data on the dose-rate dependence of void swelling in pure Ni such that the exposure temperature of 550\textdegree C is chosen here to promote the most swelling at the measured average dose rate of $7.2 \times 10^{-4}$ dpa/s averaged over the acoustic analysis region [182]. The beam
Figure 7-11: Ion beam current, SAW speed, and surface temperature during Ni exposure to 31 MeV self-ions at 550°C as a function of dose linearly averaged over the acoustic excitation depth. Doses are calculated by cumulatively integrating the ion beam current as a function of time to recover the applied fluence at each TGS measurement. All data is scaled linearly in dose resulting in a non-linear time axis as the beam current increases during exposure. The trend observed in the SAW speed as a function of dose, an initial increase followed by a slow decrease, is consistent with expectations for void swelling during exposure.

energy is chosen here to match the end of the damage range with the acoustic penetration depth, such that the entire damage profile is captured in the TGS measurement. For this exposure, on-line beam current recording is implemented as described in Section 7.2.2 and accumulated charge on the BPM is recorded in 10 second intervals continuously throughout the test. The average ion beam current incident onto the sample is 33.7 nA over a 1.6 mm diameter spot, leading to a total applied fluence of $5.7 \times 10^{16}$ ions/cm$^2$ at the conclusion of the exposure. Although the sample is the same in this experiment as that used in the static temperature test, it was remounted between the two, leading to an acoustic polarization of $13 \pm 1°$ from $\langle 100 \rangle$ for in situ TGS measurements. TGS measurements are recorded in 1000 laser shot batches which, for this experiment, are placed on 1 minute intervals. This leads to about 25 seconds of down time between subsequent measurements, allowing for optical or sample adjustment should thermal drifting occur. The applied grating spacing is again $\Lambda' = 4.54 \mu$m and temperature is again recorded in 2 second intervals.

Fig. 7-11 shows the ion beam current, SAW speed as measured by TGS, and surface temperature measured for this in situ exposure. Continuous current monitoring allows the accumulated dose in the acoustic analysis region
to be calculated at each TGS measurement point. Since the current during this experiment is drifting upwards, measurements are not linearly sampled in dose; measurements of SAW speed made near the end of the exposure have a slightly larger spacing than those near the beginning. For this exposure, a total of 453 individual TGS measurements are collected over the 7.7 hour exposure duration. The total average dose received in the acoustic analysis region is 19.9 dpa, with a peak dose in the analysis region of 51.0 dpa. The trend seen in the SAW speed as a function of dose is consistent with previous work using benchtop, post-irradiation TGS to measure the effect of ion-induced void swelling in pure copper [67]. In both studies, the measured SAW speed initially increases at low doses due to the formation and interaction of small defect clusters with dislocations. At higher doses, this trend turns over as volumetric swelling occurs and softens the crystal, reducing the measured acoustic velocity. Where many common PIE methods report changes in material properties as a function of dose for materials experiencing 10s of dpa at the fidelity of 1-10 dpa/measurement, the average dose accumulated between subsequent data points in this in situ experiment is 0.04 dpa.

The TGS-measured thermal diffusivity for this exposure is shown in Fig. 7-12. In contrast to the acoustic measurements, little change is notable in the high-temperature thermal transport properties of Ni as a function of exposure. The final dose in the thermal analysis region is 5.8 dpa. Although defect scattering is expected to reduce the thermal diffusivity of pure metals, this effect is mitigated at elevated temperatures due to the temperature dependence of electron-electron and electron-phonon scattering [127]. Additionally, as defects agglomerate into large clusters, as are expected in ion-induced void swelling in Ni, the relatively large distance between defect clusters (voids) will serve to reduce defect effects on thermal transport. In the light of these factors, the lack of a measurable change in thermal diffusivity here is consistent with expectations. One feature of note, however, is the small jump in diffusivity around 1 dpa. This jump is not ascribed to a sudden material change, but rather to a slight optical pointing adjustment made at that time during the exposure to combat a drop in TGS signal intensity noted during online measurement.

\[2\text{See Footnote 1.}\]
Figure 7-13: Two cross sectional SEM images of {001} Ni exposed to 31 MeV self-ions taken after irradiation with in situ TGS monitoring. The large, faceted voids are expected after high temperature exposure, but are localized significantly beneath the thermal wave penetration depth as indicated in the right image. This swelling is, however, responsible for the reduction in SAW velocity shown in Fig. 7-11.

However, this change is still within the few percent error expected using the method of thermal diffusivity extraction from TGS signals of this character [59]. The presence of volumetric void swelling was confirmed in this sample post-exposure using cross-sectional imaging following focused ion beam milling as shown in Fig. 7-13. In the exposed area, faceted voids several hundreds of nanometers in diameter were observed, but at a low number density, consistent with previous defocused-beam irradiations in metallic single crystals [17,67]. The majority of these voids are observed below the thermal diffusion depth, which is likely another factor in the value of the recorded thermal diffusivity remaining constant throughout in situ exposure.

7.5 Conclusions and implications

In this chapter, a new in situ ion irradiation transient grating spectroscopy (I^3TGS) facility which is operational at the Sandia Ion Beam Laboratory has been described. This facility has the ability to continuously monitor the thermal and elastic properties of materials, on the micron length scale, as they are being exposed to a variety of ion beams. While the thermal diffusivity of the samples may be measured directly, changes in elastic properties manifest themselves through changes in the surface acoustic wave speed(s). As both of these may change as a function of radiation-induced microstructural evolution, this facility offers a powerful tool to observe that evolution at a dose fidelity not previously possible.

Following the commissioning of this facility, several improvements have been implemented, and more are under consideration, to increase its flexibility in terms of types of experiments possible to perform. The most significant upgrade which was necessary following these initial tests is in sample handling and staging. Although the sample management system described in this chapter is sufficient for high temperature in situ experimentation, it relies on a reappropriated four-axis stage from an older experiment. This stage could use improvements in both high-temperature stability and positioning accuracy. Tests described in following chapter will show evidence of ion beam-laser misalignment due to coupling between translational degrees of freedom using this older staging. Modern analytical staging would allow for more precise position control as well as liquid nitrogen cooling for cryogenic exposure experiments (and
cooling for room temperature experiments) and azimuthal rotation in the plane of the sample surface. This extra degree of freedom becomes important when attempting to optimize fourth-order elastic properties from SAW velocity measurements. The current sample management system, as of the date of the completion of this thesis, will be described in detail in Chapter 8.

One particular weakness in applying the transient grating method in this context is the averaging of material properties over a surface layer which has been non-uniformly damaged by the ion beam. The simple linear average over SRIM calculated dose profiles to provide an effective dose for each measurement is likely not the best metric of comparison for materials being more uniformly damaged, e.g. from neutrons. Other factors such as surface denuded zones are common issues which this technique simply averages over. Engineering solutions exist for some of these issues, but not all. Further work in constructing an optimized dose correlation between samples exposed to ions or neutrons at various energies is currently underway. The initial considerations for this advanced correlation capability are described in Section 8.4. However, it should be emphasized that this facility does not preclude the use of traditional PIE that is commonly used for bulk ion irradiated specimens. As the monitoring method is both non-contact and non-destructive, samples exposed in the IP TGS facility may be removed and analyzed in the same manner as any single-beam irradiation.

