Multidisciplinary Research in Raman Spectroscopy, Phase Imaging and Their Applications in Heat Transfer

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Abstract

Recent advances in micro-to-nanoscale heat transfer have led to tremendous research interests in the high spatial resolution thermal characterization techniques. Although great improvement has been made in temperature probe, heat flux measurement and thermophysical properties characterization especially for solid-state materials and structures, precision thermal characterization is still challenging due to the presence of multiphysics coupling, the limitation of resolution and the restriction of materials that can be studied. The goal of this thesis is to explore more possible opportunities for advanced thermal measurement techniques. Specifically, this thesis mainly focuses on the development of Raman spectroscopy and phase imaging and demonstrates their applications to micro-to-nanoscale heat transfer.

Due to the superior spatial resolution and the non-contact nature, micro-Raman spectroscopy has been widely applied for local temperature measurement. However, the presence of multiphysics coupling to the optical phonon modes and the necessity to have Raman signature for the test materials limit the application of micro-Raman thermometry to simple solid-state devices. In this thesis, we present several advancements which extend the capability of Raman spectroscopy to multiphysics coupling systems, Raman-inactive materials and nanoscale thermometry. Specifically, we simultaneously measured the temperature, stress and electric field in GaN HEMTs and the linear thermal expansion coefficient of MoS$_2$ monolayer flake using the multiple peaks fit method. We presented a method to interface micro-Raman system with a phase change heat transfer test setup and used this integrated setup to study the thin film evaporation on structured surfaces. To measure the temperature of Raman-inactive materials, we used nanoparticles as the Raman agent. We measured the temperature distribution of the optically transparent and thermally insulated silica aerogel. Additionally, this thesis also proposed a concept of nanoscale Raman thermometry using plasmon enhanced gold-silicon nanoparticles. The electric field concentration properties and in situ measurement capability were proven using simulation and experiments.
Attributed to the high sensitivity to geometrical structures and refractive index of materials, phase imaging techniques were useful for weakly scattering systems. Although the property of imaging transparent materials has been well-demonstrated, the application of nanoscale detection using phase imaging is lacking. In this thesis, we developed robust phase imaging method based on transport of intensity equation and depth scanning technique and proved the ultrahigh sensitivity of phase in nanoscale inspection. This developed technology was validated through a number of simulations and experiments, including detecting the deep-subwavelength defects on 9 nm semiconductor wafers. The thesis finally shows the opportunity of using phase imaging to study micro-to-nanoscale phase change heat transfer. The dynamic interactions and growth of condensing droplets were investigated using the phase imaging enhanced environmental scanning electron microscopy.

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Chapter 1

1. Introduction

1.1 CHALLENGES AND MOTIVATION

Measuring heat transfer is difficult even at the macroscale because thermal characterization is typically associated with multiphysics processes (electrical heating, fluid transport, mass transfer and phase change etc.) and many key quantities (temperature, heat flux, thermal physical properties such as specific heat, linear thermal expansion and thermal conductivity etc.) [1]. Recent advances in heat transfer physics, energy transport in semiconductor materials, micro-to-nanoscale heat transfer and phase change heat transfer lead to new challenges to theoretical and experimental techniques. Here, we summarized several key challenges covered by this thesis,

(1) Significant progress made in micro-to-nanoscale heat transfer, leading to new physical insights which cannot be well-interpreted by established macroscale theories. To better understand the thermal transport at such small scales, in situ, high spatial resolution and noninvasive thermal probe shows great necessity for scientific researches and industrial applications [1-16].

(2) The massive application of semiconductor materials in integrated circuits motivate the need for thermal characterization and management in transistor devices. Specifically, the high power density presented in the gate region of the semiconductor power amplifier leads to highly localized temperature, which should be precisely characterized to estimate the lifetime of the device. The multiphysics coupling effects, i.e., the interactions between local temperature rise, thermal and mechanical stress, and internal electromagnetic field are important to understand the carrier dynamics and explain the failure mechanism of devices. Additionally, the discoveries of 2D materials such as graphene, phosporene and transition metal dichalcogenides (TMDs) show great potential for next generation solid state devices. For this reason, measuring the thermophysical properties of 2D atomic monolayer is of both fundamental and application significance [17-28].

(3) The application of nano-to-microscale structured surfaces leads to significant improvement in liquid-vapor phase change heat transfer. Recent experimental achievements in dropwise and jumping-droplet condensation, thin film evaporation, pool boiling and flow boiling show more efficient phase change processes by altering surface chemistry and micro-to-nanoscale morphology. Consequently, comprehensive theoretical frameworks should be developed to understand phase change at the micro and nanoscale. Additionally, physics at the liquid vapor interface on the structured surfaces is of particular interest, for understanding the thermal fluid transport at small scales and interfacial transport
phenomena. Thus, experimental techniques which are capable of directly probing liquid-vapor interface or capturing the dynamic evolution process at micro-to-nanoscale are of great importance [29-41].

In this thesis, we focused on the above three challenges in heat transfer problems and presented some theoretical and experimental endeavors to show possible directions and opportunities in future research. Specifically, for experimental studies, our key idea is to use optics for advanced thermal characterization from semiconductor materials to liquid-vapor phase change heat transfer at micro-to-nanoscale, because the sensitive, noninvasive and noncontact properties of light can provide accurate measurements with a minimized disturbance to the physical fields to be probed. The optical tools developed in this study is mainly Raman spectroscopy and phase imaging, which will be introduced in detail as follows.

Raman spectroscopy is one of the most common tools for material characterizations, which is capable of measuring the optical phonon frequency of Raman-active materials directly. As the phonon, the quasi quantum particle representing the atomic motion, is highly temperature sensitive, the Raman spectroscopy was widely used to local temperature measurement with a superior spatial resolution of ~1 μm. In this work, we developed the Raman thermometry as the microscale thermal probe. This micro-Raman thermometry was first applied to studied semiconductor materials due to the strong Raman activity of these materials. The multiphysics process of temperature rise, complex stress and internal electric field presented in gallium nitride (GaN) high electron mobility transistors (HEMTs) was characterized using micro-Raman spectroscopy. To validate the capability of the developed technique in measuring the thermophysical properties, we measured the linear thermal expansion coefficient of monolayer MoS₂ flakes, which is difficult to be measured by traditional techniques due to the atomic thickness of 2D materials.

However, the ability of micro-Raman thermometry is not limited in semiconductor materials. In this work, there were also many experimental efforts carried out to better understand the thermal issues of the other complex systems. In the first attempt, we interfaced the micro-Raman thermometry to a phase change heat transfer test rig, and measured the thin film evaporation process on the micro-structured surfaces. Thanks to the high-spatial resolution thermal probe, the local wall superheat near the three-phase contact line was accurately measured, which is difficult using previous contact mode temperature sensors. The temperature variation on the structured surfaces was also obtained with microscale resolution. This micro-Raman measurement reveals the effect of surface structure on heat transfer enhancement, and shows the possibility of using micro-Raman for phase change heat transfer in the future. In the second attempt, we extended the ability of micro-Raman thermometry to Raman-inactive systems. We measured the conduction and radiation conjugate heat transfer in an optically transparent silica aerogel. The temperature distribution
inside the aerogel cannot be measured by traditional contact mode temperature sensors due to the super low thermal conductivity of silica aerogel. However, with the help of micro-Raman thermometry, the interaction between radiation and conduction can be clearly resolved in this work.

We not only developed micro-Raman thermometry for both Raman-active and inactive systems, but are also working on extending the spatial resolution from the microscale to nanoscale. In this work, we designed a nano-Raman sensor by combining the Raman effect with the surface plasmon resonance effect. This nano-Raman sensor can be used to study either the temperature distribution of any Raman-inactive materials or the nanoscale thermal transport problems with reasonable resolution.

On the other hand, however, for many complex heat transfer processes, such as droplets growth during vapor condensation and bubbles departure in pool boiling, directly “seeing” what happens during those heat transfer phenomena is always of fundamental interests. For this reason, advanced imaging techniques will be very helpful for revealing more physical insights. In this thesis, particular theoretical and experimental imaging efforts were carried out for phase change heat transfer analysis. We discovered the potential of phase imaging in detecting nanoscale features at deep-subwavelength. Theoretical and numerical validation were carried out to validate the sensitivity of phase imaging. Experimental endeavors were firstly conducted for deep-subwavelength defects inspection on 9 nm semiconductor wafers. The ultrahigh sensitivity of phase imaging for nanoscale detection was proven. After these preliminary tests, this developed phase imaging technique was then used to improve the performance of environmental scanning electron microscopy (ESEM) and study the dynamics of condensing droplets in the ESEM chamber. The dynamic behaviors of condensing droplets, such as the nucleation sites on the nanostructured surfaces, single droplet growth and droplets coalescence, which are of particular interests in predicting the overall heat transfer performance of condensation, were experimentally characterized using the developed phase imaging technique.

1.2 RAMAN SPECTROSCOPY: THEORY AND APPLICATIONS

1.2.1 Overview of the Raman effect

The Raman scattering refers to a kind of inelastic light-matter interaction process, in which the molecules or atoms in the material system are excited to higher vibrational or rotational (only for molecules) energy levels by the incident light. In a particle viewpoint, we use photon-phonon interaction to express this inelastic scattering process, where the photon and phonon are the quantized quasi-particle of electromagnetic wave and lattice vibrations. The Raman process can be explained where the incident photon (excitation) with frequency (energy) $\omega_0$ is scattered to a photon with frequency $\omega_s$ by emitting (Stokes
process) or absorbing (anti-Stokes process) a phonon in the material. The change in frequency between the incident and the scattered photon \([42-45]\),

\[
\omega = |\omega_0 - \omega_s|
\]  

(1.1)
is equal to the phonon frequency (vibrational energy levels) emitted or absorbed in the Raman scattering process according to the conservation of energy. To better understand the Raman scattering process with respect to the point of energy levels transition and particle interactions, we provide the following schematic demonstration which qualitatively describes the physics during the scattering. As shown in Figure 1.1, the entire scattering process can be divided into three categories \([46]\). Initially, the electrons and nuclei stay in their ground state. In the second stage, the ground electron cloud state is perturbed by incident electromagnetic field and absorb the energy of a photon \(h\omega_0\). The electron cloud is distorted and form an unstable “virtual state”. As the response time of electrons is much faster than that of the nuclei, the electrons will oscillate with the external field but the nuclei approximately stay at the same position. Thus the electrons-nuclei system excited by the external field behaves like an oscillating dipole which emits electromagnetic radiation to outer field, known as the scattering. Once the electron cloud changes back to its original configuration (see the stage 3), it will emit one photon. For the majority of emission processes, the scattered photon frequency \(\omega_s\) is the same as the incident photon frequency \(\omega_0\), which is known as the inelastic Rayleigh scattering. However, due to the interaction between electrons and the nuclei, part of the energy absorbed from the external field can be transferred to the nuclei and change the ground vibrational energy state to the first vibrational state of nuclei through electron-phonon scattering as shown in stage 3. In this situation, the scattered photon has a different frequency with the incident photon, and this scattering process referring to the excitation of a vibrational energy level is known as the Raman effect. Finally, the nuclei will transit to their ground state through thermal relaxation \([47]\).
The Raman effect can be well-described under the classical framework by considering the electric dipole radiation of molecules or lattices. We assume the incident electromagnetic wave is expressed as,

\[ P = \alpha E \]  \hspace{1cm} (1.2)

where \( P \) is the electric dipole moment vector, \( \alpha \) is the polarizability tensor, and \( E \) is the external electromagnetic field. To simplify the problem, we consider the relation shown in Equation (1.2) in an isotropic system,

\[ P = \alpha E \]  \hspace{1cm} (1.3)

and we express the plane wave incident field as,

\[ E = E_0 \cos(\omega_0 t - k_0 \cdot r). \]  \hspace{1cm} (1.4)

It should be noted that due to the atomic oscillation, the distribution of charges will change and as a consequence, the polarizability \( \alpha \) of the material is not a constant but a function of atomic oscillation which is given by,
\[ \alpha = \alpha_0 + \sum_i \left( \frac{\partial \alpha}{\partial Q_i} \right)_0 Q_i + \frac{1}{2!} \sum_i \sum_j \left( \frac{\partial^2 \alpha}{\partial Q_i \partial Q_j} \right)_0 Q_i Q_j + \cdots \]  

(1.5)

where \( \alpha_0 \) is the polarizability of the material when its atoms stay at their equilibrium positions. \( Q_i \) is the normal (nuclear) coordinates of the \( i^{th} \) vibrational mode of the atoms, which is expressed as,

\[ Q_i = Q_{i,0} \cos(\omega_{i,q} t - q_i r). \]  

(1.6)

For the 1st order Raman effect, we only consider the harmonic terms of Equation (1.5).

Combining Equations (1.3), (1.4) and (1.7), the time-dependent electric moment of the material system is given by,

\[ P = \alpha_0 E_0 \cos(\omega_0 t - k_0 \cdot r) + \frac{1}{2} \sum_i \left( \frac{\partial \alpha}{\partial Q_i} \right)_0 Q_{i,0} E_0 \cos \left( (\omega_0 - \omega_{i,q}) t - (k_0 - q_i) \cdot r \right) + \frac{1}{2} \sum_i \left( \frac{\partial \alpha}{\partial Q_i} \right)_0 Q_{i,0} E_0 \cos \left( (\omega_0 + \omega_{i,q}) t - (k_0 + q_i) \cdot r \right). \]  

(1.8)

As depicted in Equation (1.8), for each vibrational mode, the oscillating electric dipole \( P \) emits radiation with three different frequencies, i.e., \( \omega_0, \omega_0 - \omega_{i,q} \) and \( \omega_0 + \omega_{i,q} \), where radiation with frequency \( \omega_0 \) is the Rayleigh scattering, with frequency \( \omega_0 - \omega_{i,q} \) is the Stokes process and with frequency \( \omega_0 + \omega_{i,q} \) is the anti-Stokes process. Equation (1.8) also provides the selection rule of Raman scattering,

\[ \omega_s = \omega_0 \pm \omega_{i,q} \]  

(1.9a)

\[ k_s = k_0 \pm q_i \]  

(1.9b)

where Equations (1.9a) and (1.9b) represent the conservation of energy and momentum during the Raman scattering process, respectively. The positive sign represents the anti-Stokes process and negative sign is the Stokes process. It is worthy to mention that the photon can carry a large amount of energy but little momentum, and most of phonons have relatively low energy but large momentum. Restricted by the selection rules expressed in Equation (1.9), only the optical phonons near the center of the first Brillouin zone which is known as the \( \Gamma \)-point for crystals can interact with the incident photons. For this reason, the number of vibrational modes can be measurement through Raman process is limited.
Figure 1.2 shows a typical Raman spectrum of silicon excited by 633 nm laser. The x axis of the Raman spectra is denoted as “Raman shift” with a unit of cm\(^{-1}\), which is the relative difference in wavenumber between the absorbed and emitted photons [48],

\[
\omega = \frac{1}{\lambda_0} - \frac{1}{\lambda_s}.
\] 

(1.10)

The Raman shift is directly proportional to the frequency of phonon (in THz) which is emitted or absorbed during Raman scattering. There is a sharp peak located at the center with a Raman shift about 520 cm\(^{-1}\). According to Figure 1.2, there are several key properties that characterize the Raman peak. One of the most important properties is the central peak position (around 520 cm\(^{-1}\)) referring to the vibrational energy level of the molecules or lattices, which is also known as “Stokes/anti-Stokes position”, “Raman peak position”, or “phonon frequency”. The second spectrum property is the intensity of the Raman peaks, which represents the average population of the excited phonons in the molecules or lattices described by the Boson-Einstein distribution. The Raman peak is not a perfectly sharp peak but has specific linewidth and lineshape depending on different vibrational modes and materials.
Figure 1.2. A typical Raman spectrum of silicon excited by 633 nm laser. The strongest peak marked as a star is the silicon Raman peak. The other three sharp peaks are emission lines from the neon calibration lamp.