The demonstration tests offered in this chapter serve as initial examples of the types of experiments that this facility is capable of handling. A wide variety of tests are currently being considered for the future. The most promising use for the experimental ability demonstrated here, and indeed the driving motivation for this facility’s construction, may be as a rapid down-selection tool for engineering relevant alloys. Normally, it would take months or years of testing to discover what effects processing, or minor alloying, or surface coatings have on segregation, precipitation, swelling, or a host of other radiation-induced effects. By using in situ TGS, microstructural changes as expressed through thermomechanical properties may be monitored continuously. Such real-time data will enable detailed PIE to be focused on the particular conditions of dose, temperature, etc., where non-linear changes in microstructure begin to occur. This synergy of real-time testing informing detailed analysis should allow for better mechanistic understandings of radiation-induced degradation to be developed.
Chapter 8

Further *in situ* TGS beamline results

The stated major goal of this thesis – showing the capability to track multi-property evolution in real-time during ion beam irradiation – is demonstrated in the work presented in Chapter 7. However, in that chapter, only two simple test cases were described to show the nominal performance of the I\(^3\)TGS facility. Following those demonstrations, a series of experiments were planned as the first full demonstration of this new capability. These tests were chosen to match the conditions of the work presented in Chapter 4, as the high-temperature void swelling behavior of self-ion irradiated copper had already been explored in detail using transient grating spectroscopy (TGS). In essence, this study sought to reproduce Fig. 4-2 with the dose fidelity shown in Fig. 7-11. The design of, parameters for, and results from that series of experiments are detailed in Section 8.1. As alluded to in the concluding remarks of the previous chapter, these experiments failed due to coupled geometric degrees of freedom in sample staging which lead to ion-beam laser misalignment during the *in situ* exposure. Following these experiments, a new sample handling system was installed and new alignment protocols implemented to combat the behavior observed in the failed experiments. These are described in detail in Section 8.2.

With this upgraded experimental implementation in place, an new experimental matrix has been designed as the first study of interest. In an effort to move towards more engineering-relevant material systems, this new matrix no longer focuses on pure copper, but rather on nickel-based concentrated solid-solution alloys (CSAs). The availability of oriented single crystal samples of a variety of alloy compositions, as well as the presence of recent post-irradiation examination on similar samples showing the presence of volumetric void swelling, make these samples an attractive target case for the new technology developed here. Preliminary testing on these alloys and the experimental test conditions being planned for future *in situ* irradiations are described in Section 8.3.

Finally, in response to concerns about the non-uniform sampling of surface layers using TGS, particularly with regards to the assignment of an ‘applied dose’ for *in situ* experiments, a new dose assignment methodology is proposed. The method relies on using depth dependence of the physical displacement profile associated with the surface acoustic waves induced in TGS experiments to compute a weighted average of the ion-applied dose profile. This method is intended to return a more physically meaningful dose value than the simple linear averaging used in all of Chapter 7. This method is currently a proposal only and a schematic for future validation studies are presented as well.

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8.1 *In situ* void swelling in pure copper

Although the new *in situ* ion irradiation TGS (I³TGS) facility described in Chapter 7 was validated using two exposures with varying conditions of temperatures, ion species, and ion energies, the cases presented to this point have been rather limited in scope. With a functional facility in hand, a more detailed series of experiments were conducted with the intention of fully benchmarking the new *in situ* performance against prior studies. Earlier work in this thesis provides just such a benchmark. In Chapter 4, a series of \{111\} oriented single crystal copper specimens were exposed to high levels of self-ion irradiation at a temperature where volumetric void swelling was expected to occur. Post-exposure electron microscopy confirmed that a significant amount of swelling was present in the more heavily exposed samples. TGS measurements showed a non-uniform change in surface acoustic wave (SAW) velocity across different polarizations with a trend of decreasing crystal anisotropy as a function of exposure.

Here, a series of *in situ* exposures are carried out on single crystal copper specimens of the same type as those used in Chapter 4. Namely, these samples are again purchased from the MTI corporation, are >99.999% pure, are mechanically polished to <3 nm surface roughness, and have surface orientations within 2° of \{111\}. Unlike the post-irradiation examination carried out in Chapter 4, *in situ* TGS experiments may currently measure only one acoustic polarization continuously as a function of applied ion fluence. As the prior results indicated that the greatest relative change in SAW velocity should be observed along \langle 11\overline{2} \rangle \{111\}, copper crystals will be oriented in the beamline target chamber such that SAWs are generated at roughly this polarization. The polarization may only roughly be determined due to a limitation in sample staging. For these experiments, samples are exposed at high temperature using the staging pictured in Fig. 7-4. This sample holder has no azimuthal rotation control – rotation in the plane of the \{111\} crystal surface – such that samples must be manually rotated on the face of the heating element and clamped prior to target chamber pump-down and exposure. These samples are shipped from the manufacturer with no indication of the sample edge relationship to surface angle such that for a square sample there is no way to determine by inspection whether a macroscopic square edge corresponds to a \langle 11\overline{2} \rangle polarization, \langle 1\overline{1}0 \rangle, or some intermediate angle. This being the case, samples must be iteratively positioned on the heater surface, with each iterative step involving a physical stage removal and vacuum break. As a result, each sample exposure described here has a real surface polarization, found by comparing the measured SAW velocity to that expected from literature elastic constants, within 3–4° of \langle 11\overline{2} \rangle. This sample alignment procedure is both time-consuming and imprecise and improvements to it will be described in the following sections.

Initially, an experimental campaign was designed such that multiple samples would be exposed at the same temperature, 400°C, as used in Chapter 4 to multiple dose levels such that end-state microstructures would be comparable to those observed already. Compared to the experiments in Chapter 4, the implantation ion energy is modified due to the difference in applied grating spacings available on the *in situ* and *ex situ* TGS experiments used for this thesis. The applied *in situ* grating spacing for these experiments is calibrated as $\Lambda = 4.546 \mu\text{m}$. For this spacing, an ion beam energy of 31 MeV is selected to again match the acoustic interrogation depth to the applied dose profile. The SRIM calculated dose profile, as well as the out-of-plane SAW displacement profile calculated by the method described in Section 8.4 are shown in Fig. 8-1. An initial screening experiment was planned up to the highest dose of interest, around 100 dpa at the damage peak, such that dose levels of particular interest could be identified and targeted during further experiments. One such dose of interest would be the dose at which the SAW speeds are observed to
transition from stiffening to softening, behavior seen in both Fig. 4-2 and Fig. 7-11. However, this initial screening experiment did not proceed as planned and the rest of the experimental campaign for these samples was modified accordingly. Table 8.1 lists the parameters for the three experiments that were eventually carried out on this matrix of samples.

The major difference between each of the experiments which were conducted is the exposure temperature. The initial experiment at 400°C was run to a linearly averaged dose of 34.0 dpa (95.0 dpa at the damage peak), well within the rage at which significant swelling should have occurred. The continuously-monitored ion beam current, SAW velocity, and surface temperature for this exposure are shown in Fig. 8-2(a). Unlike prior in and ex situ void swelling experiments on pure metals, the SAW velocity in this experiment is not observed to increase slightly and then turn over and decrease with applied dose, but rather to continually increase and possibly saturate near the end of the experiment. This result was counterintuitive, and no mechanistic explanation was readily apparent. A series of older works on self-ion irradiation of copper by Glowinski and coworkers stresses the importance of residual

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface polarization</th>
<th>Ion species</th>
<th>Ion energy</th>
<th>Temp.</th>
<th>Spot diameter</th>
<th>Ave. beam current</th>
<th>Meas. time</th>
<th>Meas. interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC Cu</td>
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<td>Cu^{5+}</td>
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<td>400°C</td>
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<td>44 nA</td>
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<td>60 sec</td>
</tr>
<tr>
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<td>Cu^{5+}</td>
<td>31 MeV</td>
<td>425°C</td>
<td>2.2 mm</td>
<td>80 nA</td>
<td>35 sec</td>
<td>60 sec</td>
</tr>
<tr>
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<td>Cu^{5+}</td>
<td>31 MeV</td>
<td>475°C</td>
<td>2.0 mm</td>
<td>56 nA</td>
<td>35 sec</td>
<td>60 sec</td>
</tr>
</tbody>
</table>

Table 8.1: In situ TGS exposure parameters for the single crystal (SC) pure copper sample matrix designed to reproduce the results of Chapter 4. ‘Spot diameter’ refers to the measured ion beam spot size in the sample plane. The continuously-monitored ion beam current, as seen in Fig. 8-2, is averaged over the time of exposure to generate the ‘Ave. beam current’ column.
Figure 8-2: Applied ion beam current, measured SAW velocity, and surface temperature for single crystal copper exposed at (a) 400°C, (b) 425°C, and (c) 475°C to 31 MeV Cu^{5+} self-ions. In all cases the measured SAW velocity is observed to increase as a function of applied dose, but not turn over and decrease as expected when volumetric void swelling is occurring. In the 475°C exposure, thermal drifting necessitated an optical re-alignment at two individual times, both of which caused notable shifts in the measured acoustic response. In addition, at around 5.5 hours into the 475°C exposure, an accelerator tank spark caused a sharp drop in ion beam current.

oxygen content on the swelling behavior of pure copper [145,147,148]. Combined with a confirmation from the sample manufacturer that only characteristic, and not particular, sample purity data was readily available during the time frame of this experimental campaign, an initial postulation was formed that differences in residual oxygen content between samples used in Chapter 4 and those used here were causing different swelling behavior. As one of the few experimental controls expected to influence this behavior, sample temperature was varied during subsequent exposures in an attempt to induce swelling in this matrix. Practically, to utilize all of the available beam time during the two-week experimental campaign, little extra time was available on-site at Sandia to conduct companion testing on this first sample.