We would like to provide more explanations to the lineshape of the Raman spectra. As mentioned earlier, the behavior of the electron-nuclei system can be depicted classically as an oscillating electric dipole. For this reason, the motion of electrons during the radiation is modeled by a damped oscillator which is given by [49],

\[ \ddot{x} + \gamma_i \dot{x} + \omega_i^2 x = 0 \]  \hspace{1cm} (1.11)

where \( x \) is the electron coordinate relative to the nuclei, \( \gamma_i \) is the damping ratio, and \( \omega_i \) is the vibrational frequency of \( i^{th} \) mode. When the damping ratio is small, the electronic motion can be expressed as,

\[ x = a_0 \exp \left(-\frac{\gamma}{2} t\right) \cos(\omega_i t). \]  \hspace{1cm} (1.12)

In the frequency domain, we can obtain the spectrum of the electrons radiation, which is given by,

\[ A(\omega) = \int_{-\infty}^{+\infty} x(t) \exp(-i\omega t) \, dt = a_0 \left( \frac{1}{\frac{\gamma}{2} - i(\omega - \omega_i)} + \frac{1}{\frac{\gamma}{2} - i(\omega + \omega_i)} \right). \]  \hspace{1cm} (1.13)

As the magnitude of dipole radiation is proportional to the amplitude of the electrons oscillation, because the electric dipole moment can be also expressed as \( P = ex \) where \( e \) is the elementary charge of electron. The scattering intensity of phonon mode \( i \) at frequency \( \omega \) can be approximated as,

\[ I_i(\omega) \propto A(\omega)A^*(\omega) = \frac{a_0^2}{(\omega - \omega_i)^2 + \left(\frac{\gamma}{2}\right)^2}. \]  \hspace{1cm} (1.14)

As the total scattering intensity is,

\[ I_0 = \int_{-\infty}^{+\infty} I_i(\omega) \, d\omega \propto a_0^2 / \gamma_i \]  \hspace{1cm} (1.15)

Thus the spectrum of the scattering intensity is given by,
which is known as the Lorentzian lineshape of spectrum at the vibrational mode \( i \). Therefore, the Lorentzian lineshape gives the intrinsic spectrum broadening profile of a Raman peak. According to Equation (1.16), there are two parameters characterizing the lineshape, i.e., \( \omega_i \) and \( \gamma_i \). It is clear that \( \omega_i \) is the central peak position of the Raman peak corresponding to phonon frequency \( \omega_i \), and \( \gamma_i \) is the full width half maximum (FWHM) or linewidth of the peak. It is of great interest to discuss the physical meaning of linewidth shown in Figure 1.2. According to the Heisenberg uncertainty principle to the vibrational energy level \( E_i \) corresponding to phonon the mode \( \omega_i \),

\[
\Delta E_i \tau_i \approx \hbar
\]  

(1.17)

where \( \tau_i \) is the lifetime of energy level \( \Delta E_i \) and \( \hbar \) is the reduced Planck constant. The phonon energy at the \( i^{th} \) mode is expressed as \( E_i = \hbar \omega_i \). Therefore, the uncertainty of energy level \( i \) is,

\[
\Delta E_i = \hbar \delta \omega_i
\]  

(1.18)

According to Equations (1.17) and (1.18), we can relate the broadening of the Raman peak to the lifetime of energy level \( i \),

\[
\gamma_i \approx \delta \omega \approx 1/\tau_i
\]  

(1.19)

where the linewidth of the Lorentzian profile represents the lifetime of the vibrational energy level [50-52]. The larger of the linewidth is, the shorter lifetime of the energy level will be. The ground energy level, for example, has a very large lifetime, and thus has very small uncertainty in the energy band. For this reason, the ground energy level should have a very sharp peak observed in the spectrum. From a practical consideration, the Raman spectra have to be measured by a spectrograph which typically consists of a spectrometer and a CCD camera. According to the imaging principle, the measured Raman spectra \( I_s(\omega) \) should be a convolution of intrinsic Raman spectrum \( I_i(\omega) \) and the response function of the spectrograph system \( I_{sys}(\omega) \), which is arising from the (1) intrinsic response of spectrograph (such as the CCD camera) and (2) the diffraction effect (known as the point spread function (PSF)) of the other optical components.

\[
I_s(\omega) = I_i(\omega) * I_{sys}(\omega)
\]  

(1.20)
The intrinsic response of the spectrograph system is known as the Doppler effect due to the thermal motion of atoms, which can be expressed as a Gaussian lineshape. The PSF of the optical components is given by the square or the hyperbolic sine function. For the practical convenience, however, the total response of the spectrograph is still approximated with a Gaussian profile expressed as Equation (1.21). Then, the measured Raman spectrum is described by the Voigt lineshape, which is the convolution of Lorentzian and Gaussian lineshapes.

\[ I_{\text{sys}}(\omega) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left( \frac{-(\omega - \omega_{0})^{2}}{2\sigma^{2}} \right) \]  

(1.21)

It should be noted that the classical theory as described above can only provide a qualitatively understanding for the normal Raman scattering process. The fully quantitative description of a variety of Raman effects such as the hyper Raman effects, coherent Stokes Raman scattering (CSRS) and coherent anti-Stokes Raman scattering (CARS) need the implementation of quantum mechanics and the perturbation theory, which can be found in The Raman Effect: A unified Treatment of the Theory of Raman Scattering by Molecules (2002) [53].

1.2.2 Micro-Raman Spectroscopy

Micro-Raman spectroscopy is one of the most common experimental techniques for Raman effect measurements by detecting the relative change in wavenumber of a photon before and after a Raman scattering event according to Equation (1.10). Figure 1.3 shows the schematic diagram of the micro-Raman spectroscopy setup. For solid state material measurement, the backscattering configuration is typically used. As shown in Figure 1.3, the laser excitation is focused to a small spot on the top surface of the sample. The spot is typically at the microscale (for visible excitation) which is restricted by the diffraction limit. The Raman scattering within the focused spot is excited. The scattering light propagates along the reverse path relative to the incident excitation and is collected by the same objective. The strong Rayleigh scattering at wavelength \( \lambda_{0} \) is blocked by an edge filter. The Raman scattering, which enters the spectrometer, is dispersed into the spectrum.
Figure 1.3. Schematic demonstration of a micro-Raman spectroscopy setup for solid-state material measurement.

The precision of the micro-Raman measurements depends on the spatial resolution and spectra resolution. The spatial resolution is mainly determined by the microscope objectives. Specifically, the lateral spatial resolution is usually defined by the diffraction limited laser spot size in diameter, which is given by [54],

\[ d_l = \frac{1.22\lambda_0}{NA} \]  \hspace{1cm} (1.22)

where \( d_l \) is the laser spot diameter and \( NA \) is the numerical aperture of the microscope objective. Typically, microscope objectives of 10× to 100× magnifications with \( NA \) of 0.5 to 0.8 are used, leading to \( d_l \) of \( \approx 0.8 \, \mu m \) to \( 1.5 \, \mu m \) for visible excitations. The spatial resolution in the vertical direction (along the optical path) is defined by the depth of field (DOF), which can be expressed as [54],

\[ d_v = \frac{4\lambda_0}{NA^2} \]  \hspace{1cm} (1.23)

where \( d_v \) is the DOF which is often \( \approx 2 \, \mu m \) to \( 5 \, \mu m \) depending on the laser wavelength and microscope objective. Due to the restriction of spatial resolution, the Raman scattering collected by the objective is the volumetric average within a cylinder whose diameter is about \( d_l \) and height is about \( d_v \).
The spectra resolution refers to the number of data points that resolve the Raman peaks, which is determined by the optical properties of the spectrometer (grating groove density, focal length and slit width), and pixel size of the detector (CCD camera). The Raman peaks are fitted by a certain lineshape functions, such as a Lorentzian, Gaussian or Voigt profiles, and the center of the peaks (known as the Raman peak position) can be accurately determined. With the use of long focal length spectrometers, high groove density grating and high spatial resolution detectors, the uncertainties of the Raman peak position from multiple measurements can be as small as 0.01 cm⁻¹.

As the Raman peak position measured by the spectrometer represents the vibrational or the phonon modes of the molecule/lattice, which is related to the thermal motion of atoms, micro-Raman spectroscopy can be used as a thermometry technique. For micro Raman thermometry technique, the accuracy of temperature measurement not only depends on the spatial and spectra resolutions which have been discussed above, but an accurate relationship correlating the temperature to the Raman peak properties. In previous Raman thermometry research, there have been many theoretical or empirical relationships provided based on comparing the Stokes-to-anti-Stokes intensity ratio, fitting the linewidth, and fitting the center of the peak.

The first method by comparing the Stokes-to-anti-Stokes intensity ratio is based on the fact that the intensity of Raman signal is proportional to the corresponding phonon population, which is given be Boson-Einstein distribution. For this reason, the Stokes-to-anti-Stokes intensity ratio is equal to the phonon population ratio after the Stokes/anti-Stokes process at the same temperature [55],

\[ \frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = \frac{\langle n_s \rangle}{\langle n_a \rangle + 1} = \exp\left(-\frac{\hbar \omega_{ph}}{k_BT}\right) \]  \hspace{1cm} (1.24)

where \( I_{\text{anti-Stokes}} \) and \( I_{\text{Stokes}} \) are the Raman signal intensity of anti-Stokes and Stokes processes respectively. \( \langle n_a \rangle \) is the average phonon population containing in the detected volume. \( \omega_{ph} \) is the corresponding phonon frequency. Equation (1.24) gives a pure theoretical relationship between Raman peak and temperature from the principle of solid-state physics. However, in real practice, there are several factors that restrict the application of Equation (1.24) for temperature measurement. Firstly, to implement the Stokes-to-anti-Stokes intensity ratio method, we need to measure both the Stokes and anti-Stokes peaks, which means the range of the wavelength measured by the spectrometer should at least be twice larger than if only the Stokes/anti-Stokes peaks are measured. However, the larger range of wavelength can be measured, the worse spectra resolution will be. Thing will be even worse when the phonon frequency is
very high. Secondly, for most of the temperature measurements (especially for semiconductors measurements), the temperature of interests is from the ambient temperature to two or three hundreds Celsius degree, which is in a low temperature regime. According to Equation (1.24), however, when the temperature is low, the anti-Stokes peak intensity will be very weak compared the Stokes peak, and sometimes it is very challenging to detect such weak signal. For those reasons, principle based on Equation (1.24) is not widely applied for micro-Raman thermometry [52, 54, 55].

It has been found experimentally that linewidth (inverse proportional to the lifetime of corresponding energy level) of the Raman peak becomes larger when temperature increases, which makes physical sense because the higher energy level is more unstable at higher temperature. There are linear or parabolic empirical relationships between temperature and linewidth provided for temperature measurement. However, current experimental results show that the uncertainties in the temperature measurement using linewidth fitting method were very large, which demonstrates this linewidth based method is still not ideal for accurate temperature measurement.

Not only the linewidth, but the center peak position, i.e., the phonon frequency, changes with temperature, which gives a possibility to correlate the Raman peak position to temperature rise. Physically, there are two mechanisms that contribute to the change of phonon frequency, i.e., the strain effect $\Delta \omega_{\text{strain}}$ and the phonon-phonon scattering $\Delta \omega_{\text{ph-ph}}$ effect, which are expressed as [56, 57],

$$\Delta \omega = \omega(T) - \omega(T_0) = \Delta \omega_{\text{strain}} + \Delta \omega_{\text{ph-ph}}$$

where $T_0$ is the reference temperature. The thermal expansion induced strain changes the interatomic potential and force constants between atoms which leads to the shift of phonon frequency $\Delta \omega_{\text{strain}}$ with temperature. The $\Delta \omega_{\text{strain}}$ usually behaves linearly with the change of temperature due to the linear dependence between thermal strain and temperature rise. More generally, however, any sources such as mechanical stress, electric field that can induce strain, will contribute to the shift of phonon frequency $\Delta \omega_{\text{strain}}$. The phonon frequency shift $\Delta \omega_{\text{ph-ph}}$ depends on temperature rise because the phonon-phonon scattering rate is related to the phonon occupation possibility. In principle, the temperature rise nonlinearly affects the $\Delta \omega_{\text{ph-ph}}$ [56, 57]. However, in the framework of perturbation theory, when the temperature is relatively low (which is true for most of temperature measurement study on semiconductors), $\Delta \omega_{\text{ph-ph}}$ also shows a linear dependence on temperature. For example, it has been discovered that the change of phonon frequency behaves linearly with temperature rise when the temperature is between 25 °C and 300
°C for bulk GaN samples [58, 59]. As a consequence, the relation between the shift of phonon frequency
and temperature rise is,

$$\Delta \omega = \omega(T) - \omega(T_0) = A(T - T_0)$$

(1.26)

where A is a fitting coefficient obtained from calibration. It has been found that many solid-state materials,
such as Si, GaN, TiO$_2$, and MoS$_2$, show very sensitive temperature dependent Raman peaks with good
linear relationships. For this reason, fitting the Raman peak position has become one of the most convenient
and accurate techniques for temperature measurements in micro-Raman thermometry. With accurate peak
position measurement and carefully calibration, the uncertainty of temperature arising from the random
error of peak positions and the uncertainty of fitting coefficient can be as small as 0.5 °C.

In this study, we designed and developed a free-space micro-Raman thermometry setup to collect the
Raman signal of samples in the backscattering configuration. As shown in Figure 1.4, the system consists
of two single longitudinal mode diode lasers (supporting two wavelength excitation i.e., \(\lambda = 532.019\) nm
and \(\lambda = 632.904\) nm respectively, SLM-FS, REO), an optical microscope, a dichronic beam splitter (BS,
LPD02-633RU-25, Semrock), a long pass edge filter (LP02-633RU-25, Semrock), and a 750 mm focal
length spectrometer (Acton Spectr-Pro SP-2750, Princeton Instrument) equipped with a 300 G/mm and an
1800 G/mm grating and a CCD camera (PIXIS, Princeton Instrument). A variety of microscope objectives
with magnifications of 10×, 50× and 100× and with NA of 0.55 to 0.8 (LMPlanFL N, Olympus) can be
used to focus the laser excitation on the test sample and collect the Raman scattered light. The diameter of
the focused laser spot ranges from 0.8 μm to 1.5 μm depending on the objectives. A low laser power was
used to avoid laser heating effect (at such power level, the Raman peak position is not affected by the change
of probe laser power), and the Raman collection time was depended on different experimental
configurations.
We provide more explanations on the design of the optical path. Figure 1.4 show the optical path with the 632.904 nm laser excitation. An absorption neutral density filter (OD 1 to OD 3) was placed in front of the laser to decrease the laser intensity. The incident light passed through an optical isolator to avoid backscattering to the laser. A spatial filter was used to create more circular laser beam. The incident light was then reflected by a dichroic beam splitter and then concentrated to the sample surface by the objective. For thermal measurements, the sample was typically placed on a temperature controlling stage, which was held on a XYZ stage. The Raman scattering from the sample surface was collected by the microscope objective. The dichroic beam splitter is transparent to the Raman scattering. The scattered light then passed through an edge filter that the Rayleigh scattering component was blocked. The Raman signal was dispersed by the spectrometer to a spectrum and detected by the CCD camera. Figure 1.5 shows the transient measurement mode with 532.019 nm laser excitation. An acoustic optical modulator was used to convert the continuous wave to pulsed laser beam, which can be monitored by the photodetector. This transient measurement mode can be easily transformed to static measurement mode by flipping the mirror down (see Figure 1.5).
To obtain the accurate temperature measurement, we calibrated the Raman peaks with the spontaneous emission lines of a neon calibration lamp (6032, Newport, see Figures 2, 4 and 5). To find the temperature coefficient $A$ expressed in Equation (1.26), we placed our sample on a temperature stage with an accuracy of less than 0.1 °C (HCP621 V, Instec) and measured the change of Raman peak positions with temperatures. The typical range of temperature calibration is from 20 °C to 200 °C with a 20 °C increment. Figure 1.6 shows the temperature dependent Raman peak positions of bulk silicon. We found the linear temperature coefficient $A$ of bulk silicon is -$0.0225 \pm 0.002$ cm$^{-1}$/°C through fitting, which shows good agreement with the measurements performed by Beechem et al (-0.022 cm$^{-1}$/°C) [60].
1.3 **PHASE IMAGING: PRINCIPLES AND OPPORTUNITIES**

It is well-known that a monochromic electromagnetic wave is characterized by three key factors, i.e., the amplitude, frequency and phase, as expressed in Equation (1.27),

\[ E = E_0 \cos(\omega t - \phi) \]  

(1.27)

where \( E_0 \) is the amplitude of the wave and \( \phi \) is the phase. The information stored in amplitude can be directly captured by various cameras and microscopes. Spectroscopy techniques were developed to measure the electromagnetic waves in the frequency domain. The phase imaging techniques are used to visualize the phase distribution and interpret the information contained in the phase field. Phase imaging is very useful for investigating weakly scattering samples [61]. The sample does not scatter light significantly because (1) the sample is transparent to the illumination such as live cells and liquid materials, or (2) the sample is very small in geometric size such as the nanoscale features. With the phase imaging techniques, the quantitative information about the local thickness of the sample and the fluctuation of the refractive index can be well understood. Practically, there are many approaches to perform phase imaging. Interferometry is one of the most popular methods to measure the contrast precisely. Phase contrast imaging, which is developed by Zernike in 1942, is a simple experimental technique converting the phase shift to the brightness change of intensity [62]. However, as the phase information is nonlinearly coupled with the intensity information, fully quantitative imaging with phase contrast microscope is impossible.
In this thesis, however, we focused on another phase imaging technique based on the transport of intensity equation (TIE). TIE provides a mathematical formulation to compute the phase distribution from the intensity field, for which reason only the intensity field needs to be experimentally measured and the experimental setup is well-simplified. Additionally, compared to the interferometry, TIE based phase imaging has much lower requirement on the light source. Both coherent (such as the laser) and partially coherent light source (such as the white light source) can be used for TIE phase imaging.

We provide the mathematical formulation of the phase retrieval process. The propagation of light in a uniform medium can be expressed by the homogenous Helmholtz equation [63],

\[ \nabla^2 U(r) + k^2 n^2 U(r) = 0 \]  \hspace{1cm} (1.28)

where \( \nabla^2 \) is the three-dimensional Laplacian, \( U(r) \) is the electric field distribution, \( k \) is the wave number in vacuum and \( n \) is the averaged refractive index of the medium. In this study, we carried the measurement in the air, whose refraction index \( (n) \) is equal to 1. We represented the field distribution as the product of a real amplitude and a phase dependent complex exponential function,

\[ U(r) = \frac{1}{I(r)} I(r)^{\frac{1}{2}} \exp(i\phi(r)) \]  \hspace{1cm} (1.29)

where \( I(r) \) is the intensity (the square root of which is the real amplitude) of the field and \( \phi(r) \) is the phase of corresponding wave. We plugged Equation (1.29) into Equation (1.28), and picked the imaginary part,

\[ \nabla^2 \psi = 0 \]  \hspace{1cm} (1.30)

where \( \nabla \psi = I\nabla \phi \), and \( \psi \) is an auxiliary field. We assumed the light propagates along \( z \) axis and applied the paraxial approximation to simplify the expression of phase as [63],

\[ \nabla_1^2 \psi = -k \frac{\partial I}{\partial z} \]  \hspace{1cm} (1.31)

where \( \nabla_1^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \). Equation (1.31) is known as the TIE, which is a two-dimensional Poisson equation. The gradient of intensity expressed on the right hand side of Equation (1.31) can be directly measured from experiment. The auxiliary field \( \psi \) can be solved numerically using either Fourier transform or finite
difference method. According to the relation between the auxiliary field and the phase, we obtained the second Poisson equation with respect to $\phi$.

$$\nabla^2 \phi = \nabla \cdot \left( \frac{\nabla \psi}{I} \right). \tag{1.32}$$

Repeating the same numerical procedures, the phase distribution can be solved from Equation (1.32).