As a result, a second sample was exposed to an average dose of 35.4 dpa (98.7 dpa peak) at 475°C and a third to an average dose of 45.4 dpa (126.6 dpa peak) at 425°C. The results of both of these exposures are shown in Fig. 8-2 as well, from left to right in order of exposure temperature. The 475°C sample shows the same behavior as observed at 400°C, a continuous stiffening in the SAW response without any turnover expected as a result of swelling. This sample temperature corresponds to a homologous temperature of $T/\text{melting point} = 0.55$, possibly near the upper range of where volumetric swelling should occur due to the effects of thermal vacancy emission. As a result, the temperature was lowered back to 425°C for the final exposure. This exposure was allowed to reach 33% higher applied ion fluence than the initial experiment and yet the same trend in in situ measured SAW speed was observed. One feature to note across these three samples is the decrease in the initial SAW speed as a function of temperature, which is to be expected as elastic constants generally decrease more quickly than density as a function temperature (see Fig. 5-4 or Fig. 7-8). During the 475°C exposure, thermal shifting necessitated an optical re-alignment around 0.5 and 3 hours into the experiment. At those positions, marked in Fig. 8-2(c), discrete changes in recorded TGS parameters are
Figure 8-3: Optical dark field image of the \{111\} copper sample exposed at 475°C showing ion beam-fiducial marker misalignment. The square fiducial lines are scribed onto the sample surface prior to exposure and the laser measurement spot is centered within that marker during \textit{in situ} testing. Ion beam-induced surface reconstruction allows the location of the beam spot to be identified post-exposure. An approximate ion beam boundary is shown by the dashed line.

notable. These are mostly likely due to a slight change in the physical measurement position as the laser beam spot was shifted along the sample surface.

8.1.1 Ion beam-laser coincidence positioning

At the conclusion of this sample matrix, several post-irradiation examination steps were planned to attempt to determine if 1) samples truly did not undergo void swelling in these exposure conditions or 2) if something else during the \textit{in situ} TGS measurements caused the recorded signal to behave unexpectedly. Focused ion beam lift-out and electron microscopy were planned, but first the samples were viewed under an optical microscope. An optical dark field (DF) image of the 475°C sample from this matrix is shown in Fig. 8-3. To interpret this image, a description of the exact sample alignment protocol used for each of these experiments is necessary. Prior to mounting on the I³TGS sample stage, an approximately 1–1.5 mm square fiducial marker is scribed into the surface of each of the 5 × 5 × 1 mm copper single crystal samples. This square fiducial is used align the approximately 200 µm diameter TGS laser spot on the sample surface. In practice, these scribe lines strongly scatter incident laser light, which is easily notable through the I³TGS forward imaging system. Thus, they may be used to target the laser spot, in the plane of the sample surface, into the center of the square fiducial. It is at this central position that \textit{in situ} measurements are conducted. Following laser alignment, the two-position sample stage is translated up to the ion beam diagnostic position to fix beam pointing and shaping, and then back down to the sample position as described in Section 7.2.2. The square fiducial marker used for this purpose is visible in Fig. 8-3.

With the particulars of this protocol in mind, Fig. 8-3 provides an explanation for the behavior observed in this sample matrix. The second major feature of note in the DF optical image is the presence of surface reconstruction caused by the ion beam. In all of these samples, and many of the other pure metallic samples investigated in this thesis, some degree of surface modification or reconstruction is often noted in the exposed area. This type of phenomenon is
commonly observed for low-energy ion implantation and its presence in these conditions, while not directly expected, is of no great surprise [183–186]. In the case presented here, this surface reconstruction provides an indicator of where on the sample the ion beam was focused during in situ testing. The obvious interpretation of Fig. 8-3, therefore, is that the ion beam and laser measurement position were not coincident during in situ exposure and measurement. The calculated applied dose shown in Fig. 8-2 makes the assumption that the measured TGS response corresponds to an area which has seen a uniform ion beam spot with a diameter as measured on the system imaging quartz (the same as Section 7.4). In reality, due to this misalignment, the location on the sample surface measured via TGS during irradiation likely only saw a very small amount of exposure in the tails of the Gaussian ion beam spot, rendering the applied dose axis of Fig. 8-2 incorrect. What those responses are showing, then, is simply the low dose region of the irradiation response where small defect cluster interactions with dislocations are dominating the measured change in SAW velocity. Although the image is only shown for the 475°C case where the absolute surface reconstruction was the greatest, the same misalignment is observed in all three samples. Spatial dosimetry and exact laser positioning information which would allow for the true applied dose for each experiment to be calculated do not exist. Therefore, as the cause of the experimental failure is clear, no further interrogation of these samples is planned.

However, to move forward with 13TGS experiments, the root cause of this misalignment must be identified and corrected. A combination of the particular alignment protocol and a coupled geometric degree of freedom in the sample staging used for these experiment was ultimately found to be cause of the behavior observed here. The four-axis sample manipulation stage described in Fig. 7-4 operates on the following principle: the X-Y translations – which correspond, in the 13TGS facility, to the ion beam propagation direction and one surface direction on the sample plane – are induced by pivoting the actuator rod around a fixed rod attachment point. As the sample measurement surface is not co-linear with the rod on this staging, see Fig. 7-4(c), placing the sample surface at the geometric center of the target chamber requires the rod to be translated in one of the X-Y dimensions. The resulting fixed point in the X-Y translation plane will remain during Z axis translation, such as the motion necessary to switch between the sample and ion beam alignment positions. Fig. 8-4 is a 2D schematic of this process with exaggerated angles. As shown, this rod tilt causes the plane of the sample surface to move within the target chamber between sample and alignment positions. This results in a small offset, in reality on the order of 1 mm based on Fig. 8-3, between the apparent and actual ion beam position for in situ experiments. To move forward, an alternate alignment protocol must be designed which either accounts for this offset or does not rely on the translation between two positions on a single sample stage to align the TGS lasers and ion beam prior to exposure.