As shown in Equation (1.31), one of the most important procedures in the phase imaging is to measure the gradient of the intensity field along optical axis. The experimental technique for such measurement is named depth scanning. Figure 1.7 shows the schematic demonstration of the experimental setup of depth scanning in the transmission configuration. There is a thin refractive object placed on the left. The uniform incident illumination is scattered by the object. The scattering is collected by an imaging system (typically a 4f system) located at the center. In the image space, the image of this refractive object can be found at the focal plane of the imaging system. However, to measure the gradient of intensity, not only the in-focus image, but the out-of-focus images along the optical axis is required. As depicted in Figure 1.7, the image screen moves with a small increment $\Delta z$ continuously to get a large number of out-of-focus images at different positions. The gradient of intensity can be approximated by the difference between adjacent images $\Delta I$ and the scanning increment $\Delta z$,

$$\frac{dI}{dz} \approx \frac{\Delta I}{\Delta z}. \tag{1.33}$$

According to Equations (1.31) and (1.33), the accuracy of the phase calculation highly depends on the finite difference approximation term $\Delta I/\Delta z$. For this reason, the choice of the axial increment $\Delta z$ between two adjacent images should be carefully discussed. In theory, $\Delta z$ should be as small as possible, but limited by
the sensitivity of detectors, the difference in intensity between two images will be undetectable if $\Delta z$ is too small. However, on the other hand, $\Delta z$ has to be much smaller than the coherence length of the illumination, which is especially important for partially coherent light sources [64-65].

1.4 APPLICATIONS OF RAMAN SPECTROSCOPY AND PHASE IMAGING FOR HEAT TRANSFER RESEARCH

The heat transfer problems discussed in this work are mainly divided into two parts, i.e., (1) heat transfer in solid-state materials and (2) phase change heat transfer. Figure 1.8 shows the relationship between three research fields (micro-to-nanoscale heat transfer, Raman spectroscopy and phase imaging) and the belonging of specific research problems discussed in this thesis.

We developed the general Raman spectroscopy and phase imaging techniques independently in the first stage and then applied the developed techniques to several specific research problems. For the Raman spectroscopy technique, the multiphysics characterization method and the nanoscale Raman sensor were built. For the phase imaging technique, on the other hand, the nanoscale phase imaging technique and the non-paraxial TIE theory were developed. In the micro-to-nanoscale heat transfer in solid-state materials category, we investigated the simultaneous measurement of temperature, stress and electric field in GaN HEMTs and measured the linear thermal expansion coefficient of monolayer MoS$_2$ flakes using the multiphysics characterization method. We studied the radiative heat transfer in silica aerogel using the nanoscale Raman sensor. In the micro-to-nanoscale heat transfer in phase change heat transfer category, we measured the thin film evaporation on micro-structured surfaces using micro-Raman thermometry. We proposed a multiscale dynamic growth theory of droplets condensation and applied the phase imaging technique to understand the droplets growth dynamics.
In summary, the objective of this thesis is focused on the theoretically and experimentally development of advanced Raman spectroscopy and phase imaging technique for complex heat transfer related problems including thermal characterizations and multiphysics interactions in solid state material, micro-to-nanoscale temperature measurement and liquid-vapor phase change heat transfer. We would like to show the great potential of those optical based technologies for heat transfer and to inspire a new multidisciplinary direction combining Raman spectroscopy, phase imaging and heat transfer. The structure of this thesis is outlined below:

In Chapter 1, several key challenges in current heat transfer research and possible solutions of using advanced spectroscopy and imaging techniques were discussed. The theoretical principles of Raman effect and phase imaging were introduced respectively.

In Chapter 2, the application of Raman spectroscopy for thermal characterization was explored. The multiphysics interactions presented in semiconductor material was firstly studied using micro-Raman spectroscopy. The in situ simultaneous measurement of temperature rise, stress and electric field was performed on GaN HEMTs, and the linear thermal expansion coefficient of monolayer MoS2 flakes was experimentally determined. Next, this developed micro-Raman thermometry was used to study thin film
evaporation on micro-structured surfaces, and conduction-radiation conjugate heat transfer in silica aerogel. At last, a nano-Raman sensor was designed and developed for nanoscale temperature measurement.

In Chapter 3, the concept of using phase imaging for nanoscale detection was discussed. Theoretical and experimental studies was firstly carried out to prove the high sensitivity of phase imaging in nanoscale features. As a proof-of-concept study, the developed phase imaging technique was then applied to detect the deep-subwavelength defect on semiconductor wafers. This phase imaging method was finally interfaced with ESEM for condensing droplets analysis. The improvement of ESEM performance with phase imaging and the dynamic processes of droplets were discussed in details.

In Chapter 4, the future directions of Raman spectroscopy and phase imaging for heat transfer research were discussed. The thesis was concluded in Chapter 5.
Chapter 2

2. Development of Raman Spectroscopy for Thermal Characterization

In this chapter, we introduce the development and application of Raman spectroscopy for a variety of heat transfer problems. The multiphysics characterization was firstly developed and applied to study solid state materials including GaN HEMTs and monolayer MoS$_2$ in section 2.1. We investigated the temperature, stress and electric field dependence of the Raman peaks using the phonon deformation potential theory and crystal symmetry. The simultaneous change of phonon peaks due to different physical fields was decoupled using the multipeak fit technique. We applied this multipeak fit technique to decouple the contribution of temperature, stress and electric field presented in GaN HEMTs (section 2.1.1), and measure the linear thermal expansion coefficient of monolayer MoS$_2$ (section 2.1.2). In section 2.2, we extended capability of Raman spectroscopy to phase change heat transfer by interfacing the micro-Raman setup with a thin film evaporation test rig. We investigated the effect of microstructure on evaporation by directly probing the top of the micropillar near the three-phase contact line. In section 2.3, we studied the radiative heat transfer in silica aerogel, which has super low thermal conductivity and is transparent to visible light. We used silicon nanoparticles as temperature sensors and coated them inside the aerogel. The temperature distribution of the silica aerogel was then obtained by measuring the Raman peak of silicon nanoparticles. In section 2.4, we present the design of gold-silicon nano-Raman sensor, which is used for nanoscale thermal probing.

2.1 MICRO-RAMAN THERMOMETRY FOR SOLID-STATE MATERIAL APPLICATIONS

Due to the superior spatial resolution, micro-Raman spectroscopy has been extensively used for measuring the local temperature rise in high power radio frequency amplifiers and high voltage power conversion applications, in which devices high power dissipation is concentrated in a small area [66]. However, it has been demonstrated that the change of Raman peak positions not only depends on temperature rise, but the complex stress state and internal electric field [66], which makes it challenging to measure the local temperature independently. For this reason, we studied the coupling effects of multiphysics fields on Raman peak positions according to the symmetry of the lattice structure of corresponding materials. We showed the example theoretical analysis on wurtzite GaN and monolayer MoS$_2$. The temperature, stress and electric field in GaN HEMTs were measured using the simultaneous change in the Stokes peak position of three
phonon modes [66]. The linear thermal expansion coefficient of MoS$_2$ were measured by decoupling the thermal stress effect on the change of Raman peaks. In section 2.1.1, we would first present the theoretical analysis of the phonon frequency response to temperature, stress and electric field of wurtzite GaN using phonon deformation potential theory and group theory. Then we show the micro-Raman measurement in the ON state of the GaN HEMTs based on the three-peak fit method. In section 2.1.2, similar theoretical analysis on the phonon response of MoS$_2$ is provided. We carried out micro-Raman measurement on monolayer MoS$_2$ by transferring the sample on different substrates with different thermal expansions, in which way the effect of thermal stress on the change of phonon frequency was decoupled.

2.1.1 Simultaneous Measurement of Temperature, Stress and Electric Field in GaN HEMTs

GaN HEMTs are a promising solid-state transistor application which provides higher power density and efficiency than silicon based devices. However, the high power densities presented in GaN HEMTs lead to elevated channel temperatures, which are believed to degrade device performance and accelerate device failure through thermoelastic stresses. It has also been found other mechanisms such as the electromechanical and electrochemical processes driven by the strong piezoelectricity contribute to the failure of the device. For these reasons, an experimental approach which is capable of measuring the electro-thermal-mechanical coupled phenomena in GaN HEMTs is of great necessity. Previous studies reported the micro-Raman thermometry as useful a tool for measuring temperature rise in GaN HEMTs, which believed the change of Raman peak positions attributed to the temperature alone. Subsequent studies showed the importance of accounting for inverse piezoelectric and thermoelastic stresses in the change of phonon frequency, and demonstrated the ability to simultaneously measure the temperature rise and thermoelastic stresses in the ON state. However, large discrepancies in the inverse piezoelectric stress was found between the electro-mechanical model predictions and micro-Raman measurements. In a recent study, Bagnall et al. showed that the vertical electric field along the c-axis can strongly affect the Stokes peak position of wurtzite GaN independently of the inverse piezoelectric stress. They accounted the accounted a term depending on the electric field and validated their concept with the measurement of vertical electric field and in-plane inverse piezoelectric stress in GaN HEMTs using micro-Raman spectroscopy [66, 67].

In this work, we demonstrate the simultaneous measurement of temperature rise, in-plane stress, and the vertical electric field in GaN HEMTs using the simultaneous change in the position of three phonon modes, i.e., $E_2$ (high), $A_1$ longitudinal optical (LO), and $E_2$ (low), at any arbitrary gate and drain bias [68]. This technique overcomes the limitation of previous approaches that measuring the temperature rise in GaN HEMTs in the ON state relies on the unpowered pinched OFF state as a reference [69]. Although the
concept of simultaneous measurement was demonstrated on GaN HEMTs, this technique can be generally applied to any solid-state materials with reasonable Raman response.

We first present theoretical analysis of the phonon frequency response to temperature, stress and vertical electric field using wurtzite GaN as an example. Wurtzite GaN has a hexagonal lattice structure which is depicted in Figure 2.1. The unit cell of wurtzite GaN is characterized by two lattice parameters $a$ and $c$. Each unit cell contains two Ga and two N atoms where bond length between Ga and N along the $c$-axis is denoted by the internal structural parameter $r$ [68, 70]. The hexagonal lattice structure belongs to $C_{6v}$ point group. The Raman-active zone-center optical phonon can be classified by the irreducible representations $A_1$, $E_1$ and $E_2$ of group $C_{6v}$ where $A_1$ represents the totally symmetric mode, $E_1$ represents a doubly degenerate mode and $E_2$ represents the other doubly degenerate modes. As the incident photon is along $c$-axis in the backscattering configuration, the phonon modes $A_1$ (TO), $E_1$ (TO) and $E_1$ (LO) cannot be excited. Thus, only the $A_1$ (LO), $E_2$ (high) and $E_2$ (low) can be observed in the backscattering configuration [70, 71].

\[
\begin{align*}
&\text{(a)} \\
&\text{(b)} \\
\end{align*}
\]

Figure 2.1. The crystal structure of wurtzite GaN material. (a) The unit cell of wurtzite GaN where the large blue and small red spheres represent Ga and N atoms respectively. (b) The hexagonal lattice structure of GaN crystal [72].

According to the linear deformation potential theory, the perturbation potential arising from the internal strain is given by [68],

\[
V = \sum V_{ij} \epsilon_{ij}, \quad i, j = x, y \text{ or } z
\]

(2.1)
where $\epsilon_{i,j}$ is the strain tensor and $V_{i,j}$ is the deformation potential. According to the symmetry of the lattice, the deformation potential created by $V_{i,j}$ can be represented by $\Gamma_V = 2A_1 + E_1 + E_2$. According to the basis function of each irreducible representation, the Equation (2.1) can be explicitly expressed as [68],

\[
V = \frac{1}{2} (V_{xx} + V_{yy})(\epsilon_{xx} + \epsilon_{yy}) + V_{zz}\epsilon_{zz} + 2[(V_{yz}\epsilon_{yz} + (-V_{xz})(-\epsilon_{xz})]
\]

\[
+ \frac{1}{2} [(V_{xx} - V_{yy})(\epsilon_{xx} - \epsilon_{yy}) + (2V_{xy})(2\epsilon_{xy})]
\]

where the potential components $(V_{xx} + V_{yy})$ and $V_{zz}$ belong to $A_1$ irreducible representation, terms $V_{yz}$ and $-V_{xz}$ belong to $E_1$ irreducible representation, and $(V_{xx} - V_{yy})$ and $-2V_{xy}$ belong to $E_2$ irreducible representation respectively.

According to the perturbation theory, the effect of the deformation potential on the change of Raman peak positions is related to the matrix element $\langle \phi_{\Gamma_{phonon}} | V | \phi_{\Gamma_{phonon}} \rangle$, where $\phi_{\Gamma_{phonon}}$ is the eigenfunction (basis function) of phonon mode $\Gamma_{phonon}$, and $\Gamma_{phonon} = A_1$ or $E_2$ in this study. Thus, the change of phonon frequency due to deformation potential is given by,

\[
\Delta \omega_{A_1} = \langle \phi_{A_1} | V | \phi_{A_1} \rangle
\]

(2.3)

and,

\[
\Delta \omega_{E_2} = \langle \phi_{E_2} | V | \phi_{E_2} \rangle.
\]

(2.4)

Performing the calculation expressed in Equations (2.3) and (2.4), some matrix elements $\langle \phi_{\Gamma_{phonon}} | V_{i,j} | \phi_{\Gamma_{phonon}} \rangle$ will vanish due to symmetry, which can be determined by calculating the direct product $\Gamma_V \otimes \Gamma_{phonon}$. For the non-degenerate phonon mode $A_1$, the change of phonon frequency is given by [68],

\[
\Delta \omega_{A_1} = \langle \phi_{A_1} | V | \phi_{A_1} \rangle = a_{A_1 \sigma} (\epsilon_{xx} + \epsilon_{yy}) + b_{A_1 \sigma} \epsilon_{zz}
\]

(2.5)

Where $a_{A_1} = \frac{1}{2} \langle \phi_{A_1} | (V_{xx} + V_{yy}) | \phi_{A_1} \rangle$, and $b_{A_1} = \langle \phi_{A_1} | V_{zz} | \phi_{A_1} \rangle$ are the deformation potential constants.

According to degenerate perturbation theory, a secular equation $| V_{kl} - \Delta \omega_{E_2 \ell} \delta_{kl} | = 0$ should be solved to
determine the change of phonon frequency of two-fold degenerate mode $E_2$, where $V_{kl} = \langle \phi_{E_2}(l) | V | \phi_{E_2}(k) \rangle$ and $\delta_{kl}$ is the Kronecker delta tensor. Specifically, this secular equation of the $E_2$ phonon response is given by [68],

$$\begin{vmatrix} a_{E_2}(e_{xx} + e_{yy}) + b_{E_2} e_{zz} + c_{E_2}(e_{xx} - e_{yy}) - \Delta \omega_{E_2} & \frac{2c_{E_2} e_{xy}}{2c_{E_2} e_{xy}} \\ \frac{2c_{E_2} e_{xy}}{2c_{E_2} e_{xy}} & a_{E_2}(e_{xx} + e_{yy}) + b_{E_2} e_{zz} - c_{E_2}(e_{xx} - e_{yy}) - \Delta \omega_{E_2} \end{vmatrix} = 0 \quad (2.6)$$

where $a_{E_2}$, $b_{E_2}$, and $c_{E_2}$ are the deformation potential constant for $E_2$ mode. Corresponding change of phonon frequency of $E_2$ is given by,

$$\Delta \omega_{E_2} = a_{E_2}(e_{xx} + e_{yy}) + b_{E_2} e_{zz} \pm c_{E_2} \left[ (e_{xx} - e_{yy})^2 + 4e_{xy}^2 \right]^{1/2} \quad (2.7)$$

Equations (2.5) and (2.7) provide the relationship between change of Raman peak positions and the strain perturbation. To show the temperature and stress dependence of Raman peak position, the strain tensor $\epsilon_{i,j}$ should be expressed as a function of temperature and stress tensor though the constitutive relation [73],

$$\begin{align*}
\epsilon_{xx} &= S_{11} \sigma_{xx} + S_{12} \sigma_{yy} + S_{13} \sigma_{zz} + \alpha_{xx} \Delta T \\
\epsilon_{yy} &= S_{12} \sigma_{xx} + S_{11} \sigma_{yy} + S_{13} \sigma_{zz} + \alpha_{xx} \Delta T \\
\epsilon_{zz} &= S_{13} \sigma_{xx} + S_{13} \sigma_{yy} + S_{33} \sigma_{zz} + \alpha_{zz} \Delta T \\
\epsilon_{xy} &= (S_{11} - S_{12}) \sigma_{xy}
\end{align*} \quad (2.8)$$

where $S_{i,j}$ is the component of the elastic compliance constant tensor, $\sigma_{i,j}$ is the stress tensor, $\alpha_{i,j}$ is the component of linear thermal expansion coefficient, and $\Delta T$ is the temperature rise relative to the reference temperature. Substitute Equation (2.8) into Equation (2.7), the relationship between change of Raman peak position and temperature and stress is obtained [66],

$$\Delta \omega_{A_1} = \frac{1}{2} K_{A_1}(\sigma_{xx} + \sigma_{yy}) + b_{A_1} \sigma_{zz} + A_{A_1} \Delta T \quad (2.9)$$
\[ \Delta \omega_{E_2} = \frac{1}{2} K_{E_2}(\sigma_{xx} + \sigma_{yy}) + \bar{b}_{E_2} \sigma_{zz} \pm \bar{c}_{E_2} \left[ (\sigma_{xx} - \sigma_{yy})^2 + 4\sigma_{xy}^2 \right]^{1/2} + A_{E_2} \Delta T \]  

(2.10)

where \( \frac{1}{2} K_i = a_i(S_{11} + S_{12}) + b_i S_{13} \), \( \bar{b}_i = 2a_i S_{13} + b_i S_{33} \), and \( A_i = 2a_i \sigma_{xx} + b_i \sigma_{zz} \) for \( i = A_1, E_2(t) \) or \( E_2(h) \). \( K_i \) and \( A_i \) are the biaxial stress and the temperature coefficients of mode \( i \) respectively. According to Bagnall et al., the vertical electric field can affect the change of Raman peak position independently, another term about the effect of vertical electric field should be added to Equations (2.9) and (2.10) [66],

\[ \Delta \omega_{A_1} = \frac{1}{2} K_A(\sigma_{xx} + \sigma_{yy}) + \bar{b}_{A_1} \sigma_{zz} + B_{A_1} E_z + A_{A_1} \Delta T \]  