Before describing the experimental configuration implemented to combat this coincidence issue a notable question remains to be answered in light of the geometry described above: if this alignment protocol resulted in misalignment for this copper sample matrix, how did the demonstration experiments from Chapter 7 reflect the actual ion-exposed area? Recall that post-exposure cross sectional imaging did indeed reveal the presence of void swelling commensurate with the trend observed through in situ TGS. The unsatisfying answer to this question comes in the details of the alignment protocol. While the copper sample matrix was precisely positioned to the scribed fiducial, the initial experiments did not include this sample fiducial and positions were not tracked on the video screen from the forward imaging system between sample and alignment positions. These initial experiments, then, were aligned with a guess and a degree of luck. In trying to design a more repeatable alignment protocol for these later samples, the effect of the inherent geometric coupling of the physical staging was more obvious.
8.2 Current experimental configuration

To combat the systemic misalignment discovered in the tests described above, several improvements in sample management and handling have recently been implemented in the I$^3$TGS facility. Most importantly, a second independently controlled, five-axis sample positioning stage was installed on the target chamber from the bottom. The new stage has been designed with an improved sample management system. The original, reappropriated four-axis stage mounted to the top of the target chamber is still in place and has been re-designed with a single mounting point for a piece of targeting quartz. Independent control of the sample position and imaging quartz allows for an alignment protocol which is able to fix the sample position once laser alignment is achieved. This protocol is shown schematically in Fig. 8-5. After a sample is mounted, the bottom stage is used to place it at the correct laser measurement position. The use of a fiducial marker on which the laser measurement spot is centered is retained. Next, the top stage is used to lower the imaging quartz into position directly in front of the sample. How close this quartz may be to the sample is restricted by the clips used to hold samples in place. The bend radius of those clips is approximately 1/8" and the imaging quartz is normally translated to be in contact with those points for alignment; this makes the ion beam imaging plane as close to the sample surface plane as possible. Following ion beam positioning, the upstream Faraday cup is inserted, the quartz translated upwards to a parking position, and the in situ exposure started whenever the desired sample temperature is reached. In this new protocol, the sample being investigated need not be moved from its TGS-aligned position once that position is optimized. To the accuracy of the dosimetry currently available, the difference in ion beam shape and size over the short offset distance between quartz and the sample surface is assumed to be negligible in the calculation of the applied ion dose.

The newer, bottom-mounted stage is chosen as the sample management stage – as opposed to leaving sample management on the already-installed staging – because it has five manually controllable degrees of freedom. This staging has the same linear (×3) and tilt (×1) axes as the original stage. In addition, it also has an in-plane, azimuthal rotation degree of freedom. This extra rotation allows the effective SAW polarization vector to be modified external to the sample.
Figure 8-5: Diagram of ion beam-laser alignment procedure used with the current two-stage target chamber. Following alignment of samples at the TGS measurement position, (a) the imaging quartz is lowered in front of the sample and sample staging. In this position the ion beam shape, size, and alignment is set using ion beam luminescence. (b) After alignment, the quartz is retracted to leave the ion beam path to the sample surface unobstructed.

To the chamber without making a vacuum break. Importantly, this staging uses a removable platen/docking point mechanism such that samples may be exchanged through the large side door in the target chamber (see Fig. 7-3(b)), rather than by removing the whole stage at each sample exchange as was done previously. This new sample staging is shown in Fig. 8-6 both with and without the sample platen attached. The staging retains the ability to reach high temperature through the use of a bare tungsten wire heating element placed directly behind the sample platen. The platen is pure molybdenum and suitable for high-temperature operation. The azimuthal rotation operates with the use of the geared rod which runs through the center of the larger actuation rod on the stage. Translating this rod external to the chamber causes the docking mount point to rotate about the fixed heating element. As this rotation is controlled manually, it could not easily be used for an in situ sweep of SAW polarizations during exposure. However, it can be used to more quickly find and fix the correct polarization during initial sample alignment. This capability makes the newer staging the best choice for sample management, leaving the older staging to be used for imaging quartz positioning. Practically, this newer staging was necessarily placed on the bottom of the chamber as it tall enough to impact ceiling-mounted piping were it to be placed on top. The mechanical staging was produced by Thermionics Northwest, Inc. (Richland, WA) in the early 1990s for experiments at the Sandia Ion Beam Laboratory. For this facility, a new custom heating element (0.8" diameter) and high temperature Mo sample platens were purchased from the same vendor.

At the time of the writing of this document, this new sample management and coincidence position system has not been utilized for any in situ experiment in the I$^3$TGS facility. One current limitation of this new staging is the temperature monitoring system. As the sample platen is removable from the stage itself, a thermocouple mounted directly to the sample surface becomes more difficult to implement. As such, the temperature is currently controlled
from a thermocouple embedded in the rear of the heating element. Since a surface temperature measurement is preferred for the surface layer-sensitive TGS measurements, an extra set of 0.01" type K thermocouple wires have been included on the staging, as seen in Fig. 8-6, should a connectorized, platen mount thermocouple be designed in the future. An initial conditioning of the new heating element up to 600°C resulted in the fracture of the tungsten filament. The cause of this failure was determined to be an insufficiently low vacuum pressure in the target chamber. To achieve a more appropriate ultimate pressure, an additional turbomolecular vacuum pump will be installed onto the chamber itself. Once this component has been installed, a new tungsten filament will be conditioned and future in situ TGS tests may be conducted.

8.3 Ni-based concentrated solid-solution alloys

With the new staging and sample management system in place at the I³TGS facility, the next target study is currently being designed. An obvious choice would be to attempt the same copper self-ion irradiation as described in Section 8.1. However, in an attempt to move more quickly to materials with a practical engineering interest for future nuclear systems, the focus for the immediate future study has shifted to high entropy alloys (HEAs) and their precursors. These materials promise unique structural and functional properties by combining five or more roughly equiatomic constituent elements [187,188]. Precursor alloys to HEAs which still combine roughly equiatomic components of two to four elements are commonly referred to as single phase concentrated solid-solution alloys (CSAs). CSAs and HEAs are of great interest for extreme environments with high radiation exposure as many works have shown a decreased sensitivity to radiation effects with increasing chemical complexity [33,189–195]. Mechanistically, this radiation tolerance is imparted due to inhomogeneous potential energy landscapes resulting from randomized atomic arrangements. This inhomogeneous landscape inhibits fast 1D defect diffusion and therefore promotes local recombination of generated point defects [195]. Despite the advantages of these materials, the high number of
The desire for faster screening of radiation-induced effects in these alloys make them attractive targets for testing using the I²TGS facility. Additionally, the Energy Dissipation to Defect Evolution (EDDE) Energy Frontier Research Center at Oak Ridge National Laboratory has the ability to grow well-oriented single crystals of Ni-based CSAs with up to four equiatomic components. Samples of this nature provide an intermediate step for in situ TGS testing where the protocols developed for pure single crystal metals may be utilized in materials with more future utility. In addition to enhanced defect recombination on short timescales, these materials have also been shown to be resistant to long time scale defect evolution in the form of void swelling. Recently, Yang and coworkers carried out a series of Ni ion irradiation experiments on several Ni and Ni-based CSAs intended to gauge the amount of void swelling resistance imparted by chemical complexity [198]. Samples were exposed at an intermediate temperature of 500°C to 3 MeV Ni²⁺ ions up to a peak damage level of 53 dpa. Cross sectional high angle annular dark field (HAADF) STEM images showing a reduction in overall swelling in these materials with increasing complexity are reproduced in Fig. 8-7.

The next sample matrix to be exposed in the I²TGS facility will include four compositions of Ni or CSA sourced from collaborators at EDDE. The goal of the experiments will be to reproduce the conditions explored by Yang et al. changing only the ion implantation energy to match the TGS acoustic length scale. Sample compositions and intended exposure conditions are listed in Table 8.2. The total fluences necessary to reach the intended maximum dose level are calculated from SRIM simulations carried out for each composition assuming the same relative temperature dependence of density as described in Section 7.4.1 for pure Ni. Samples are provided with {001} surface orientations, but the selection of the ⟨100⟩{001} surface polarization for in situ testing is worthy of note. This polarization was chosen by taking the optimized elastic constants for Cu exposed to 90 dpa at peak as shown in Table 4.4 and