(2.11)

\[ \Delta \omega_{E_2} = \frac{1}{2} K_{E_2}(\sigma_{xx} + \sigma_{yy}) + \bar{b}_{E_2} \sigma_{zz} \pm \bar{c}_{E_2} \left[ (\sigma_{xx} - \sigma_{yy})^2 + 4\sigma_{xy}^2 \right]^{1/2} + B_{E_2} E_z + A_{E_2} \Delta T \]  

(2.12)

where \( B \) is the electric field shift coefficient. In general, the top surface of the device is free of stress so the \( \sigma_{zz} \) is about zero. The asymmetry of the stress in the c-plane \( |\sigma_{xx} - \sigma_{yy}| \) and the shear stress \( \sigma_{xy} \) are small compared to the average stress in the c-plane \( |\sigma_{xx} + \sigma_{yy}| \) so the third term in Equation (2.12) can be neglected. Therefore, Equations (2.11) and (2.12) can be simplified as [66],

\[ \Delta \omega_{i} = \frac{1}{2} K_i(\sigma_{xx} + \sigma_{yy}) + B_i E_z + A_i \Delta T, \quad i = A_1(LO), E_2(high) \text{ or } E_2(low) \]  

(2.13)

Equation (2.13) provides the basic principle of simultaneous measurement of temperature rise, stress and electric field. It should be noticed that there are three phonon modes can be measured by Raman spectroscopy, i.e., \( A_1(LO) \), \( E_2 \) (high) and \( E_2 \) (low) and there are three unknowns, i.e., \( \Delta T, \frac{1}{2}(\sigma_{xx} + \sigma_{yy}) \) and \( E_z \). Therefore, if the temperature \( A_1 \), biaxial stress \( \frac{1}{2} K_i \) and electric field shift \( B_i \) coefficients for each phonon modes are known and the change of Raman three peaks are fitted simultaneously, the unknown temperature, stress and electric field can be obtained by solving the system of equations [66],

\[
\begin{bmatrix}
\Delta T \\
(\sigma_{xx} + \sigma_{yy})/2 \\
E_z
\end{bmatrix} = \begin{bmatrix}
A_{E_2(h)} & K_{E_2(h)} & B_{E_2(h)} \\
A_{A_1(LO)} & K_{A_1(LO)} & B_{A_1(LO)} \\
A_{E_2(h)} & K_{E_2(h)} & B_{E_2(h)}
\end{bmatrix}^{-1} \begin{bmatrix}
\Delta \omega_{E_2(h)} \\
\Delta \omega_{A_1(LO)} \\
\Delta \omega_{E_2(h)}
\end{bmatrix}
\]  

(2.14)
Before performing the three-peak fit measurement, it is important to know the coefficient matrix in Equation (2.14). In this work, we measured the temperature coefficients of $A_1$ (LO), $E_2$ (high) and $E_2$ (low) modes. The biaxial stress coefficients were retrieved from Choi et al. [57] and the electric field shift constants were calculated by Bagnall et al. [66] based on density functional theory (DFT). These coefficients are listed in Table 2.1.

Table 2.1. Biaxial stress, temperature, and electric field coefficients for the zone center optical phonon modes of wurtzite GaN from experimental measurement and theoretical calculation [66].

<table>
<thead>
<tr>
<th></th>
<th>$K$ (cm$^{-1}$/GPa)</th>
<th>$A$ (cm$^{-1}$/K)</th>
<th>$B$ [cm$^{-1}$/(MV/cm)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_2$ (high)</td>
<td>-3.27±0.15</td>
<td>-0.0138±0.0001</td>
<td>-1.36</td>
</tr>
<tr>
<td>$A_1$ (LO)</td>
<td>-2.21±0.10</td>
<td>-0.0263±0.0001</td>
<td>2.09</td>
</tr>
<tr>
<td>$E_2$ (low)</td>
<td>-0.28±0.01</td>
<td>-0.0034±0.0001</td>
<td>-0.26</td>
</tr>
</tbody>
</table>

To validate the proposed three-peak fit method, we performed micro-Raman measurements for GaN HEMTs in the ON state and compared the experimental results with electro-thermo-mechanical model predictions. In this experiment, the micro-Raman spectroscopy setup was integrated with a precision source/measure unit (SMU, B2902A, Agilent), which was used to bias the GaN devices. The micro-Raman system used for this study has been introduced in chapter 1. The GaN HEMTs device was mounted on a thermal electric cooler and the backside of the device was maintained at 20.0±0.1°C. We focused the laser spot on the source-connected field plate in the gate-drain access region (see the inset of Figure 2.2(a)) and measured the Raman peak positions of $E_2$ (high), $A_1$ (LO) and $E_2$ (low) simultaneously. When the test device is in the ON state, the gate bias was set to $V_{gs} = -2.85$ V, while the drain bias $V_{ds}$ was changed from 0 V to 40 V. The temperature, stress and electric field were measured by solving the system of equations (2.14). Typical uncertainties (95% confidence intervals from the standard deviation of ten spectra) for the change in Raman peak positions were within ±0.01 cm$^{-1}$ for the $E_2$ (high) and $E_2$ (low) modes and within ±0.05 cm$^{-1}$ for the $A_1$ (LO) mode. As shown in Figure 2.2, we compared the three-peak fit experimental results with the electro-thermo-mechanical model simulation. The measurement results show reasonably good agreement with model simulation. It was found from this experiment that the peak temperature rise presence in GaN HEMTs can be as high as 150 °C even the dissipated power is only 2.5W.
Experiment $V_g = -2.85$ V

Simulation $V_g = -2.9$ V

(a)

(b)
Figure 2.2 Micro-Raman measurements of (a) vertical electric field, (b) in-plane stress and (c) temperature rise of GaN HEMTs in ON state (gate voltage $V_{gs} = -2.85$ V) using three-peak fit method.

2.1.2 Measuring the Linear Thermal Expansion Coefficient of Monolayer MoS$_2$

Recent research advances in atomically thin two-dimensional (2D) crystals, such as graphene, transition-metal dichalcogenide (TMD) semiconductors, and boron-nitride (BN) revealed the extraordinary physical properties and promising application possibilities, which inspired tremendous research interests in the past decade [74-80]. It has been proven that some TMD materials, such as MoS$_2$, have high mobility at room temperature which is comparable to graphene nanoribbons. Compared to graphene, the presence of band gap in TMDs is more desired for low band gap transistor applications. Additionally, it was found from experiments and theoretical calculation that the TMDs transit from indirect to direct electronic bandgap when thickness of material reduces from bulk to monolayer. MoS$_2$, as one of the most stable TMDs, transforms from indirect bandgap of about 1.3 eV to direct bandgap of about 1.8 eV with the decrease of the number of layers. These unique properties of MoS$_2$ show great potential for nanoelectronics and next generation of low-power transistors. For this reason, understanding the thermophysical properties of MoS$_2$ is very important for the thermal management of MoS$_2$ based electronics. Although the thermal transport properties, such as the thermal conductivity of MoS$_2$ have been widely studies [81-83], the linear thermal expansion coefficient of MoS$_2$, which is of great necessity for estimating the thermal stress within the atomically thin material was not well understood. In this work, we measured the linear expansion coefficient of monolayer MoS$_2$ using micro-Raman spectroscopy. The theory about the temperature and stress dependent Raman peak positions proposed in section 2.1.1 was applied to study MoS$_2$. The technique
developed in this section can not only be used for measuring MoS$_2$, but can be generally used to measure the linear temperature coefficient of any Raman-active thin film materials.

As shown in Figure 2.3, MoS$_2$ has hexagonal lattice structure with a unit cell consisting of one Mo and two S atoms. The MoS$_2$ crystal structure belongs to the D$_{6h}$ symmetry point group, and the Raman-active zone-center optical phonon can be classified by the irreducible representations $A_{1g}$, $E_{1g}$ and $E_{2g}$ of group D$_{6h}$ where $A_{1g}$ represents the gerade totally symmetric mode, $E_{1g}$ represents a gerade doubly degenerate mode and $E_{2g}$ represents the other gerade doubly degenerate modes. In the backscattering configuration, however, $E_{1g}$ mode is forbidden which represents the phonon propagating in the c-plane. Thus, only $A_{1g}$ and $E_{2g}$ modes can be observed. Performing the similar analysis using deformation potential and group theory, the phonon frequency response of MoS$_2$ to the temperature and stress can be expressed as,

$$\Delta\omega_i = K_i\sigma + A_i\Delta T, \quad i = A_{1g}, \text{or} \ E_{2g}$$  \hspace{1cm} (2.15)

where $K_i$ is the biaxial stress coefficient and $A_i$ is the temperature coefficient of corresponding phonon mode. Following the same principle presented in section 2.1.1, we found the $A_i = 2a_i\alpha_{xx} + b_i\alpha_{zz}$ where $a_i$ and $b_i$ are the deformation potential of corresponding phonon modes and $\alpha_{xx}$ and $\alpha_{zz}$ are the in-plane and out-of-plane thermal expansion coefficients respectively. In Equation (2.15), the shear stress term $\sigma_{xy}$ was neglected due to the symmetry of stress state in most of conditions. The normal stress $\sigma_{zz}$ is also negligible because the top of the surface is free of stress. We also assumed $\sigma = \sigma_{xx} \approx \sigma_{yy}$ due to the symmetry of the operation state.

![Figure 2.3. Unit cell and crystal structure of MoS$_2$.](image)
It can be found from Equation (2.15) that the thermal expansion coefficient can affect the change of Raman peak position through the temperature coefficient $A_i$. Measuring $A_i$ accurately is very important to quantify the effect of thermal expansion. However, as shown in Equation (2.15), the effect of (1) biaxial stress and (2) out-of-plane thermal expansion also contribute to the change of Raman peak positions, making it difficult to measure the in-plane thermal expansion coefficient directly. In this study, we suspended the MoS$_2$ flake to keep the sample in stress-free state and decouple the effect of biaxial stress. As shown in Figure 2.4, the single crystal MoS$_2$ monolayer flake was transferred on the 300 nm SiO$_2$/Si substrate which was grown on a 500 µm silicon wafer. Circular holes with 5 µm diameter were patterned on the SiO$_2$/Si substrate using e-beam lithography, and the suspended area of MoS$_2$ flake was defined by the top of the hole (see Figure 2.4(b)). The 532 nm laser excitation was focused on the suspended MoS$_2$ by a 50x objective (NA=0.55). The laser power was maintained to be below 0.1 mW to avoid laser heating effect.

As shown in Figure 2.4, the test sample was placed on a temperature stage (HCP621 V, Instec). To measure the temperature coefficient expressed in Equation 2.15, we measured the change of Raman peak position with the temperature increased from ambient to 200 °C. The Raman peak positions of E$_{2g}$ and A$_{1g}$ modes of MoS$_2$ varying with temperature were depicted in Figure 2.5. The temperature coefficients of these two modes were obtained by linearly fitting the slope. In this work, the temperature coefficients are -0.0144±0.0003 cm$^2$/K and -0.0148±0.0002 cm$^2$/K for E$_{2g}$ and A$_{1g}$ modes respectively. As shown in Table 2.2, the measurements in this work shows reasonably good agreement with previous studies [81, 82].
To measure the in-plane thermal expansion coefficient of MoS₂, we transferred the MoS₂ flakes on 500 μm fused silica and 500 μm pure copper (99.999% in purity) wafer respectively in the ambient temperature (see Figure 2.6). Due to the strong Van der Waals force between the MoS₂ flake and the substrate, the sample is believed to be well bounded by the substrate. The fused silica and the copper sample were placed on the temperature stage. When the temperature of the stage increases, both the bottom substrate and the transferred MoS₂ will thermally expand. As the thermal expansion coefficients of the substrate and MoS₂ flake are different, in-plane thermal stress forms at the interface. However, as the substrate is much thicker than that of the MoS₂ flake, i.e., 500 μm ≫ 0.8 nm, the substrates can be regarded as free expansion. At the interface, the bottom of the flake and the top of the substrate share the same strain rate,

\[ \varepsilon_1 = \alpha_{x\chi} \Delta T + \frac{1 - \nu}{E_{xx}} \sigma_1 \approx \alpha_{SiO_2} \Delta T \]  

(2.16)
\[ \varepsilon_2 = \alpha_{xx} \Delta T + \frac{1 - \nu}{E_{xx}} \sigma_2 \approx \alpha_{Cu} \Delta T \]  

(2.17)

where \( \varepsilon_1 \) and \( \varepsilon_2 \) represent the in-plane strain rates at the SiO_2-MoS_2 and Cu-MoS_2 interfaces respectively. \( \alpha_{xx} \) and \( E_{xx} \) are the in-plane thermal expansion coefficient and the in-plane elastic modulus of monolayer MoS_2 respectively, which are unknown previously. \( \nu \) is the Poisson ratio of the MoS_2 flake. \( \sigma_1 \) and \( \sigma_2 \) are the in-plane biaxial stress in the MoS_2 flake on fused silica and copper respectively. As there are no constraints to the side walls of the substrate, \( \sigma_{xx} \approx \sigma_{yy} = \sigma \). \( \alpha_{SiO_2} \) and \( \alpha_{Cu} \) are the thermal expansion coefficients fused silica and copper respectively. \( \Delta T \) is the temperature increase compared to ambient.

Figure 2.6. Schematic demonstration of the experimental method for measuring the thermal expansion coefficient of monolayer MoS_2. (a) The MoS_2 transferred on fused silica substrate. (b) The MoS_2 transferred on the pure copper substrate.

According to Equations (2.16) and (2.17), the induced in-plane thermal stress on the flake is given by,

\[ \sigma_1 = \frac{(\alpha_{SiO_2} - \alpha_{xx})E_{xx}}{1 - \nu} \Delta T \]  

(2.18)

\[ \sigma_2 = \frac{(\alpha_{Cu} - \alpha_{xx})E_{xx}}{1 - \nu} \Delta T \]  

(2.19)

Substituting Equations (2.18) and (2.19) into Equation (2.15), the relationship between the in-plane thermal expansion coefficient and change of Raman peak position is given by,
\[ \Delta \omega_{1i} = K_i^b \sigma_1 + A_i \Delta T = K_i^b \left( \alpha_{SiO_2} - \alpha_{xx} \right) E_{xx} \frac{\Delta T}{1 - \nu} + A_i \Delta T = A_{i, SiO_2} \Delta T \]  \hspace{1cm} (2.20)

\[ \Delta \omega_{2i} = K_i^b \sigma_2 + A_i \Delta T = K_i^b \left( \alpha_{Cu} - \alpha_{xx} \right) E_{xx} \frac{\Delta T}{1 - \nu} + A_i \Delta T = A_{i, Cu} \Delta T \]  \hspace{1cm} (2.21)

where \( \Delta \omega_{1i} \) and \( \Delta \omega_{2i} \) are the change of Raman peak positions on the SiO\(_2\) and Cu substrates for phonon mode \( i \), which can be directly measured by micro-Raman spectroscopy. \( A_{i, SiO_2} \) and \( A_{i, Cu} \) are the equivalent temperature coefficients on SiO\(_2\) and Cu substrates respectively. For convenience, we denote term \( \beta = \frac{K_i^b E_{xx}}{1 - \nu} \), which can be obtained by fitting the relation when \( \alpha_{Cu} \) and \( \alpha_{SiO_2} \) are known,

\[ \Delta \omega_{2i} - \Delta \omega_{1i} = \left( \alpha_{Cu} - \alpha_{SiO_2} \right) K_i^b E_{xx} \frac{\Delta T}{1 - \nu} = \left( \alpha_{Cu} - \alpha_{SiO_2} \right) \beta \Delta T \]  \hspace{1cm} (2.22)

According to Equations (2.20), (2.21) and (2.22), the in-plane thermal expansion coefficient of monolayer MoS\(_2\) is thus given by,

\[ \alpha_{xx} = \alpha_{SiO_2} - \frac{A_{SiO_2} - A_i}{\beta} = \alpha_{Cu} - \frac{A_{Cu} - A_i}{\beta} \]  \hspace{1cm} (2.23)

### 2.2 MICRO-RAMAN THERMOMETRY FOR PHASE CHANGE HEAT TRANSFER

In this section, we introduce the experimental endeavors of using micro-Raman thermometry to study phase change heat transfer. In this work, we mainly focused on the thin film evaporation on micro-to-nanostructured surfaces. Thin film evaporation is an effective phase change heat transfer process in which the liquid is driven by the capillary force due to the microstructure. A thin film region with microscale thickness liquid film forms near the three-phase contact line, which provides very low thermal resistance and high heat transfer performance. As the heat is mainly transferred through the thin film region, it is of fundamental interests to probe the temperature and energy transport near the three-phase contact line. However, characterizing the heat and mass transport crossing the liquid-vapor interface is always challenging. As the laser beam of optical probe can be easily focused on submicron regions and has negligible effect to the local heat transfer, micro-Raman thermometry shows great potential for thin film evaporation investigations. In section 2.2.1, we show that the micro-Raman thermometry system was
integrated to a thin film evaporation setup. The effects of microstructure on thin film evaporation was characterized by micro-Raman spectroscopy. In sections 2.2.2 and 2.2.3, we discuss future directions of using hierarchical structures to enhance thin film evaporation and using micro-Raman spectroscopy to probe the liquid-vapor interface directly.