<table>
<thead>
<tr>
<th>Material</th>
<th>Peak dose (dpa)</th>
<th>Number of voids counted</th>
<th>Area examined (µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCoFeCr</td>
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<td>97 ± 0.06</td>
<td>2.88 ± 0.05</td>
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<tr>
<td>NiFe</td>
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<td>144 ± 0.04</td>
<td>3.57 ± 0.05</td>
</tr>
<tr>
<td>NiCo</td>
<td>17 ± 0.01</td>
<td>240 ± 0.03</td>
<td>3.33 ± 0.04</td>
</tr>
<tr>
<td>Ni</td>
<td>17 ± 0.00</td>
<td>42 ± 0.02</td>
<td>6.82 ± 0.06</td>
</tr>
<tr>
<td>NiCoFeCr</td>
<td>17 ± 0.01</td>
<td>17 ± 0.01</td>
<td>8.2 ± 0.05</td>
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<td>144 ± 0.04</td>
<td>3.57 ± 0.05</td>
</tr>
<tr>
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<td>240 ± 0.05</td>
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<tr>
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<td>42 ± 0.06</td>
<td>6.82 ± 0.06</td>
</tr>
<tr>
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<td>69 ± 0.07</td>
<td>2.05 ± 0.04</td>
</tr>
<tr>
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<td>42 ± 0.18</td>
<td>6.82 ± 0.06</td>
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Figure 8-7: HAADF STEM cross-sectional images of Ni and CSA single crystals irradiated up to a peak damage of 53 dpa at 500°C using 3 MeV Ni²⁺ ions. Voids are the lighter, faceted regions and total swelling is observed to decrease as a function of chemical complexity. Figure from [198].
<table>
<thead>
<tr>
<th>Material</th>
<th>Surface polarization</th>
<th>Ion species</th>
<th>Ion energy</th>
<th>Temp.</th>
<th>Peak dose</th>
<th>Total fluence (×10¹⁶ ions/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC Ni</td>
<td>~ ⟨100⟩{001}</td>
<td>Ni⁵⁺</td>
<td>31 MeV</td>
<td>500°C</td>
<td>50 dpa</td>
<td>5.60</td>
</tr>
<tr>
<td>SC NiFe</td>
<td>~ ⟨100⟩{001}</td>
<td>Ni⁵⁺</td>
<td>31 MeV</td>
<td>500°C</td>
<td>50 dpa</td>
<td>5.71</td>
</tr>
<tr>
<td>SC NiCoCr</td>
<td>~ ⟨100⟩{001}</td>
<td>Ni⁵⁺</td>
<td>31 MeV</td>
<td>500°C</td>
<td>50 dpa</td>
<td>5.68</td>
</tr>
<tr>
<td>SC NiFeCoCr</td>
<td>~ ⟨100⟩{001}</td>
<td>Ni⁵⁺</td>
<td>31 MeV</td>
<td>500°C</td>
<td>50 dpa</td>
<td>5.70</td>
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</table>

Table 8.2: Target ion irradiation parameters for Ni concentrated solid-solution alloy sample matrix based on previous conditions used in the literature. Ion energies must be higher for *in situ* TGS experiments compared to traditional exposures to match the damage and acoustic length scales.

recalculating the SAW response on the {001} surface. These calculations indicated that similarly to the ⟨112⟩{111} polarization, ⟨100⟩{001} is the direction of greatest change in SAW speed for anisotropic FCC metals with a significant degree of void swelling. In addition, as shown in Fig. 7-6, pure Ni only exhibits pure SAW mode propagation out to about 25° from ⟨100⟩{001}, transitioning to pseudo SAW (PSAW) propagation around the other primary direction, ⟨110⟩{001}. SAW modes are those interest for *in situ* testing as they remain more localized to the near surface region than PSAWs, making ⟨100⟩{001} the obvious polarization choice for these future experiments.

As mentioned previously, the polarization optimization during I³TGS experiments is carried out by rotating the crystal surface until a SAW velocity is measured which is as close as possible to that calculated for the target orientation. Even though this procedure will be made easier in future experiments with the additional azimuthal rotation degree of freedom, the target SAW speed must still be a known quantity. Literature values for all fourth-order elastic constants for these CSAs do not exist. Therefore, the acoustic response across all surface polarizations on these materials must be characterized to provide this set point. The results of these angular sweeps, carried out in increments of 5° using an applied grating of Λ = 4.82 µm on the bench top TGS facility at MIT are shown in Fig. 8-8. By inverting and fitting the SAW region data to a Gaussian profile, the target optimization velocities are identified as 2351.7 m/s, 2845.8 m/s, and 2730.9 m/s for NiFe, NiCoCr, and NiFeCoCr, respectively. The pure Ni target velocity of 2740.8 m/s is calculated using the method and values described in Section 7.4.1. During these measurements, fiducial marks were scribed onto the sample surfaces to indicate the rough orientation at which they should be mounted on the sample platen. These fiducials in concert with the new azimuthal rotation ability will make initial sample alignment in the I³TGS chamber much more efficient.

With the information provided in Table 8.2 and Fig. 8-8 in hand, no barriers exist to conducting this study on Ni-based CSAs the next time an experimental campaign may be conducted. These experiments will allow the new capability at the I³TGS facility to be demonstrated on potentially engineering-relevant alloys while still targeting the radiation-induced degradation mode into which significant insight has been gained over the course of this thesis.

8.4 Sampling depths and assigning dose

One of the major complications in using ion beam irradiation to emulate bulk irradiation effects seen from neutrons is the non-uniformity of the applied dose profile. Imposed damage levels, as shown in several places in this thesis, may vary drastically between a material surface and the ion range. This most challenging neutron-atypical effect
is commonly combated by a modification or control of the sample length scale under analysis. When irradiating
bulk samples, small regions on the order of 100-200 nm thick, sampled from a depth into the material where the
imposed damage profile is relatively uniform, may be extracted and used for either microscopy or nanomechanical
testing [14,168]. During in situ TEM experiments, exposure conditions may be chosen such that ions pass completely
through thin-foil samples depositing a uniform level of damage [18,21]. An alternative approach is to use sequential
ion exposures at multiple energies to create an effectively uniform dose profile over some longer length scale [66]. In
this case the temporal accumulation of damage is not consistent and may be drastically different than that expected
in the neutron case.

The use of in situ TGS to quantitatively monitor radiation-induced microstructure evolution is challenged by this
non-uniformity. With continuous monitoring, it is not possible to select a specific interior layer of material to measure.
Rather, a TGS measurement will return in fact some non-uniform sampling of a non-uniformly applied damage profile.
The sampling of effective material properties is non-uniform as both the applied temperature profile and the induced
mechanical displacement decay exponentially from the surface down. These non-uniformities motivate the question:
of what ‘dose’ are TGS measurements indicative for a given ion fluence, ion energy, and measurement grating spacing?
Instead of addressing this quantitatively, two methods have been used so far in this thesis in the assignment of dose
values. In Chapter 4, the applied grating spacing was matched to the depth of the damage layer and the peak dose
simply reported as the sample dose. In Chapter 7, this method was modified and instead of the peak dose per sample,
the dose averaged linearly from the sample surface to a depth of one grating spacing was reported. This method was
chosen as previous studies have shown that it is only this layer – one grating spacing thick – that should contribute
to the effective bulk material properties that may be extracted from TGS measurements [66]. However, this simple
linear averaging is entirely phenomenological and does not take into account any of the physics of the TGS excitation
or detection process.

Figure 8-8: Experimentally measured SAW velocity versus angles on Ni-based solid-solution alloys as measured using
$\Lambda = 4.82 \text{\ mu m}$. The pure Ni response is calculated using room temperature elastic constants. Here, 0° surface rotation
responds to the $\langle 110 \rangle \{001 \}$ polarization and 45° corresponds to the $\langle 100 \rangle \{001 \}$ polarization. Data are collected
without prior knowledge of these polarizations and shifted until the minimum SAW velocity is located at 45°.
In light of these shortcomings, this section proposes a new method of assigning dose to TGS measurements of ion implanted materials based on a SRIM-calculated applied dose profile and the mechanical actuation associated with an imposed SAW. In essence, this procedure will be a further modification of the linear averaging method used in Chapter 7. The driving postulation is that the depth-dependent SAW displacement serves as a reflection of how significantly the properties of a layer at a given depth affect the non-linearly-averaged material properties extracted from TGS measurements. In the following, a SAW is considered which is excited on an infinite half-space with surface normal along the \( \hat{z} \) direction and the acoustic polarization along \( \hat{x} \). Such a SAW will have a separable displacement profile of the form
\[
    u_j(x, z, t) = U_j(z)V_j(x, t),
\]
where \( j = (x, z) \). Depth-dependent applied dose profiles, \( D(z) \), will be taken based on SRIM outputs. Since the response monitoring technique in TGS is only sensitive to out-of-plane displacement – which may cause diffraction of the quasi-CW probing laser – it is \( u_z(x, z, t) \) which is of interest when seeking to determine to what contribution a non-uniform surface layer is sampled. Since the depth-dependence of this displacement profile is of interest in particular, the contribution \( U_z(z) \) will be used to weight the average of \( D(z) \) in this new dose assignment method. That displacement-weighted average is given by
\[
    D = \frac{\sum D(z)U_z(z)}{\sum U_z(z)},
\]
where numerically the summation is run from \( z = 0 \) (the free surface), to the total depth included in the SRIM calculation of \( D(z) \). As the SRIM depth sampling is not a controllable parameter, this average will be conducted computationally by re-sampling \( D(z) \) through linear interpolation at the pre-selected step size which is used to calculate \( U_z(z) \). For the examples below, this step size is fixed at 10 nm. Under this formulation, the problem is reduced to finding \( U_z(z) \) based on acoustic physics for whatever material is being investigated. Below, these forms are provided for both isotropic media and anisotropic single crystals where the particular SAW polarization vector plays an important role.