2.2.1 A Micro-Raman Study of Thin Film Evaporation on Micro-structured Surfaces

Thermal management of high-performance electronics is increasingly challenging due to the increasing power density in these devices. Heat dissipation strategies that utilizes liquid-to-vapor phase change process is promising because it harnesses the large latent heat of vaporization. [84] Significant efforts have focused on creating micro and nanostructures in boiling and evaporation to enhance the heat transfer coefficient (HTC) and critical heat flux (CHF). [32, 36, 85-87] In particular, the enhancement mechanisms have generally been attributed to the ability of the micro and nanostructures to create curved menisci of the liquid-vapor interface (Figure 2.7), enhancing thin-film evaporation area and introducing capillarity which delays dry-out. Direct support of these arguments requires the ability to probe the local wall superheat on the structures. However, heat transfer measurements are typically performed remotely (i.e., away from the three-phase contact line) due to limitations of conventional contact-mode temperature sensors such as thermocouples and resistance temperature detectors (RTDs) [88], or are averaged over an area of 20-50 μm with infrared cameras [89]. As evaporation mainly occurs in the thin-film region near the three-phase contact line, fundamental understanding of the enhancement mechanism requires a microscopic measurement technique capable of probing temperature near the contact line with high spatial resolution.
The high spatial resolution (~1 μm) and noncontact nature of micro-Raman spectroscopy has made Raman thermometry one of the most popular techniques to probe localized temperature during the last decade [90-93]. The temperature can be interpreted by analysing the change of Raman spectra, i.e., peak position, linewidth or the ratio of the intensity of Stokes to anti-Stokes peaks. Although previous studies show that micro-Raman thermometry has been successfully applied to a variety of semiconductors [81, 82, 94], microelectronic [95-96] and optoelectronic devices [97], its capability of probing local temperature during liquid-vapor phase change heat transfer in micro-fluidic system has not been demonstrated. Considering the strong Raman scattering cross section and temperature dependent Raman spectrum of silicon based micropillars, we can directly focus the laser excitation onto the top of each micropillar and probe the temperature close to the three-phase contact line in situ. The physical insights during phase change, including both the local temperature near the thin film region and temperature distribution on the entire sample, thus, can be well-understood through micro Raman measurements.

In this work, we performed in situ temperature measurement of micropillar wick structures during evaporation using a custom micro-Raman thermography, and investigated the effect of microstructure geometry on local wall superheat. We fabricated 1×1 cm silicon micropillars with varying pitches, and built a thermo-fluidic test block to house the sample and interface with the micro-Raman system. Local wall temperature on the top surface of the micropillars near the three-phase contact line was measured in situ during thin-film evaporation. The results show that local wall superheat reduced as the pitch of micropillars

Figure 2.7. Schematic of liquid-to-vapor phase change in micro/nanostructures and conventional contact-type temperature sensors with a large area and a distance to the liquid-vapor interface where evaporation occurs.
reduced, which is a result of increased thin-film area. The local, in situ temperature measurement platform presented in this study serves as a new tool for mechanistic understanding of the microscopic phase change heat transfer phenomena, and potentially could be extended for boiling and condensation process as well.

To investigate the effect of microstructure geometry on local wall superheat during evaporation, silicon samples with micropillar arrays (diameters $d$ of 20 $\mu$m, heights $h$ of 50 $\mu$m and pitches $l$ of 30-100 $\mu$m) were designed with a heater on the backside. Each sample has an area of $2 \times 2$ cm and a thickness of 600 $\mu$m. The micropillar arrays have an area of $1 \times 1$ cm. The fabrication process is briefly as follows:

(a) Micropillars with heights of 50 $\mu$m were etched out in a 600 $\mu$m thick silicon wafer with 1 $\mu$m thermal oxide using Deep Reactive Ion Etching (DRIE) method. (b) Teflon residue on the sidewalls of the micropillars was removed by oxygen plasma. (c) A thin thermal oxide (~20 nm) was grown on the sidewalls of the micropillars to enhance the wettability. (d) A layer of 150 nm platinum was deposited on the backside of the wafer to serve as the heater ($1 \times 1$ cm) with E-beam evaporation and lift-off technique. Figure 2.8(a) shows a front side image of a representative, fabricated sample (diameters of 20 $\mu$m and pitches of 50 $\mu$m). In the following sections, all samples were named in the form of “diameter - pitch”. For example, we denoted the sample shown in Figure 2.8(a) as “20-50”. The micropillar arrays are located inside the dotted square ($1 \times 1$ cm). The back side of the sample is shown in Figure 2.8(b), where the heater is aligned with the micropillars shown in the dotted square. Figure 2.8(c) shows a scanning electron micrograph (SEM) of the fabricated micropillars.

![Figure 2.8](image)

Figure 2.8. Images and SEM of a representative, fabricated sample. (a) front and (b) back side view image. Dotted line highlights the micropillar arrays and the heater. (c) SEM of the micropillars on the front side.

To quantitatively investigate the thin film evaporation process, we built a thermo-fluidic test setup shown in Figure 2.9(a). Figure 2.9(b) shows a detailed image of the sample fixture. De-gassed and de-ionized (DI) water (Chromasolv for HPLC, Sigma-Aldrich) was used as the working fluid. The test setup consists of
two syringe pumps (PHD ULTRA 4400 Programmable Syringe Pump, Harvard Apparatus), two glass syringes (Cadence Science), a vacuum degasser (Analytical Stand Alone Degasser 2 Channel, SYSTEC) and an Ultem sample fixture. During the experiment, water was first pumped to the vacuum degasser. The degassed water then entered the reservoir on the sample fixture through the bended needle held on the XYZ stage (see Figure 2.9(b)). The reservoir was heated to maintain a constant sub-cooling. To ensure contact between the fluid and the sample while avoiding flooding, the water level in the reservoir was precisely controlled by a second syringe pump which withdrew excess liquid when it contacted the needle (see the bended needle held on the other XYZ stage in Figure 2.9(b)). A heated glass was placed above the sample to prevent the evaporating vapor from condensing on the objective of the micro-Raman system. The test sample was placed adjacent to the reservoir, and sealed by two O-rings on the top and bottom side respectively. Spring loaded pogo-pins (HPA-1D and SPR-1W, Everett Charles Technologies) were fitted into the bottom fixture for providing electrical contact between a power supply and the heater on the sample.

![Figure 2.9. (a) Schematic and (b) image of the thermo-fluidic test setup to be interfaced with the micro-Raman setup.](image)

In this study, we interfaced a micro-Raman thermometry setup to the thin film evaporation test rig to collect the Raman signal of silicon micropillars in the backscattering configuration. As shown in Figure 2.10, A 50X microscope objective with a numerical aperture (NA) of 0.55 (LMPlanFL N, Olympus) was used to focus the 633 nm laser excitation on the micropillar and collect the Raman scattered light. The diameter of the focused laser spot was about 1.5 μm, which enabled high spatial resolution. A low laser power (0.5 mW) was used to avoid laser heating effect (at such power level, the Raman peak position is not affected by the change of probe laser power), and the Raman collection time was 1 s. It has been found that at a low
temperature range (0-200 °C), the shift of peak position $\Delta \omega$ of silicon has a linear dependence on the change of temperature [60], which is expressed as,

$$\Delta \omega = A(T - T_0)$$  \hspace{1cm} (2.24)

![Schematic of the micro-Raman thermometry setup. Inset: an example Raman spectrum of silicon micropillar with neon emission lines.](image)

In this study, the uncertainty of the peak position can be controlled within 0.01 cm$^{-1}$, which arises from the random error of multiple measurements. An example of Raman spectrum of silicon (marked by a star) with a Neon calibration line collected by our micro-Raman setup is shown in the inset of Figure 2.10. For the measurement of linear temperature coefficient $A$, we placed our sample on a temperature stage with an accuracy of less than 0.1 °C (HCP621 V, Instec) and measured the change of Raman peak positions with temperature in the range of 20 °C to 200 °C. As shown in Figure 2.11, we fitted the linear temperature coefficient and repeated the calibration procedure on different micropillars and samples to ensure that the results are consistent and repeatable. The linear temperature coefficient in this study is found to be $-0.0225 \pm 0.002$ cm$^{-1}$/°C, which shows good agreement with the measurements performed by Beechem et al ($-0.022$ cm$^{-1}$/°C) [60]. The uncertainty in temperature measurement is within ±0.9 °C, accounting for both the random error associated with Raman peak positions, fitting error in linear temperature coefficient and uncertainty of the temperature stage.
Before each experiment, a standard cleaning procedure was carried out to avoid contamination. The test sample, syringes, sample fixture and cover plate were rinsed with acetone, methanol, isopropanol (IPA), and DI water. The sample was further cleaned with oxygen plasma (PDC-001, Harrick Plasma) for 20 minutes. After the cleaning procedure, the fixture with the sample was assembled on an XYZ stage under the microscope. The syringe pumps, vacuum degasser and assembly were connected by tubing (Tygon Laboratory Tubing E-3603, Harvard Apparatus) through Luer locks (Luer Type 316 Stainless Steel Adapter, Harvard Apparatus). After the experiment, the tubings were sealed by closed-end Luer locks to avoid contamination.

We first set the XY coordinate on the sample plane and moved the focused laser spot to the center of the micropillar array using the XYZ stage. To obtain a reference point, Raman peak position was measured and repeated a few times with ambient temperature (see Equation (2.24)). The glass which prevents vapor from contacting the objective was heated to about 110 °C (measured by a K-type thermocouple) by a resistive Kapton heater. The degassed DI water was then infused into the reservoir until water contacted and wicked onto the microstructured surface via capillary wicking. Simultaneously, the withdrawing syringe pump was switched on to maintain the water level in the reservoir and avoid flooding. The flow rates for both infusing and withdrawing syringe pumps were set to 0.5 ml/min. Water in the reservoir was heated and maintained at 40 °C (measured by a K-type thermocouple).

Figure 2.11. Calibration of silicon Raman peak position as a function of temperature.
When the water in the reservoir reached thermal equilibrium (at 40 °C), we started heating the sample using a DC power source (N5752A, Agilent Technology). The heat flux $q''$ is calculated from power source voltage $V$, current $I$ and heated area $S$ (1×1 cm² in this work) as,

$$q'' = \frac{VI}{S}$$

(2.25)

The heating power was gradually incremented and the corresponding Raman peak position of micropillar (located at the center of the microstructured surface) was measured in situ. For each constant heat flux, Raman measurement was performed 5 minutes after the power was adjusted to allow adequate time for the system to reach thermal equilibrium. The spectrum in each measurement is the average of three successive collections (each collection duration is 1 s), and each temperature measurement was repeated for 6 times. The uncertainty of the fitted peak position from multiple measurements at each power level is less than 0.01 cm⁻¹. For each microstructured sample, we increased the heating power input until drying out occurred. The temperature of the top of micropillar is calculated from Equation. (2.24) with a known reference (the ambient).

In this work, we experimentally characterized the effects of wick structure on heat transfer performance during steady state thin-film evaporation. We measured the local wall temperature at the center of the micropillar top surface at various heat flux conditions using micro-Raman spectroscopy. We compare the measured local wall temperature on micropillars with different pitches (40 to 100 μm) but same diameter (20 μm) and height (50 μm). Based on the measured result, the effect of micropillar pitch which corresponds to different thin-film area on heat transfer efficiency was discussed.

Figure 2.12 shows the measured local wall temperature during thin-film evaporation for a few different samples as the applied heat flux increased from 0 to 30-40 W/cm². This local wall temperature was measured from a pillar at the center of the structured surface which was accurately controlled by the motorized XYZ stage (marked by the dot in the inset of Figure 2.12), and the laser was focused at the center of the top surface of the micropillar. The experiments were stopped when drying out was observed at the end of the structures (longest distance from the reservoir).

When the temperature was low (<90 °C), the wall temperature increased almost linearly with the applied heat flux. This suggests that the increase of temperature was mainly due to the sensible heat of the fluid in this regime. The wall temperature was slightly different among the samples with sample 20-100 ($l=100 \mu$m)
being the hottest and sample 20-40 ($l=40 \mu m$) being the coldest. This is likely because samples with smaller pitch has more total surface area of the micropillar side walls which enhanced the convective heat transfer with the fluid.

![Figure 2.12. Applied heat flux as a function of the measured temperature of the micropillar top surface (located at the center of the structured surface) for various samples investigated](image)

When the temperature increased further (>90 °C), the slope of the evaporation curve increased sharply (Figure 2.12). This is mainly because the liquid temperature approached the saturation temperature (100 °C at 1 atm) and evaporation became the dominating heat transfer mode. The difference in the local wall temperature among different samples is more significant. At 27 W/cm², the temperature of sample 20-100 is approximately 10 °C higher than sample 20-40. The result suggests that evaporation from the thin-film area plays a significant role in the overall thermal resistance. For evaporation from micropillar arrays, liquid film is thin (up to a few microns) in a region surrounding the top circumference of a micropillar. Capillarity generates curved meniscus which increases thin-film area around a micropillar. For dense micropillar arrays such as sample 20-40, the total three-phase contact lines is longer and there is more thin-film area which facilitates efficient evaporation. Therefore, the total thermal resistance is smaller. For sparse micropillar arrays such as sample 20-100, thin-film area is greatly reduced and this increased the overall thermal resistance significantly. We anticipate that the temperature difference would be more severe at higher heat flux conditions. In addition, for the sample with pitch of 100 µm, the maximum local wall temperature reached about 106 °C before drying out. Since silicon pillars have a higher thermal conductivity ($\approx 152$ W/mK at 20 °C and $\approx 100$ at 100 °C) than water ($\approx 0.6$ W/mK), the temperature of the liquid film very
close to the contact line should also be approximately 106 °C. This superheated thin liquid film verifies the existence of thermal resistance at the liquid-vapor interface.

To optimize the wick structure for enhanced heat transfer coefficient, the wall temperature should be minimized. Figure 2.13 shows the local wall temperature for samples with different pitches at various heat flux conditions. The effects of small pitch in reducing the wall temperature is more significant at high heat flux (25-30 W/cm²) than at low heat flux conditions (11 W/cm²). For example, when the heat flux is 30 W/cm², the wall temperature can be reduced by about 8 °C when the pitch is reduced from 80 μm to 40 μm.

In summary, direct measurement of the local wall temperature during evaporation from micropillar wick structures with micro-Raman thermometry suggests that reducing the spacing between microstructures can enhance the thin-film area and lower the wall temperature significantly. This new platform provides important insight into optimizing micro and nanostructures to enhance the heat transfer coefficient in liquid-to-vapor phase change systems for thermal management of high flux electronic devices. For these applications, designing the target surface structures should also takes into consideration the requirement for dryout heat flux, where an optimal pitch which balances the capillarity with viscous drag have been shown previously.

![Figure 2.13. Measured temperature at the center of a micropillar top surface for samples with different pitch.](image)

Different lines represent different heat flux conditions.

Owning to the unique property of micro-Raman thermometry, it is possible to focus the laser excitation on any arbitrary pillars and measure the temperature distribution on the structured area. As shown in Figure
2.14, we measured the temperature distribution along the flow direction at a constant flux of 26.5 W/cm². It can be found that the temperature distributes uniformly along the flow direction because the heat flux acting on this sample is much smaller than its dry-out heat flux. The meniscus shape of the liquid-vapor interface does not change. However, when the pitch increases, the temperature at each pitch increases accordingly because of the decrease of solid fraction. According to Figure 2.14, along the flow direction, the temperature increases firstly due to the sensible heating. The temperature then decreases gradually. The thermal resistance of the thin film around the micropillar decreases accordingly because the contact angle approaches receding contact angle gradually along flow direction when the sample approaches drying out.

![Figure 2.14](image)

Figure 2.14. Temperature distribution along the flow direction on different structured samples when the heat flux is 26.5 W/cm².

In this work, we developed a platform using micro-Raman spectroscopy to perform in situ temperature measurement of micropillar structures during thin-film evaporation for the first time. We built a custom micro-Raman spectroscopy with a spatial resolution of 1.5 μm. By measuring the temperature on the top of silicon micropillars near the liquid-vapor interface on different samples at various heat flux conditions, we observed that local wall temperature reduced as the pitch of micropillars reduced, which is a result of increased thin-film area. The method presented in this work serves as a high resolution and local temperature probing platform to gain new insight into phase change heat transfer.
2.2.2 Thin Film Evaporation on Hierarchical Structured Surfaces: A Future Direction

In this section, we would like to introduce a possible future direction that enhances the thin film evaporation heat transfer by using the hierarchical structured surfaces. As shown in Figure 2.15, this hierarchical structure consists of silicon micropillar with silicon nanowire arrays fabricated on the top. As both the micro and the nanostructure have high wickability. The liquid water will be firstly driven into the micropillar structure by the capillary force and then flows into the nanowire arrays. It has already been observed that the heat transfer is mainly contributed by the thin film region near the micropillar. With the existence of the nanostructure, the thin film region will be extended to the nanowire arrays, which covers the top of the micropillar as depicted in Figure 2.15. Therefore, the total heat transfer performance is possible to improve with the increase of thin film region. To validate this concept, the developed micro-Raman thermometry technique demonstrated in section 2.2.1 can be directly used to characterize the evaporation process on the hierarchical structured surfaces. The superior resolution of micro-Raman spectroscopy also provides great convenience to measure the temperature distribution on each micropillar and investigate the effect of nanostructure on heat transfer.

![Figure 2.15. Thin film evaporation on the micropillar structure and hierarchical structure.](image)

2.2.3 Direct Micro-Raman Measurements on the Liquid-vapor Interface: A Future Direction

In this section, we discuss the possibility of direct liquid-vapor interface probing with micro-Raman thermometry. Although we have shown the temperature at the three-phase contact line can be measured by
micro-Raman technique, it is still very difficult to measure the local heat flux at the thin film region and the
interfacial thermal resistance. To better understand the interfacial transport properties, measuring the
temperature distribution along the entire meniscus interface is critical. It has been demonstrated by Smith
et al. that the O-H bending vibrational mode of water molecule is sensitive to temperature rise, which
provides possibility to probe the water temperature by measuring the temperature dependence of the O-H
bending mode using Raman spectroscopy. Combining the temperature of the silicon micropillar and the
temperature along the liquid-vapor interface, the heat transfer problem of the liquid in the micro structures
is well defined. The local heat flux and the interfacial thermal resistance can be easily computed by solving
the heat conduction in liquid water governed by the Fourier’s law.

2.3 MICRO-RAMAN THERMOMETRY FOR CONDUCTION-RADIATION
CONJUGATE HEAT TRANSFER IN SILICA AEROGEL
Silica aerogel is a promising solar-thermal application attributed to its unique properties of high optical
transparency and low thermal conductivity [98]. It has been found that the silica aerogel has hierarchical
structures. A mesoporous structure (2-50 nm) with 80-99% porosity is supported by solid network, which
is comprised by cross-linked primary particles. The primary particles are aggregated by secondary particles
with 1-10 nm diameter. Due to the high porosity, the heat conduction through solid is significantly reduced.
The air is trapped to nanoscale pore which is smaller than the mean free path of air, leading to very low
gaseous thermal conductivity as well. As the silica particles have high absorptivity in infrared (IR)
wavelength, the radiative thermal conductivity is also reduced [98, 99].

Heat transfer in silica aerogel relies on both conduction and radiation. The coupling of conduction and
radiation leads to nonlinear temperature distribution and size/boundary dependent thermal conductivity of
silica aerogel. For this reason, it is of great fundamental interests to understand the conjugate heat transfer
at different temperature. However, due to the low thermal conductivity of silica aerogel, it is challenging to
measure the temperature using contact mode sensors such as thermal couples or resistive temperature
detector (RTD). Micro-Raman, which uses noncontact laser probe as the detector, shows great possibility
to measure the temperature distribution and heat transfer in silica aerogel. In this section, we show the
experimental technique to measure the temperature profile in silica aerogel using micro-Raman
spectroscopy.

As the silica aerogel is Raman-inactive material and transparent to visible light, direct temperature
measurement is difficult. In this work, we used silicon nanoparticles as the temperature agent, which
produce strong temperature dependent Raman scattering but have negligible effects on the heat transfer
performance of bulk silica aerogel. Figure 2.16 shows the schematic of the experimental technique. In Figure 2.16(a), the dilute silicon nanoparticles solution is deposited in the middle of the silica aerogel forming a very thin Raman-active layer. The sample is held by two heaters on both sides, one is held at high temperature $T_h$ and the other is at low temperature $T_c$. To measure the temperature of silica aerogel, we focused the 633 nm laser excitation on the middle layer and captured the Raman signal from silicon nanoparticles. Figure 2.16(b) shows the LED light focused on the silicon middle layer using 50x objective (NA = 0.55). The temperature can be obtained from Equation (2.24), with the calibrated temperature coefficient of silicon nanoparticles (NP).

To measure the temperature of silica aerogel accurately, two factors should be carefully considered. Firstly, the silicon nanoparticles solution should be dilute enough that it has negligible effect to the properties of silica aerogel. Secondly, the heat induced by the probe laser should be negligible. In this study, we used 100 nm diameter silicon nanoparticles as the temperature agent, which generates strong Raman scattering but has negligible effect to the performance of silica aerogel properties. To determine the concentration of silicon nanoparticle solution, we performed simulation to predict the coefficient of silicon nanoparticles solution and silica aerogel. Figure 2.17 depicts the extinction coefficients of different materials varying with wavelength. According to Figure 2.17, in the 3-10 μm wavelength in which range the thermal radiation is strong, the extinction coefficient of silica nanoparticle is larger than that of silicon nanoparticles solution when the concentration is $10^{12}$/cm$^3$, indicating the radiation heat transfer in the silica aerogel mixed with silicon nanoparticles mainly relies on silica particles. For this reason, we used silicon nanoparticles solution with $1.24\times10^{12}$/cm$^3$ in our experiments.
For the second consideration, we studied the laser heating effect on the silicon nanoparticles. Figure 2.18 shows the center of the silicon Raman peak varying with laser probe power. It can be seen when the laser power is smaller than 0.1 mW, the laser heating effect becomes negligible. For this reason, we used 0.05 mW laser power for the measurements. Figure 2.19 shows the calibration of the silicon nanoparticles. The temperature coefficient of 100 nm diameter silicon nanoparticle is -0.0232 cm¹/C from linear fitting which is slightly different to the that of the bulk silicon due to the size effect.
2.4 GOLD-SILICON NANO-RAMAN SENSOR: A TOOL FOR NANOSCALE THERMAL PROBING

The recent advances in nanoscale heat transfer attract tremendous attentions for academia research and industrial applications. Experimental techniques which is capable of measuring the heat transfer at nanoscale are thus of great importance. Although Raman spectroscopy is a powerful tool to measure the temperature with high accuracy, the best resolution is about 1 μm which is restricted by diffraction limit. To measure the temperature at nanoscale using Raman thermometry, in this section, we propose a concept of using gold-silicon nano sensor to achieve in situ nanoscale probe or extend the temperature measurement on Raman-inactive materials.

Figure 2.20 shows the conceptual demonstration of the nano-Raman sensor. This nano-Raman sensor is composed by a gold nanosphere and a silicon nanocone. The gold nanoparticle behaves like a "nano lens" which concentrates the electromagnetic field within a deep-subwavelength region due to the surface plasmon resonance (SPR) effect (see the left side of Figure 2.20). On the other hand, the silicon nanocone acts as a Raman reporter. As the silicon nanocone is bonded by the gold nanosphere, the enhanced near field will significantly affect the silicon nanocone and excite strong Raman scattering. For this reason, although the silicon nanocone is very small, the Raman scattering from a single nano-Raman sensor is still detectable due to the SPR enhancement. The diameter of this nano-Raman sensor is about 200 nm. If this sensor can be placed on a nanoscale heater, although the laser spot is limited at microscale, the temperature at nanoscale can still be precisely reported by this nano-Raman sensor.
To make the nano-Raman sensor work properly, the material and the size of the sensor should be optimized. There are several factors should be considered. Firstly, the field enhancement effect of the SPR should be maximized. Secondly, the absorption of the nanosphere to the external field should be small enough to minimize the heating effect. Thirdly, the SPR can be excited by the probe laser. Based on the above criterion, we carried out simulation on the gold and silver nanosphere with different wavelength. Figure 2.21 shows the optical performance of the gold nanospheres varying with incident wavelength at different size. For the laser excitation ranging from 532 nm to 633 nm, absorption of nanospheres becomes very small when the diameter of nanosphere is larger than 50 nm. The scattering is maximized when the diameter ranges from 150 nm to 200 nm and 633 nm wavelength is a better choice of laser excitation than 532 nm wavelength due to the low absorption but high scattering.
Figure 2.21. Optical performance of (a) 50 nm (b) 100 nm (c) 150 nm (d) 200 nm and (e) 250 nm gold nanospheres. (f) The peak scattering coefficient and the SPR frequency varying with incident laser wavelength.

Similar theoretical analysis was carried out on silver nanospheres with the diameter ranging from 50 nm to 250 nm. Following the same criterion, as shown in Figure 2.22, the optimized diameter of silver nanosphere is 200 nm to achieve the best scattering but lowest absorption.
Figure 2.22. Optical performance of (a) 50 nm (b) 100 nm (c) 150 nm (d) 200 nm and (e) 250 nm silver nanospheres. (f) The peak scattering coefficient and the SPR frequency varying with incident laser wavelength.

To validate the optimized results from simulation, we carried out Raman measurements on 150 nm, 200 nm gold spheres and 200 nm silver nanospheres with 633 nm laser excitation. The nanospheres was coated...
on the bulk silicon wafer and the Raman scattering of silicon was enhanced by the nanospheres. The concentration of the different nanosphere solutions is maintained the same. The enhancement can be quantified by comparing the nanospheres enhanced silicon Raman peak to the Raman scattering from bulk silicon reference. Figure 2.23 shows the silicon Raman peak measured on different conditions. The best enhancement was found for 200 nm gold nanosphere which provides more than two times improvement for Raman signal. According to this experimental characterization, the 200 nm gold nanosphere should be the optimized size for the nano-Raman sensor.

Figure 2.23. Raman signal of silicon enhanced by 150 nm and 200 nm gold nanospheres and 200 nm silver nanospheres.

To quantitatively predict the optical and the heat transfer performance of the gold-silicon nano-Raman sensor, we developed a numerical solver based on rigorous electromagnetic wave simulation and heat transfer physics. Figure 2.24 shows the simulated electric field distribution and the temperature distribution. The electric field is excited by 633 nm incident plane wave. In the heat transfer model, the nanosensor was placed on a 20 nm width GaN nanoheater with a heat generation of $3 \times 10^{13}$ W/cm$^3$ which is embedded into a GaN wafer. According to Figure 2.24, the SPR was excited at the silicon-gold interface with more than 7 times field enhancement, which can excite strong Raman scattering in silicon nanocone. The average
temperature of the silicon nanocone is only about 3 K less than the average temperature on the top of the nanoheater, indicating this nano-Raman sensor is a good agent for temperature measurement.

![Figure 2.24. The electric field and temperature field simulation of the gold-silicon nano-Raman sensor.](image)

To fabricate the proposed nano-Raman sensor, we presented the following fabrication formulation. As shown in Figure 2.25, the 200 nm nanospheres were firstly coated on the silicon wafer using spin coater. Then we elevated the ambient temperature to anneal the gold nanospheres. The gold nanospheres were bonded on the silicon wafer. After that, the sample was put into KOH solution and the silicon wafer was etched by KOH with the gold spheres as the mask. Finally, the gold-silicon nano-Raman sensors were collected using filter. As shown in Figure 2.26, the developed nano-Raman sensors can be either used to \textit{in situ} probe the temperature at nanoscale (see Figure 2.26(a)) or to map the temperature distribution on Raman-active/Raman-inactive materials (see Figure 2.26(b)).
Figure 2.25. Fabrication process of the gold-silicon nano-Raman sensor.

Figure 2.26. (a) Schematic demonstration of the in situ measurement using single nano-Raman sensor. (b) Schematic demonstration of the mapping measurement using nano-Raman sensors ensemble.
Chapter 3

3. Development of Phase Imaging for Nanoscale Detection

In this chapter, we introduce the theory and application of phase imaging in nanoscale detection. The phase imaging process was achieved combining the depth scanning experiment and TIE algorithm which have been discussed in the chapter 1. In section 3.1, we developed a rigorous vectorial imaging simulator which is capable of computing the imaging process through a high NA optical system. The sensitivity of phase imaging was proven through numerical simulation and experiments. In section 3.2, we applied the developed phase imaging technique to detect the deep-subwavelength defects on 9 nm semiconductor wafer. Section 3.3 presents the application of phase imaging in heat transfer researches. We used the developed phase imaging technique to enhance the performance of environmental scanning electron microscopy and analyzed the droplets dynamics during condensation. To validate the experimental results obtained from phase imaging, we developed a dynamic growth model for condensing droplets. Both experimental and numerical results reveal great potential of phase imaging technique in studying phase change heat transfer.

3.1 THE POTENTIAL OF USING PHASE IMAGING TO RETRIEVE NANO SCALE FEATURES

In this section, we performed numerical and experimental studies to demonstrate the high sensitivity of phase to nanoscale perturbations. We developed a numerical solver to simulate the propagation of electromagnetic (EM) field within the optical system. The conventional scalar diffraction theory, which is based on Fresnel and thin lens approximations, can only be applied to model the low numerical aperture imaging system (NA < 0.5) [100]. To accurately simulate the imaging process of our system (NA > 0.5), we should consider the rigorous vectorial diffraction theory [101, 102]. As depicted in Figure. 3.1, our simulation consists of four parts. In the first part, we calculated the near-field scattering, at which region the non-propagating evanescent field is important. We then propagated the field where the evanescent component has died out to a virtual plane (plane S) at far-field region. The area of plane S is assumed to be large enough to collect all the radiative scattering from the sample. In the third part, the electric field at plane S is transformed to the image plane geometrically through the 4F imaging system with vectorial ray tracing method. Finally, we used Debye-Wolf integral, which takes the diffraction into account, to calculate the image field distribution at the detector [100].
Figure 3.1. Schematic demonstration of the rigorous vectorial diffraction method for the imaging simulation.

(1) The light scattered by the sample at the near-field region is first calculated using method of moments (MOM). (2) The scattering at near-field region is propagated to a virtual plane S at far-field. (3) Geometric optics electric field is transformed from the S plane to the image space using vectorial ray tracing method. (4) The image field is calculated using Debye-Wolf integral.

A more detailed description on the imaging simulation is provided in the following section. We calculated the scattering at the near field using the method of moment (MOM), which is useful in dealing with open-region electromagnetic problems such as wave scattering and antenna radiation [103]. Considering the complexity of the IDA wafer geometry and the high computational cost, we also applied the multilevel fast multipole algorithm (MLFMA) to accelerate the process in solving the moment-method matrix equations [104]. The role of plane S is to eliminate the effects of the evanescent components on the far-field propagation and resample all the radiations from the oscillating magnetic dipoles on the sample. In this work, we positioned the plane S at 10λ far from the sample surface where λ is the wavelength of the incident wave. To calculate the field distribution on plane S, we performed Stratton-Chu integral, which can be expressed as [105],

$$E_s(r_s) = \frac{1}{4\pi} \oint \oint [i\omega \mu (n \times H)G + (n \times E) \times \nabla G + (n \cdot E) \nabla G] dS_0$$  (3.1)

where $E_s(r_s)$ is the field distribution at plane S, ω is the angular frequency of the wave, μ is the magnetic permittivity, n is the surface normal of the sample plane. E and B on the right-hand side represent the...
electric and magnetic fields on the sample plane, which is calculated by the MOM theory. \( G \) is the free-space Green’s function where \( G = \exp(ikr)/r \) and \( r \) is a vector points from an arbitrary surface element on the sample plane \( r_s \) to a surface element on the \( S \) plane \( r_s \).

In the high NA imaging system, the optical components will change the polarization state of the EM field. For this reason, we carried out the vectorial ray tracing method to study the radiation through the 4F system. As shown in Figure 3.1, the polarization change by rotation, refraction and reflection of an optical ray in a meridional plane can be described by Jones matrices. The field distribution (the image field without diffraction) \( e(\theta_2, \phi) \) on the focus of the detector lens with respect to the Gaussian reference sphere is given by Foreman et al. [101],

\[
e(s) = \sqrt{\frac{\cos \theta_2}{\cos \theta_1}} R^{-1}(\phi)L(\pi - \theta_2)L(\pi - \theta_1)R(\phi)\tilde{E}(\theta_1, \phi)
\]

(3.2)

where \( \tilde{E}(\theta_1, \phi) \) is the Jones vector on the plane \( S \), which is converted from the field distribution obtained from Stratton-Chu integral. The definition of the coordinate system related to \( \theta_1, \theta_2 \) and \( \phi \) are shown in Figure 3.1. The unit vector \( s \), which depicts the propagation direction of the wavevector through the imaging system is defined as \( s = (s_x, s_y, s_z) = (\sin \theta_2 \cos \phi, \sin \theta_2 \sin \phi, \cos \theta_2) \). \( R \) and \( L \) are the Jones matrices, which represent the rotation of the meridional plane (\( \phi \)) around the optical axis and the rotation of a ray (\( \theta \)) with respect to an axis perpendicular to the meridional plane respectively. The rigorous electromagnetic field distribution with the diffraction induced by limited NA at the focal region in the image space is given by Debye-Wolf integral [100],

\[
E(r) = -\frac{if_2}{\lambda} \int \int \frac{e(s)}{s_z} \exp(iks \cdot r) ds_x ds_y \quad \text{(3.3)}
\]

where the integral is performed over all the rays reaching the image space. \( \frac{ds_x ds_y}{s_z} = \sin \theta d\theta d\phi \) is the differential element in the solid angle \( \Omega \). Substituting Equation (3.2) into Equation (3.3), we can get the analytical expressions of the field distribution in the image space.
\[ E_x(r) = \overline{E_x}[L_1 + L_2 \cos(2\varphi)] + \overline{E_y}L_2 \sin(2\varphi) \]
\[ E_y(r) = \overline{E_y}[L_1 - L_2 \cos(2\varphi)] + \overline{E_x}L_2 \sin(2\varphi) \]
\[ E_z(r) = -2iL_3[\overline{E_x} \cos(\varphi) + \overline{E_y} \sin(\varphi)] \]  

(3.4)

and

\[ L_1 = \frac{if_2\pi}{\lambda} \int_{\pi-a}^{\pi} \sqrt{\frac{\cos^2\theta_2}{\cos\theta_1}} \sin\theta_2 \cos(\theta_1 + \cos\theta_2) J_0(kr \sin\theta_2) \exp(ikz \cos\theta_2) d\theta \]
\[ L_2 = \frac{if_2\pi}{\lambda} \int_{\pi-a}^{\pi} \sqrt{\frac{\cos^2\theta_2}{\cos\theta_1}} \sin\theta_2 \cos(\theta_1 - \cos\theta_2) J_2(kr \sin\theta_2) \exp(ikz \cos\theta_2) d\theta \]
\[ L_3 = \frac{if_2\pi}{\lambda} \int_{\pi-a}^{\pi} \sqrt{\frac{\cos^2\theta_2}{\cos\theta_1}} \sin^2\theta_2 J_1(kr \sin\theta_2) \exp(ikz \cos\theta_2) d\theta \]  

(3.5)

where \( J_n \) is the n-order Bessel function of the first kind, \( \alpha \) is the convergence semi-angle (aperture angle) of the detector lens (\( NA = \sin\alpha \)), and \( k \) is the wavenumber. We superposed the all the fields emitted by the dipoles on plane \( S \) and obtained the vectorial image of the IDA wafer with arbitrary \( NA \).

To demonstrate the high sensitivity property of phase imaging, we simulated the image field of a magnetic dipole (MD) square array consisting of 1, 4, 9, 16 and 25 MDs respectively. We defined the in-focus image plane located at \( z = 0 \), and the out-of-focus planes of interests are located at \( z_0 \) which ranges from -10 mm to 10 mm with 0.67 mm increment. In each simulation, the amplitude and initial phase of each MD are randomly chosen in the range of 0 to 1 V/m and 0 to \( \pi \) respectively. The wavelength of the illumination is 405 nm whereas the NA and magnification of the microscope objective are 0.9 and 100 respectively. We defined the figure of merit (FOM) which represents the strength of the differential field,

\[ FOM = \sum \frac{L_{\text{max}} - L_{ij}(I_{z_0}(i,j) - I_{z_0-\delta}(i,j))^2 + L_{\text{max}} - L_{ij}(I_{z_0}(i,j) - I_{z_0+\delta}(i,j))^2}{L_{\text{max}}} \]  

(3.6)

where the summation is over all pixels \((i,j)\). \( L_{\text{max}} \) is the length of the image, \( L_{ij} \) is the distance of pixel \((i,j)\) relative to the center of the image. \( \delta \) is a small offset quantity which is fixed at 1 \( \mu \)m in this simulation. Figure 3.2 shows the FOM at the in-focus and the out-of-focus image planes. The peak value of FOM was always found at the focal plane, indicating the effects of out-of-focus information arising from defects or
noises were effectively removed through the center difference process. As a result, the contrast of image at
the focal plane was substantially improved. It is known that the differential field of intensity is related to
the phase of the field through the TIE,

$$\nabla_{\perp} [I(x, y) \nabla_{\perp} \phi(x, y)] = -k \frac{\partial I(x, y; z)}{\partial z},$$

(3.6)

which indicates that the phase of the field remains the high contrast property of the differential field.