For the case of an isotropically elastic medium, Lin provides a detailed description of the derivation of both the in-plane (along the acoustic polarization direction) and out-of-plane (normal to the acoustic polarization direction, out of the free surface) displacement of Rayleigh-type SAWs [199]. Following Lin’s derivation, these two profiles are given analytically as
\[
    u_x(x, z, t) = A \left[ -q e^{-qs} + \left( \frac{2k_R^2q}{s^2 + k_R^2} \right) e^{-sz} \right] \exp \left[ i(\omega t - k_R x) \right],
\]
\[
    u_z(x, z, t) = A \left[ -k_R e^{-qs} + \left( \frac{2k_R^2q}{s^2 + k_R^2} \right) e^{-sx} \right] i \exp \left[ i(\omega t - k_R x) \right],
\]
where \( k_R = 2\pi/\Lambda \) is the Rayleigh wave vector, \( \omega \) is the Rayleigh wave frequency, and \( q \) and \( s \) are values defined by
\[
    q^2 = k_R^2 - \frac{\omega^2}{v_p^2},
\]
\[
    s^2 = k_R^2 - \frac{\omega^2}{v_s^2},
\]
where \( v_p \) and \( v_s \) are the bulk longitudinal and shear wave velocities in the material in question, respectively. For this
isotropic case, the bulk longitudinal and shear wave velocities are most easily given in terms of the Lamé constants \( \lambda \) and \( \mu \) as

\[
\begin{align*}
v_p^2 &= \frac{\lambda + 2\mu}{\rho}, \\
v_s^2 &= \frac{\mu}{\rho},
\end{align*}
\]

where \( \rho \) is the material density. These constants are related to the cubic fourth-order elastic constants in Voigt notation as

\[
\begin{align*}
C_{11} &= \lambda + 2\mu \\
C_{12} &= \lambda \\
C_{44} &= \mu.
\end{align*}
\]

In this isotropic case, then, the series of equations above can be used in concert with a method to calculate the isotropic Rayleigh wave velocity to determine the physical displacement associated with these Rayleigh modes as a function of depth into a surface on which they are induced. There are several polynomial approximations from which Rayleigh wave velocities may be calculated easily. Malischewsky provides one such approximation as

\[
v_R = v_s \left(0.874 + 0.196\nu - 0.043\nu^2 - 0.055\nu^3\right),
\]

where \( v_R \) is the Rayleigh wave velocity and \( \nu \) is the Poisson’s ratio [86]. This form has been shown in good agreement with exact numerical solutions to Rayleigh’s equation for all possible values of Poisson’s ratio \( \nu \in [-1, 0.5] \). Therefore, from a given experimental TGS measurement from which the grating wavelength \( \Lambda \) may be calculated, Eq. (8.7) may be used to calculate the Rayleigh wave velocity for known elastic constants. From \( v_R \) and a known \( k_R \), \( \omega = v_R k_R \) may be calculated, and Eq. (8.3) used to calculate the displacement profiles. An inspection of the forms of Eq. (8.3) also reveals that the in- and out-of-plane displacements oscillate out of phase with one another due to the phase factor accompanying the oscillatory term in \( u_z(x, z, t) \).

However, as many experiments considered in this thesis – and those being planned for the future – are conducted on anisotropic, single crystal materials, the isotropic displacement case described above is insufficient to describe the induced mechanical actuation. For the anisotropic case, Royer and Dieulesaint provide analytical forms for Rayleigh wave displacements polarized along arbitrary directions in orthorhombic, tetragonal, hexagonal, and cubic crystal symmetries [137]. Given the particular boundary conditions for SAWs propagating in a semi-infinite half-space, only four of the anisotropic elastic constants will be necessary to solve for Rayleigh wave displacements. These constants are \( C_{11}, C_{12}, C_{22}, \) and \( C_{44} \). For the high symmetry cubic crystal cases considered thus far in this thesis \( C_{11}=C_{22} \), which need not necessarily be true for all cases where the following analysis applies. For this system, the secular equation based on a plane-wave solution to the Christoffel equation (Eq. (3.5)) reads

\[
C_{22}C_{44}q^4 + \left[ C_{22} (C_{11} - \zeta) + C_{44} (C_{44} - \zeta) - (C_{12} + C_{44})^2 \right] q^2 + (C_{11} - \zeta) (C_{44} - \zeta) = 0,
\]

where \( \zeta \) is a directionally-dependent effective modulus for the Rayleigh wave propagation velocity in that direction.
given by
\[ \zeta = \rho v_R^2. \quad (8.9) \]

A composite elastic constant \( C \) will also be used in the forms for the displacement profiles with a value
\[ C = C_{11} - \frac{C_{12}^2}{C_{22}}. \quad (8.10) \]

In this formulation, the directionality of the acoustic wave polarization is determined by the elastic constants themselves. To explore SAW properties as a function of surface angle and polarization, the elastic constant tensor must be rotated to a frame of reference where the appropriate crystal plane is normal to the \( \hat{z} \) (or index 2) direction. The framework developed here for controlling tensor rotations and direction assignments will be described following the forms for Rayleigh wave displacement profiles.

Solutions to Eq. (8.8) are of two forms: cases where the roots \( q^2 \) are real and cases where they are imaginary. Each case has independent solutions for \( u_j(x, z, t) \). For the case where \( q^2 \) are real, values must be negative such that the roots may be written as
\[ q_r = -i\chi_r, \quad (8.11) \]
for \( r = (1, 2) \), such that \( \chi_r \) are real and positive. In this case, the displacement profiles are given by
\[ u_x(x, z, t) = A \left[ e^{-\chi_1 k_R z} - \frac{a_1}{a_2} e^{-\chi_2 k_R z} \right]^{1/2} \exp \left[ i (\omega t - k_R x) \right], \quad (8.12) \]
\[ u_z(x, z, t) = aA \left[ e^{-\chi_2 k_R z} - \frac{a_1}{a_2} e^{\chi_1 k_R z} \right] i \exp \left[ i (\omega t - k_R x) \right], \]

where
\[ a = \left( \frac{C}{\zeta} - 1 \right)^2, \quad (8.13) \]
\[ a_r = \frac{C_{11} - \zeta - C_{44}\chi_r^2}{(C_{12} + C_{44})\chi_r}, \]
again for \( r = (1, 2) \). In the case that the roots \( q^2 \) are complex, then the valuable roots must necessarily be conjugate and can be written as
\[ q_1 = -q_2^* = -g - ih, \quad (8.14) \]
and the corresponding mechanical displacement profiles given by
\[ u_x(x, z, t) = 2A \left[ e^{-hk_R z} \cos (gk_R z + \xi) \right] \exp \left[ i (\omega t - k_R x) \right], \quad (8.15) \]
\[ u_z(x, z, t) = 2aA \left[ e^{hk_R z} \cos (gk_R z - \xi) \right] i \exp \left[ i (\omega t - k_R x) \right], \]

where \( \xi \) is given by
\[ \tan \xi = \frac{C_{22}(C - \zeta) + C_{12}\zeta}{C_{22}(C - \zeta) - C_{12}\zeta} \frac{h}{g}. \quad (8.16) \]