![Figure 3.2 Normalized FOM varying with the position of image plane \(z_0\). Inset: the definition of the pixel
distance relative to the on-axis MD. The schematic of the MD array.](image)

We further demonstrate the high sensitivity property of phase imaging through experiments. We
reconstructed the phase perturbed by nanoscale line edge roughness (LER) structures. Figure 3.3(a) shows
an optical image \((NA = 0.75)\) of a standard NIST reference sample which is used for testing the
performance of imaging system. Each parallel LER (see the red-dash box in Figure 3.3(a)) is a square-wave
like nanoscale pattern. Along each column, the pitch of each square-wave pattern remains the same but the
amplitude of each square wave increases from 0 to 60 nm with 10 nm increment. Alone each row, however,
the amplitude of each pattern remains the same but its pitch increases from 50 nm to 260 nm with 10 nm
increment. The intensity images of the nano-pattern array are shown in the left side of Figure 3.3(b) and the
top of Figure 3.3(c) respectively. It can be seen that the intensity is uniformly distributed along each square-
wave pattern as the scattering from 10 nm change in the pattern is too weak to be detected. However, this
change can be clearly observed if we retrieved the phase from intensity by solving TIE. More quantitative
investigation is also possible if we examine the phase and intensity distribution along the dash line shown
in Figures 3.3(b) and 3.3(c). The magnitude of intensity almost remains constant alone the column and row.
However, a linear decay in phase can be clearly seen from Figures 3.3(b) and 3.3(c), which was in good accordance with the 10 nm uniform change in amplitude and pitch of each square-wave pattern. Therefore, the sensitivity of phase imaging and the capability of phase imaging through TIE were further proven.

Figure 3.3. Intensity and phase images of nanoscale line edge roughness (LER) pattern. (a) The optical image of NIST standard testing sample. (b) Intensity and phase images of LER pattern along the column. (c) Intensity and phase images of LER pattern along the row.
3.2 DEEP-SUBWAVELENGTH DEFECTS INSPECTION ON 9 NM SEMICONDUCTOR WAFER USING PHASE IMAGING

Nanoscale feature detection is an important technique relevant to many fields, including nanostructure fabrication [106, 107], biomedical observation [108, 109] and nanoscale physics [110, 111]. Among these applications, defect inspection of semiconductor wafer, which is critical for both academia and industry, has attracted increasing attentions [107, 112-115]. Despite numerous efforts have been made in advanced microscopy, the rapid progress in integral circuit (IC) predicted by Moore’s law continuously pushes the limit of fabrication to smaller size, and brings new challenges for defect inspection [106, 116]. Conventional techniques, such as scanning electron microscopy (SEM) [117], transmission electron microscopy (TEM) [118], as well as small angle X-ray scattering (SAXS) [119] severely suffer from the drawbacks of low efficiency, high cost and high system complexity, which prevent their massive industrial application to the wafer-level inspection. Besides, the inspection process with these techniques may contaminate or even damage the fragile nano structures due to the high energy exposure [107]. Here, we demonstrate a high sensitive cost-worthy optical method to probe the perturbation of wavefront induced by nanoscale features. A wide-field white light depth-scanning (WLDS) technique and a phase retrieval algorithm were applied to identify and locate a variety of defects and even dust particles on 9 nm intentional defect array (IDA) wafers. Experimental results showed that this wide-field technique can achieve an image field 625 times (in area) larger than that of traditional SEM. An accurate electromagnetic (EM) wave simulation predicted that our method is possible to detect even smaller size defects down to 5 nm.

The fabrication defects on wafers often lead to short circuit or disconnection, which can severely degrade the performance of chips [120-122]. Therefore, defect inspection is always significant in the process of semiconductor fabrication. Recent advances in multiple patterning ultra-violet (UV) lithography and extreme-UV (EUV) lithography enables fabricated wafers with node size below 10 nm [112, 114]. To spot the defects on the semiconductor wafer with such small node size, techniques based on electron-beam (e-beam) scanning, such as SEM, TEM are reported to be used for wafer inspection [117, 118, 123]. Although these techniques can often achieve nanoscale resolution, the efficiency and cost are inevitably sacrificed [115, 124, 125, 126]. For example, a typical SEM can resolve nanoscale structures down to the size of nearly 10 nm. However, the image field of SEM has to be shrunk to about 1 μm × 1 μm to reach such high resolution (with a pixel size about 1 nm accordingly), which means it will take over a month to scan only one 5-inch wafer. Multiple electron beams (more than 100) were proposed to boost the efficiency, but the detection cost per area with this method increased dramatically. Similar problems occur when using TEM. SAXS is a promising technology because this technique enables the entire three-dimensional imaging of
IC with very high resolution (~ 14 nm) [119]. Unfortunately, the necessity to use synchrotron light sources limits its broad application.

Attributed to the noninvasive and large-field-of-view nature, optical microscopy is also intensively applied in semiconductor wafer inspection and other nanostructure characterizations [112, 115, 127, 128]. However, there are two technical limitations for optical microscopes to spot nanoscale defects: one is resolution and the other is sensitivity. The resolution of optical microscopes is restricted by diffraction limit, and the best resolution of optical microscopy using visible light is typically 100-200 nm [129], which is not enough to visualize nanostructures under 100nm. To improve the resolution, several optical techniques based on UV and even EUV illumination were proposed for nanostructure observation, which can find defects down to 20 nm [114, 130, 131]. However, the instrument complexity and high cost prevent their further industrial applications. As for sensitivity, it is characterized by the signal to noise ratio (SNR) of the optical microscope [132]. Mechanical vibrations, laser speckles and even the quantum uncertainty of photons can introduce noises, which will degrade the performance of instrument in detecting weak signals [133, 134]. In fact, for wafer inspection, sensitivity is much more important than resolution since what we are really interested in is the existence and position of defects rather than their geometrical features. Thus, an ideal probe for defects inspection does not necessarily have ~10 nm resolution, but it should be sensitive enough to the perturbation of nanoscale defects. It has been proven that the phase of optical field is a proper agent for such weak wavefront perturbations [135], and phase measurements with high sensitive optical apparatus such as interferometers have been extensively used in biomedical researches for qualifying nanoscale membrane fluctuations [136-138]. Furthermore, it was reported that interferometry method was also successfully applied to 20 nm node wafer defect detection [115].

To enable the deep-subwavelength probe with high efficiency but low cost and minimum invasion, we developed a WLDS apparatus to map the perturbed wavefront using phase retrieval method. Figure 3.4 presents the basic concept of this measurement. When the incident wave interacts with the nano feature on the wafer, the light is scattered. This scattering is so weak that it cannot be detected directly from the intensity of scattered wave. However, the scattered wavefront is distorted due to the phase shift during interaction, providing a possibility to find corresponding defects. The schematic of the WLDS setup is shown in Figure 3.4(b). The white light source (WLS) was chosen as the broad-band light source has low coherence, which can improve the spatial sensitivity by decreasing speckles in imaging. The spatial sensitivity and illumination uniformity are further enhanced by the Kohler illumination aperture diaphragm shown in Figure 3.4(b). The sample located on a linear stage can move along the optical axis with an increment of 50 nm in each step. Both the in-focal and de-focal images of the wafer are taken to construct
the entire optical field. The images form from a 4F system and then are captured by a charge-coupled device (CCD) camera. The perturbed phase field can be retrieved through the measured intensity field by transport of intensity equation [139, 140] (section 1.3 for derivations),

$$\nabla^2 \psi(x, y; z_0) = -k \frac{\partial I(x, y; z_0)}{\partial z}$$ (3.7)

where the wave propagates along $z$ axis and $\nabla \psi = I \nabla \phi$. $I$ and $\phi$ are the two-dimension intensity and phase at plane $z_0$. $k$ is the wave number. The intensity field shown on the right-hand side of Equation (3.7) can be directly measured by the WLDS apparatus, and corresponding phase can be calculated by solving Equation (3.7). To evaluate our method, we performed experiments on IDA wafers. The 9 nm (defined as the width of the top) technology node arrays were fabricated on the wafer (Figure 3.4(c)) and different types of defect were intentionally put on the wafer simultaneously (Figure 3.4(d)-(f)). One of the most common defects is the parallel bridge defect (Fig. 1d) which connects two neighboring technology nodes. The stitching error (Figure 3.4(f)) arises from the overlapping between two adjacent UV scanning in manufacture. It is also of great interest to distinguish dust particles from defects (Figure 3.4(f)), as the nanoscale dusts mixing with defects makes it hard to accurately assess the quality of the wafer.
Figure 3.4. Demonstrations of perturbed wavefront by defects, experimental techniques and 9 nm IDA wafer. (a) Conceptual sketch of wavefront distorted by the nanoscale feature. (b) Sketch of the WLDS technique. M and BS represent a mirror and a 50:50 beam splitter respectively. (c)-(f) SEM images of typical 9 nm wafers (c) without defects, (d) with parallel bridge defect (see corresponding red-dash box), (e) with stitching error (see corresponding red-dash box), and (f) with a dust particle (see corresponding red-dash box).

We first show the detection of the parallel bridge defect and stitching error (Figure 3.4(d),(e)). The in-focal intensity image of the 9 nm IDA wafer and corresponding retrieved phase are shown in Figure 3.5(a),(b) respectively. The intensity field (Figure 3.5(a)) was normalized by the maximum intensity, and the phase (Figure 3.5(b)) was solved from Equation (3.7). Thanks to the high sensitivity of phase, significant improvement in contrast was achieved from phase imaging. As expected, the intensity signal from parallel bridge defects was completely submerged into background noises (Figure 3.5(a)), but the phase shift due to the perturbation of this defect can be clearly seen at the center of Figure 3.5(b). The blurry grid pattern shown in Figure 3.5(a) arising from the stitching error (Figure 3.5(e)) was also sharpened and enhanced by this phase retrieval technique (Figure 3.5(b)). To interpret this observation mechanistically, a rigorous EM simulation of the scattered field was carried out by using vectorial optical diffraction theory [141]. Higher
sensitivity of phase compared to intensity was demonstrated through this simulation. As depicted in Figure 3.5(c), the simulated phase shift caused by the parallel bridge defect can qualitatively agree with our measurements. It should be noticed that even if our phase imaging technique can position the defect, it is still restricted by optical diffraction limit. The diffraction of light on the nanostructures leads to the loss of high frequency information. In other words, each node on the wafer will generate a large blurry spot (~200nm) on the image, and these blurry spots superpose to form a uniform background. However, the “bad node”, two adjacent nodes connected by the defect, breaks the periodic distribution of the regular nodes by creating a larger perturbation to the wavefront, for which reason the position of defect is finally seen from the retrieved phase map.

To validate our method, we compared our measurement results with SEM images at the approximately same position of the wafer. As shown in Figure 3.5(d), the position of the defect cannot be determined in this image because the pixel size (≈ 30 nm) is too large if the scanning area becomes the same as image field of WLDS, i.e., ≈ 30 μm × 20 μm. To achieve better resolution, the scanning area was decreased to ≈ 1.2 μm × 0.8 μm (see the red-dash box in Figure 3.5(d)) until the defect was clearly resolved. A parallel bridge defect was (Figure 3.5(e)) found exactly at the center of the SEM image (Figure 3.5(d)), indicating this defect can be precisely positioned through the WLDS method. The position of the stitching error detected by the WLDS method was also verified through SEM as shown in Figure 3.5(f). It worth to compare the efficiency of the proposed technique with SEM. This wide-field optical method enables the image field as large as ≈ 30 μm × 20 μm under a single shot. However, as discussed above, the area of the image field of SEM is 625 time smaller than the WLDS counterpart when the profile of the defect is well resolved in SEM. Therefore, to take an image on the same area, this WLDS method is much more time-saving than traditional SEM inspection.
We next examine the capability of the WLDS method in identifying dust particles from defects. Following the same protocol described above, we obtained the retrieved phase perturbed by a parallel bridge defect and a $\approx 200$ nm (in diameter) dust particle simultaneously. The phase was normalized by its maximum. There are two circular spots shown in Figure 3.6(a). Stronger signal always come from the dust particle because of its size ($\approx 200$ nm) is usually much larger than that of the defect ($\approx 10$ nm). As a result, the spot at the center of the phase image (Figure 3.5(a)) indicates the position of the parallel bridge defect, and the other ring-shape spot is generated by the dust particle. This result was also verified by SEM depicted in Figure 3.6(b)-(d). The scanned area shown in Fig. 3b was blocked in the red-dash box (1) of Figure 3.6(a).
The observation depicted in Figures 3.6(c) and (d) reveals the position of the defect and the dust particle by scanning the area marked by the red-dash boxes (2) and (3) respectively. The position of the defect relative to the dust particle shown in SEM images (Figure 3.6(b)-(d)) exactly agrees with what observed from the retrieved phase (Figure 3.6(a)). The ring-shape spot of the dust particle (Figure 3.6(a)) is originated from the defocused diffraction. The dark rectangular area around red-dash box (2) shows the damage after several times e-beam scanning. We also scanned the sample along the optical axis to find the focal positions of the defect and dust particle. The phase in x-z plane crossing the center of the defect and the dust particle are shown in Figures 3.6(e) and (f) respectively. The strongest signal from defects was always found at the center along the optical axis, i.e., the focal plane of the wafer. However, the dust particle has the strongest signal always off the center line because the dust locates out of the wafer plane, setting on the top of technology nodes. The repeat of the signal along z direction arising from Talbot effect, however, it usually does not interfere with the pinpoint of the focal position.

**Figure 3.6. Dust characterization using depth scanning and phase retrieval.** (a) Comparison between the weak dot-shape spot and the strong ring-shape spot generated by a defect and a dust particle respectively. (b)-(d) SEM images of the IDA wafer at the area covered by (b) red-dash box (1), (c) red-dash box (2) where a parallel bridge defect was found and (d) red-dash box (3) where a dust particle was observed. (e),(f) The x-z plane of the phase field crossing (e) the center of the parallel bridge defect spot and (f) the center of the dust spot. WLDS is along z axis.
Finally, to evaluate the limitation of our experimental technique, we performed simulations to predict the minimum detectable size of defects. We discussed two conditions. Firstly, we assumed smaller defects can be made accidentally in current fabrication technology. In the simulation, we reduced the width of the defect from 9 nm to 4 nm on the 9 nm IDA nodes wafer. Secondly, we simulated the perturbed intensity and phase on the IDA wafer with smaller node size. We kept the size of defect the same as the technology nodes but scaled down all the geometrical features from 9 nm to 5 nm simultaneously. To make the defect detectable, the strength of signal arising from the defect should be larger than the noise of instruments. According to Equation 3.7, the signal of phase depends on the gradient of intensity \(I\) relative to the background intensity \(I_0\). Here, we defined a dimensionless quantity normalized intensity \(\frac{\Delta I}{I_0}\), where \(\Delta I\) is the difference in intensity between two adjacent images and \(I_0\) is the averaged intensity of the reflected field.

As for instruments, their noise level mainly depends on the shot noise of the CCD \(\delta I\), if we assume that other sources of noise (mechanical vibration and air flow etc.) are negligible. The shot noise is determined by the full well capacity (FWC) of the CCD pixel, which can be expressed as,

\[
\frac{\delta I}{I_0} = 1/\sqrt{N},
\]

where \(N\) is the FWC (maximum photon number that can be received by a pixel). We compared the normalized intensity to the CCD shot noise. If the normalized intensity is larger than the noise level of instruments, the gradient of intensity can be measured, and the phase can be solved from. Equation 3.7 accordingly.

As shown in Figure 3.7, the normalized intensity from the defect decreases with both defect size and node size. When the defect size changes from 9 nm to 4 nm (Figure 3.7(a)), corresponding peak phase drops from 0.02 rad to 0.012 rad (inset of Figure 3.7(a)), showing an approximately linear size dependence. As the shot noise of the CCD used in this work is 0.0075, all the defects ranging from 4 nm to 9 nm on the 9 nm IDA wafer are possible to be detected using current setup. When the size of nodes changes, the signal strength of the defect becomes highly node-size dependent (Figure 3.7(b)). The strength of signal can be more than 10 times weaker if the node size decreases from 9 nm to 5 nm (Figure 3.7(b)), and the spot shown in the phase map, which indicates the defect, expands due to diffraction (inset of Fig. 4b). Although it is challenging to probe the perturbed phase using current setup if the node size is below 7 nm (Figure 3.7(b)), detecting defects down to 5 nm is still possible if current CCD is replaced by other high sensitive commercial available products, such as iXon3 897 EMCCD (ANDOR), and Newton 920 CCD (ANDOR) which have a shot noise of 0.0024 and 0.0014 respectively (inset of Figure 3.7(b)).
Figure 3.7. EM wave simulation of the normalized intensity varying with the size of defects and technology nodes. (a) Normalized intensity induced by defects with different sizes on a 9 nm IDA wafer. Insets: Simulated optical phase field at the focal plane perturbed by a 4 nm, 5 nm, 6 nm, 7 nm, 8 nm and 9 nm defect respectively (from left to right). (b) Normalized intensity of a 5 nm, 7 nm and 9 nm IDA nodes wafer. Yellow line: the shot noise (0.0024) of iXon3 897 EMCCD. Orange line: the shot noise (0.0014) of Newton 920 CCD. Insets: Simulated optical phase field of the 5 nm, 7 nm and 9 nm IDA nodes wafer (from left to right). Newton 920 CCD (left) with a FWC of 510000 and iXon3 897 EMCCD (right) with a FWC of 180000. The scale bars in all the inset images denote 1 μm.