Using the forms for Eq. (8.12) and Eq. (8.15), the procedure for finding displacement profiles for SAWs polarized along arbitrary crystal directions proceeds in the same manner as that for the isotropic case. Namely, the Rayleigh wave velocity in the particular crystal plane with the polarization of interest is solved for, and the corresponding wave
Figure 8-9: Normalized, out-of-plane SAW displacement as a function of depth into a sample surface, \( U_z(z) \), for one isotropic case (tungsten) and two anisotropic cases (copper). The isotropic profile decays relatively slowly, but the intensity is still reduced by a factor of about \( 1/e \) by one wavelength. As copper is quite anisotropic, \( A = 3.2 \), the displacement behavior varies strongly along different directions. Along \( \langle 11\bar{2}\rangle\{111\} \) the decay follows Eq. (8.12) and along \( \langle 100\rangle\{001\} \) the decay follows Eq. (8.15).

As an example, the contribution \( U_z(z) \) extracted from Eq. (8.3), Eq. (8.12), and Eq. (8.15) is plotted in Fig. 8-9 as a function of normalized depth using tungsten as the isotropic material and copper as the anisotropic material. For copper, displacement profiles along \( \langle 11\bar{2}\rangle\{111\} \) and \( \langle 100\rangle\{001\} \) demonstrate the possible different characteristics in the anisotropic crystal case. Namely, in the case that Eq. (8.15) governs \( U_z(z) \), nodes exist in the through-depth displacement such that certain depths will have out-of-plane displacements in opposite directions. The rough metric used throughout this thesis, that the acoustic actuation decays by roughly \( 1/e \) by one grating spacing into the surface, is true for each of these cases.

To show the effect of using the acoustic displacement to weight the dose average, Fig. 8-10 shows a normalized SRIM displacement profile, normalized \( U_z(z) \), and also their product \( D(z)U_z(z) \). The parameters for these cases are taken to be indicative of the experiments conducted in Chapter 4; the SRIM case is run for 35 MeV Cu self-ions into Cu, the acoustic polarization is taken as \( \langle 11\bar{2}\rangle\{111\} \), and the experimental grating spacing taken as 4.8 \( \mu \)m. The product \( D(z)U_z(z) \) is instructive to visualize as it shows the relative depths at which dose is being accumulated using this type of averaging. Despite \( D(z) \) being so heavily peaked near the end of the ion range, the competing behavior from the acoustic displacement causes the accumulated dose to be reasonably constant throughout the interrogation depth. Continuing to use parameters from Chapter 4, if a total dose at peak is assumed to be 90 dpa, then the linearly averaged dose is 30.72 dpa, and the weighted average dose is 15.36 dpa. It is unsurprising that the weighted average
returns a smaller value for the sample dose since the peak mechanical actuation is localized near the surface and the peak dose localized just before one wavelength down.

Thus far, all that has been provided here are the pieces necessary to compute a physics-inspired dose which may be assigned to samples damaged by ions and interrogated using TGS. Specifically, this method has considered the elastic properties measurable using TGS; the construction of a similar averaging technique appropriate for the measured thermal diffusivity using the thermal wave penetration as the weighting function is easy to envision. What this work has not shown is whether this new metric actually returns information useful for comparing radiation-affected microstructures subject to different conditions. To validate the utility of this metric a series of experiments using different combinations of test wavelength and spatially varying dose profiles which result in the same value $\bar{D}$ must be tested to see if the resulting optimized material properties are similar. An even more useful test would be to compare TGS measurements of a microstructure with uniform damage from neutron irradiation to an ion-exposed sample with the same degradation modes present. Using this weighted dose and testing at a variety of applied grating spacings would then give a sense of best practices when attempting to measure neutron-equivalent effects using in situ TGS.

Until one or both of these validations is carried out, the utility of the method shown above remains in question. One strong factor complicating this process will be the often-notable differences between the degree of spatially varying applied dose and the spatially varying retained damage such as voids or precipitates.

8.5 Implications

In this chapter, the work conducted to-date following the initial commissioning of the I$^3$TGS facility has been described. This work includes failed experiments, new infrastructure, baseline testing for future experiments, and a proposal for an improved dose assignment method. In general, though, all of the components of this chapter seek
either to utilize or to improve the world-unique capability available through the P^3TGS facility. Experiences like those described in Section 8.1, although frustrating in practice, are vital for garnering familiarity with any new technology. With the completion of the handling improvements described in Section 8.2 and the execution of baseline experiments on Ni-based CSAs, the next round of in situ TGS experiments on engineering-relevant materials await only facility access. The issue of assigning a meaningful ‘dose’ to ion exposed samples interrogated using TGS is yet another step in the development of a new suite of tools for monitoring material property changes in real time during irradiation.

The description of the next target matrix is included in this thesis primarily for the sake of example. The development of the new capabilities over the course of this work involved answering many interesting physics-based questions. But, the unique set of tools demonstrated in this work are just that: tools to conduct future investigations. The intended use for this technology, as described at the outset of this document, is to expedite the process of materials design for nuclear systems. Here, at the conclusion of the original work to be presented, that capability appears to be extremely promising, particularly for materials such as CSAs and HEAs where rapid screening of many combinatorial alloy variations is vital. But, the use cases of material evaluation in this broad framework moving forward need not be restricted to evaluating radiation tolerance under ion bombardment. In the final chapter of this thesis, future work which can and should be done on the facilities and methods developed here will be described. In addition, several new areas of investigation utilizing this broad framework will be enumerated, with the goal of inspiring creative science in the future.
Chapter 9

Future work and outlook

This thesis was motivated by a single driving question: can dose-property correlations for radiation-induced microstructure evolution be captured at much finer resolution, much more rapidly, than the current state of the art? The work presented here answers that question firmly in the positive. This is accomplished by shifting the emphasis away from the in situ testing of dose-structure relationships and instead seeking to measure dose-property correlations directly in situ during ion beam irradiation. Specifically, the all-optical method of transient grating spectroscopy (TGS) has been employed for this purpose in a world-unique facility capable of continuous elastic and thermal property monitoring during irradiation. In developing this capability, four necessary functionalities were systematically demonstrated: theoretical sensitivity to radiation effects, experimental sensitivity to high-dose radiation effects, time resolution, and ability to extract both elastic and thermal parameters simultaneously. The now-operational in situ ion irradiation TGS (I\textsuperscript{3}TGS) facility located at Sandia National Laboratories is poised to be utilized as a powerful tool in the design and development of materials to be used in radiation environments.

In the previous chapter, one specific weakness in the initial implementation of the I\textsuperscript{3}TGS facility related to sample positioning and management was identified and corrected. Moving forward, many more upgrades exist which would increase the stability and versatility of this facility. Most importantly, an upgrade is currently planned for the installation of a dedicated electron-suppressed beam current monitor. The in-place scheme of recording ion beam current off of the wire beam profile monitor is useful after several calibration steps, but a more direct measure of that current, which also frees the beam profile monitor for actual profile measurements, would be extremely useful. As mentioned previously, the highly non-uniform imposed damage profile from the ion beam can make quantitative analysis of radiation-induced effects challenging. As opposed to sequential exposures at different ion energies, as mentioned in the previous chapter, variable thickness energy degrading foils may also be used to implant multiple energies continuously into a sample [200]. These experimental components are often difficult to implement, but may be necessary if the other dose correlation options prove inadequate. Finally, multi-beam irradiations may be possible in the I\textsuperscript{3}TGS target chamber with significant future work. At the Sandia Ion Beam Lab, a newly-installed 1 MV tandem accelerator could be used as the source of this second beam for the purpose of H or He gas co-implantation.

Future upgrades are also under consideration for the sample handling and user protocol components of the I\textsuperscript{3}TGS facility. Although manual azimuthal rotation for acoustic wave polarization control has recently been installed, this actuation is not currently suitable for continuous rotation during exposure. Such a continuous rotation, synchronized
with the TGS measurement time step, would be necessary to measure complete fourth-order elastic tensors continuously throughout an exposure, rather than single-polarization acoustic wave speeds. Currently, samples may be exposed at intermediate or high temperatures as no active cooling system is present to combat beam heating effects at room temperature. A significant improvement would be the addition of a liquid nitrogen cooling capability such that room and cryogenic temperature in situ experiments could be conducted. Were new staging with this capability to be added, the ability to directly bias samples and collect current from the target itself would be included. This functionality could replace in-place charge collection mechanisms used for continuous beam current monitoring, or, at minimum, be used to calibrate in-place diagnostics. Finally, a functional capability to exchange samples through a load-lock mechanism in the target chamber would reduce the number of necessary system vacuum breaks, maintaining a cleaner exposure environment.

In addition to all of the specific hardware improvements mentioned above, work is ongoing to decrease the level of expertise necessary to conduct experiments at the I^3TGS facility. Advances such as automated positioning, acquisition, and diagnostics would allow this unique capability to be marketed as a user facility. Several instruments in the Ion Beam Laboratory are already available as user instruments through a variety of mechanisms. Wrapping this new capability into those programs is something all parties are interested in moving forward. As mentioned before, the major contribution made as the synthesis of the work here is a particular tool. Although its utility has been demonstrated on a few cases, opening this new capability to an interested community will dramatically increase the impact of this technology.

Several particular future studies currently under consideration stem directly from the scoping work presented in Chapter 8. The next available experimental campaign will be dedicated to Ni-based concentrated solid-solution alloys. The details for that experimental matrix have already been described and results from that study will provide some of the most relevant data for materials currently under consideration for future use in high radiation environments. Validation studies on the proposed method of dose assignment for ion irradiated materials studied using TGS must also be performed. One likely path forward is to use archival neutron-irradiated materials for comparison testing of uniformly damaged surfaces. Ideally, such validation studies – in concert with the wealth of literature on best practices for emulating neutron damage with ion beams – will provide functional design criteria for future in situ TGS irradiation experiments in terms of the selected relative ion energies and grating spacings.

Another area of future study necessary before widespread use of this technology is possible is the extension to polycrystalline materials. Although much information may be collected on single crystal materials with varying chemistry, all real structural materials being put to use in radiation environments or any other are polycrystalline. For TGS measurements, polycrystallinity only affects the material response if the grain size is smaller than the laser spot size used in experiment. Thus, for materials with large grains on the order of several hundred microns, an effectively single crystal acoustic response will most often be observed. In contrast, at very small grain sizes, the effects of anisotropic crystal responses will be averaged over, resulting in a response governed by isotropic elasticity and thermal transport. It is in the intermediate length scale in which polycrystal effects are most notable. Acoustic waves may be induced along different polarizations on multiple grains in a single excitation area, complicating quantitative analysis. For thermal transport, grain boundary character and density within the excited area may change the measured effective thermal diffusivity.
However, these challenges also present opportunities as measuring multiple acoustic polarizations in situ may provide equivalent information to a single crystal experiment with in situ azimuthal rotation. Such a polycrystal experiment would be simpler to implement. The question of how to mitigate or exploit polycrystal effects for in situ irradiation experiments is, at this moment, open and may prove either a benefit or hindrance to a wider adoption of this methodology. These effects should be explored first on model systems to reduce complexity. However, once those tests are complete, an immediate engineering alloy target for in situ TGS testing will be precipitate disordering and dissolution in Ni superalloys. Several samples of Inconel 718 have already been procured from a collaborator for this purpose. Similar to the planned testing of Ni-based CSAs, the irradiation behavior of this material has already been characterized quite well. Irradiation-induced changes to precipitate structure, size, and number density will affect the effective properties of the crystal matrix on length scales accessible through TGS, allowing a much finer time-resolved understanding of their evolution to be gathered.

With some immediate steps for future work in hand, it is useful to re-examine types of experiments which have been demonstrated thus far. The focus of the present work has mainly been in the use of highly time-resolved material property evaluation to essentially ‘fill in’ coarsely-sampled data collected post exposure. However, this is likely not the most impactful use for in situ TGS. For dynamically changing materials, the instantaneous, out-of-equilibrium material properties and microstructure are not those commonly reported in post-irradiation examination due to effects such as parasitic annealing during a high vacuum cooling cycle. That in situ TGS reports the true out-of-equilibrium properties directly is an extreme advantage in its own right. In addition, future experiments could easily conduct this type of in situ testing not only through steady-state material evolution, but also through transient conditions. Understanding the instantaneous behavior of a stainless steel structure having received twenty years of in-service radiation exposure followed by an accident scenario temperature spike of several hundred degrees is not currently possible. Although other forms of in situ interrogation exist, testing through these types of transients is often quite challenging. Specifically for in situ TEM experiments, sample geometry and drifting often prohibit dramatic condition changes. TGS is notably applicable to bulk material samples. Even through physical drifting may pose experimental challenges, it may be designed against. The ability for transient testing in in situ TGS experiments seems to be one of the most powerful future use cases of this technology.

Here at the completion of this thesis the wider implications of the materials testing framework which has been developed must be considered. What this work shows is that non-destructive, non-contact, multi-modal material property evaluation is possible on dynamically changing systems in out-of-equilibrium conditions. Although the particular out-of-equilibrium condition of interest was irradiation-induced microstructure evolution, radiation is only one of many driving forces which can cause long-term material changes. Depending on the material system in question, other driving forces during either service or manufacture include temperature, stress, high voltage switching, cyclic fatigue, extrusion processes, deposition, and additive construction. Given the versatility of time-resolved TGS as demonstrated here, experimental geometries may be envisioned which would allow testing under many combinations of these conditions. The technology described here is poised to be utilized as a powerful high-throughput design and down-selection tool for materials being developed for high radiation environments. More broadly, however, in situ all-optical property interrogation – in the form of TGS or otherwise – may be used as an extremely flexible tool to study the dynamic evolution of materials subject to many driving forces.
The final perspective motivated by this work concerns the use of synergistic or companion material testing. For a great many materials on which and conditions during which in situ TGS testing may be applied, measures of micron-scale acoustic propagation and thermal transport are not the material characteristics of interest. However, these methods, by virtue of the non-destructive nature of the interrogation, may still prove useful as highly time-resolved indirect measures of material evolution which can be used to precisely target future experiments. For example, in many chemically complex alloys the initiation location and composition of precipitation during moderate or high temperature annealing are important features which must be noted for alloy design. Locating these features temporally using standard test sampling protocols is extremely difficult. But, precipitation of this sort will likely lead to changes in the effective elastic properties of the material in question. By using an in situ TGS monitor during an annealing experiment, the precise sample history necessary for the initiation of decomposition may be established. Further experiments may be stopped exactly at this point and detailed microstructure characterization carried out to better understand mechanisms and validate models. Thinking beyond photoacoustic testing, this completely generalized type of experimental design – where achievable highly resolved testing along one process parameter is used to inform targeted evaluation – seems to be underutilized at present. Applying this experimental design philosophy across fields of materials development has the potential to drastically increase efficiency of the design process itself and produce materials fully optimized for their intended use.

In summation, this thesis has delivered a first-of-a-kind experimental capability: the ability to continuously monitor material properties changing as a result of radiation-induced or -enhanced material evolution. At the outset, this goal was targeted for its prospective ability to dramatically increase the speed at which new materials may be designed for nuclear systems of all types. This capability has been delivered and stands poised to be used in the near future as a unique tool for materials design and development. Along this pathway, advances in in situ, multi-modal non-destructive evaluation have been generated which open extremely wide areas of future research. This work began with a rather simple question of the form: can this tool exist? In answering affirmative, a much broader question now lies ahead: what can this technology do?
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References