In conclusion, we have reported wide-field deep sub-wavelength defects detection method using WLDS and phase retrieval which can achieve 625 times larger image field than traditional SEM. Our observations are in good agreement with both SEM detection and EM wave simulation. Furthermore, the predicted smallest defect that can be detected is 5 nm according to EM simulation. This work demonstrates the importance of sensitivity and the potential of phase imaging in nanoscale defects inspection. Our experimental approach can either directly locate the position of defects and dust particles or act as the pre-process of SEM detection to significantly narrow down the total area need to be scanned by e-beam. Perhaps more importantly, we anticipate this high sensitivity optical phase imaging technique will inspire a variety of promising applications, such as biological observations, material characterizations and measurement of nanoscale features.
3.3 ENHANCED ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY FOR CONDENSING DROPLETS ANALYSIS

The properties of the phase imaging technique which can substantially improve the image contrast and extract the nanoscale perturbation from noisy background have been demonstrated in sections 3.1 and 3.2. In this section, we show the application of phase imaging in heat transfer research. We improved the image contrast and suppressed the background noise of ESEM. The enhanced ESEM was used to study the dynamics of droplet condensation. To validate the experimental results, we developed a dynamic growth model to predict the droplets growth and heat transfer performance, which is presented in section 3.3.1. In section 3.3.2, the droplets growth was investigated using the enhanced ESEM. The experimental results were validated by numerical simulations, and high contrast images of condensing droplets at pressure up to 20 torr were produced.

3.3.1 Condensing Droplets Growth: A Time-dependent Multiscale Dynamic Model

Condensation of water vapor is a common phenomenon in nature and it is also widely used in various engineering systems [142-144]. Typically, two modes of condensation have been considered, i.e., filmwise condensation [145-147] and dropwise condensation [148-152]. While filmwise condensation results in a liquid film, dropwise condensation leads to discrete nonwetting droplets. Droplets are removed by gravity when they become larger than the capillary length scale (~1 mm). This mode is much more efficient than the condensate removal in the form of a liquid film, and therefore, improved heat transfer performance is expected with dropwise condensation. More recently, with certain superhydrophobic surfaces, jumping-droplet condensation [153-155] has demonstrated even better heat transfer performance than traditional dropwise condensation. These jumping-droplets grow, coalesce and spontaneously jump due to the release of excess surface energy. The coalescence induced removal of droplets occurs at small droplet radii (~10 to 100 μm) which makes the droplet removal more efficient. The smaller droplet radius also reduces the thermal resistance and promises improved condensation heat transfer performance. In addition to heat transfer enhancement, jumping-droplet condensation has also been studied for anti-icing/frosting [156-158] and self-cleaning [159].

In both dropwise and jumping-droplet condensation, droplet growth is an inevitable, yet complex process which couples the liquid-vapor phase change and fluid flow to the morphology of droplets. Therefore, continuous theoretical improvements have been made to understand the growth and energy transport in individual droplets during condensation. The early theoretical works solved the heat transfer in a droplet...
relying on a thermal resistant network by assuming 1) pure conduction at steady state, 2) a hemispherical droplet and 3) a uniform temperature along the liquid-vapor interface [160-165]. This theoretical framework was extended to beyond the hemispherical droplet assumption by Kim and Kim [166], in which the effect of contact angle on heat transfer was considered. Improvements in the thermal resistance network of an individual droplet during condensation was subsequently carried out by Enright et al. [167] and Miljkovic et al. [168] by carefully considering the wetting morphologies. Meanwhile, Chavan et al. [169] replaced the thermal resistance network by an axisymmetric two-dimension model. The assumption of uniform temperature along the interface was also eliminated by applying a convective boundary condition [169].

In all of these previous studies, heat was assumed to be transferred by pure conduction and the droplets always remained at steady state for simplification. However, the internal circulation in droplets commonly occurs in a variety of dynamic processes including droplets falling [170] and evaporating [171-174], indicating convection inside droplets is not always negligible. Furthermore, the time-dependent growth of droplets indicates that in actuality, steady state can never be reached. Even though the fluid flow caused by the pressure difference can be neglected due to the small droplet size, the fluid flow arising from several other factors can still affect energy transport as described as follows. 1) When there is a temperature gradient along the interface, surface tension gradients will lead to the Marangoni flow. 2) The contact line of the droplet can change during growth, whereas past models have assumed a static advancing contact angle for geometric calculations. The effects of the moving contact line and the corresponding dynamic contact angle have not yet been considered. 3) Condensation on the liquid-vapor interface introduces mass flow into the droplet, which can influence the convective heat transfer due to the mass and momentum of the condensed vapor transferred into the droplet. 4) The droplet growth is a dynamic and continuous multi-scale process with droplet radii ranging from several nanometers to several hundred microns. The heat transfer and fluid flow are time-dependent and strongly affected by the interface expanding during growth. However, these dynamic effects have not been captured by previous pure conduction models where steady state and negligible convection were assumed.

In this work, we developed a comprehensive model that considers the dynamics of individual condensing droplet growth with droplet radii from nucleation size of several nanometers to hundreds of microns before coalescence. This model couples the transient phase change heat transfer and two-phase flow both inside and outside the droplet. The underlying physical insights of the growth dynamics and energy transport are elucidated. We present the details of our developed dynamic growth model. We show multi-scale dynamic growth and energy transport in an individual droplet, identify the effects of convection at different length
scales and analyze the mechanics responsible for convection. Finally, we summarize the contributions of this work and provided prospects for future work.

The heat transfer in a condensing droplet is complex due to the multiple heat transfer modes inside the droplet as well as the phase change at the liquid-vapor interface. To model this conjugate mass, fluid and energy transport process, we developed a time-dependent multi-physics solver. Initially, as shown in Figure 3.8, a nucleated droplet with several nanometers radius \( R \) is placed on a solid substrate with uniform temperature \( T_s \) and in a saturated vapor environment \( (p_{\text{sat}}, T_{\text{sat}}) \). Driven by the temperature gradient between the saturated vapor and the substrate, heat flux \( q_i \) is transferred from the vapor to the droplet. The latent heat of condensation primarily carries the energy, which is delivered to the liquid through phase change at the interface. The mass flux \( M_i \) associated with the heat flux enters the liquid simultaneously, leading to a continuously growing droplet. As a result, we modeled the heat transfer (temperature distribution \( T \) ) inside the droplet bounded with phase change \( q_i \) at the liquid-vapor interface and constant temperature \( T_s \) at the substrate. As the heat transfer is coupled with fluid flow, we considered the fluid fields of both liquid \( u_l \) and vapor \( u_v \) phases. The fluid field of liquid is bounded by an expanding liquid-vapor interface where the mass flux \( M_i \) continuously flows in, and by a Navier-slip solid wall (substrate) where the three-phase contact line \( v_{CL} \) is moving. According to the above descriptions, the following physics were captured in the model. At the liquid-vapor interface, the expanding interface, mass flow and Marangoni effect were taken into account. At the contact line, the effect of the advancing contact line \( v_{CL} \) on the dynamic contact angle \( \theta \) was computed. Inside the droplet, gravity driven flow and possible internal circulations \( u_l \) were considered. The energy transport in the droplet was determined by solving the heat equation with the flow field obtained from continuity and Navier-Stokes (NS) equations. The fluid flow and heat transfer equations are coupled through the relation between the heat and mass fluxes at the interface as well as the temperature dependent properties.
Fluid flow
Open BC at
constant $p_{sat}$

Heat transfer
Saturated
vapor $p_{sat}$
Saturated
vapor $T_{sat}$
Condensing
mass flux $M$,
Condensing
heat flux $q$,
Internal liquid
flows $u_l$
Expanding
interface
Dynamic contact
angle $\theta$
Moving contact line
$\phi_c$ (Navier-slip BC)

Figure 3.8. Schematic diagram of the model capturing a condensing droplet during growth. A droplet grows in the saturated vapor environment ($p_{sat}, T_{sat}$). The coupling of fluid flow and heat transfer were modeled. In the heat transfer model (right side), transient conduction and convection in a droplet were solved. This droplet rests on a substrate at a temperature of $T_s$. The heat flux ($q_i$) arising from phase change enters the droplet through the liquid-vapor interface. In the fluid model (left side), transient fluid flow inside the droplet was solved. Mass flux ($M$) flows into the droplet during condensation leads to droplet growth. The mass conservation and the force balance were considered at the expanding interface. A Navier-slip boundary was applied on the substrate to allow the contact line to move and the contact angle $\theta$ to change dynamically according to the contact line velocity $v_{CL}$.

The heat transfer in the liquid phase is governed by the energy equation

$$\rho_l c_p \frac{\partial T}{\partial t} + \rho c_p u \cdot \nabla T + \nabla \cdot (-k \nabla T) = 0$$  \hspace{1cm} (3.9)$$

where $\rho_l$ is the density, $c_p$ is the specific heat capacity and $k$ is the thermal conductivity. The time dependent and flow related terms were involved in order to capture the transient effect and convective heat transfer. The coupled flow field $u$ was obtained by solving fluid equations as will be described later.
To model the heat transfer at the liquid-vapor interface, two effects were considered, i.e., the temperature drop arising from interface curvature and the interfacial heat transfer due to phase change. This curvature induced temperature drop is given by [165, 166, 168]:

$$\Delta T_c = \frac{2T_{sat} \sigma}{Rh_{fg} \rho_l}$$ (3.10)

where $T_{sat}$ is the saturated temperature of vapor, $\sigma$ is the surface tension, and $h_{fg}$ is the latent heat. From Equation (3.10), it can be seen that the curvature induced temperature drop is significant when droplets are as small as tens of nanometers but becomes negligible when the radius is larger than 1 \(\mu\)m.

The interfacial heat flux normal to the interface is related to the total temperature difference through the interfacial heat transfer coefficient:

$$q''_l = h_i(T_{sat} - \Delta T_c - T_i)$$ (3.11)

where the interfacial heat transfer coefficient is given by:

$$h_i = \frac{2\sigma_c}{2 - \sigma_c \sqrt{2\pi R_g T_{sat} \rho V_g T_{sat}}} \frac{1}{h_{fg}}$$ (3.12)

where $\sigma_c$ is the condensation coefficient, $R_g$ is the specific gas constant and $V_g$ is the specific volume of vapor. The condensation coefficient refers to the ratio of vapor molecules captured by the liquid to the total number of vapor molecules reaching the interface. At the saturation condition, according to Marek et al. [175], this condensation coefficient is determined from the saturation pressure. The convective heat flux boundary given by Equation (3.11) is prescribed at the liquid-vapor interface while a constant temperature ($T_i$) boundary condition is set at the liquid-solid interface.

In order to compute the flow field term $\mathbf{u}$ shown in Equation (3.9), as well as to capture the growth of the droplet interface, continuity and Navier-Stokes equations expressed in Equations (3.13) and (3.14), respectively, were solved in both the liquid and vapor phases,

$$\nabla \cdot \mathbf{u} = 0$$ (3.13)
\[
\rho \frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = -\nabla p + \mu \nabla \cdot (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) + \rho \mathbf{g}.
\]  

(3.14)

The condensing mass flux on the liquid-vapor interface (see Figure 3.8) is determined by the interfacial heat flux and the mass is conserved on the normal direction to the interface,

\[
M_i = \frac{q_i}{h_{fg}} = \rho_v (u_i^p - u_i) = \rho_l (u_i^l - u_i)
\]

(3.15)

where \(u_i^p\), and \(u_i^l\) are the normal velocities at the interface on vapor and liquid sides respectively, and \(u_i\) is the normal velocity of moving interface.

To solve the two-phase flow problem, we applied the following boundary conditions (see Figure 3.8): Navier-slip boundaries at the liquid-solid interface and the vapor-solid interface, force balance and mass conservation at the liquid-vapor interface, dynamic contact angle at the moving contact line and stress-free boundaries with constant pressure \(p_{wall}\) at the outer boundaries of the vapor domain. The temperature and pressure dependent properties were considered for both the liquid and vapor phases. We solved the heat transfer and two-phase flow coupled problem described by Equations. (3.9) – (3.15) with the finite element method in COMSOL. A 2D axisymmetric model was used for numerical calculation. To simulate the continuous growth of droplets from several nanometers to hundreds of microns, Arbitrary Lagrangian-Eulerian (ALE) method was used to adapt to the multiscale geometrical change.

We simulated an individual water droplet growing in a saturated vapor environment of 60°C, which is a common temperature for steam condenser. The temperature of the substrate in this study ranges from 53°C to 59°C and the static contact angle varies from 90° to 140°. The droplet grows from the nucleation size to the coalescence size with droplet radii from several nanometers to hundreds of microns. We show different energy transport modes in the droplet at different length scales during growth. We analyze the increasing contribution of convection heat transfer inside the droplet to the energy transport and growth dynamics. The importance of convection is further emphasized by comparing the proposed dynamic growth model with both the pure conduction and the static convection models. To better understand the driving force of convection, we examine several potential factors including interfacial mass flow, Marangoni flow, gravity driven flow as well as the dynamic contact angle, and show that the interfacial mass flow plays the key role responsible for strong convection of microscale droplets. We predict the critical radii of droplets when the
convection becomes significant under different subcooling temperatures and contact angles, providing guidelines for when convection in condensing droplets needs to be considered.

We first show the multiscale dynamic growth of an individual droplet for the following conditions. The substrate is held constant at 55°C and the static contact angle of the droplet is 120°. The condensation coefficient is ~0.35 according to the saturation pressure \([175]\) and the corresponding interfacial heat transfer coefficient is ~1 MW/m². Vertical gravity is applied. Droplet growth starting from a nucleation radius of 3.77 nm to 500 μm before coalescence is analyzed, where the nucleation radius was estimated based on Kim and Kim [166]. In order to highlight the significant effects induced by the continuous growth and capture the detailed physics, we compare the dynamic model with the pure conduction and static convection models typically used in previous works. We first describe all three models used for comparison.

(1) As described in before, the dynamic model considers time-dependent heat and mass transport with two-phase flow by solving Equations. (3.9) ~ (3.15) simultaneously. As a result, the effects of interfacial mass flow, the deforming interface and convection can be well-resolved.

(2) The pure conduction model provides a steady state solution by solving Equations. (3.9) ~ (3.12). This model treats the droplet as “solid” in steady state by eliminating the time-dependent and convection terms in Equation (3.9). Equation (3.11) acts as a convective boundary condition on the pre-defined and nondeformable interface. We highlight the contribution of convective heat transfer to droplet growth by comparing the dynamic growth model to this pure conduction model.

(3) The static convection model provides a solution to heat transfer for single phase flow in the steady state by solving Equations. (3.9) ~ (3.14) in the liquid domain only. This model is capable of studying gravity driven flows and Marangoni flows inside the droplet. However, the mass transport and resulting droplet growth expressed in Equation. (3.15) is neglected, and the transient terms in Equation. (3.9) and (3.14) are consequently eliminated. We will emphasize the importance of interfacial mass flow and droplet growth to energy transport by comparing the dynamic growth model to this static counterpart.

Before we discuss the fluid flow and energy transport in growing droplets quantitatively, we qualitatively discuss the role of convection in droplets during different stages. Figure 3.9 shows the temperature distribution inside the droplet from 50 nm to 500 μm obtained from the three different condensing models. Specifically, Figure 3.9(a) shows the temperature of the droplet predicted by the dynamic growth model.
Results of the pure conduction model (model (2)) and static convection model (model (3)) are shown in Figure 3.9(b) and 3.9(c), respectively.

Comparing the three cases, similar discrete-layer temperature distributions are observed when the droplet grows from 50 nm to 500 nm, indicating heat conduction plays a key role in energy transport. The stage of droplets smaller than ~5 μm is referred to as the “conduction-dominated stage”. This result makes physical sense as the conductive thermal resistance is small for nanoscale droplets. The temperature of the 50 nm radius droplet is much closer to the substrate than vapor environment because the thermal resistance of droplets is much smaller than that of the interface as illustrated in Equation (3.10).

When the droplet grows to 5 μm, the static convection model can still produce results similar to the dynamic growth model, but there are discrepancies between the convection model results (Figures 3.9(a) and (c)) and the conduction model (Figure 3.9(b)). Figures 3.9(a) and (c) show the cold fluid at the center is carried upwards slightly, indicating the convection occurs at the 5 μm radius droplet. This convection is mainly driven by Marangoni flow, which will be specifically discussed later. For the 50 μm radius droplet, the effects of convection can be more clearly identified from the temperature distribution, but the discrete-layer temperature distribution induced by pure conduction remains, indicating a coexisting stage of conduction and convection. Therefore, the stage of droplets between ~5 μm and ~200 μm is referred to as the “transition stage”.

As the droplet radius increases to 200 μm, as shown in Figure 3.9(a), the discrete-layer temperature distribution disappears and the cold fluid mixes with hot fluid as predicted by the dynamic growth model. This temperature distribution indicates that the convection becomes significant when the droplet grows to 200 μm and can further develop with increasing droplet size. This stage (the droplet radius is larger than ~200 μm) is referred to as the “convection-dominated stage”. The energy transport process inside the droplet can be clearly seen from Figure 3.9(a) when the droplet expands to 500 μm. As the heat is transferred into the droplet, the high-temperature fluid at the upper side is completely mixed with the bottom low-temperature fluid through convection. As a result, the temperature at the upper region of the droplet becomes uniform, and the bottom region containing the cold fluid is compressed to a very thin layer. As the temperature gradient of the liquid at the bottom of the droplet is very large, the heat flows through the thin cold liquid layer to the substrate mainly by conduction. As the temperature gradient near the top of the substrate becomes large due to convection inside droplets, the total heat transfer rate calculated by the dynamic growth model can be much higher than that estimated by its pure conduction counterpart. In addition, it is also of great interest to understand the differences predicted by the dynamic growth and static...
convection models shown in Figures 3.9(a) and (c), respectively, when droplets are larger than 50 µm. The interaction between the Marangoni flow and internal circulation driven by interfacial mass flow, which is not considered in the static convection model, is responsible for such a discrepancy, and will be discussed in detail.

![Figure 3.9. Temperature distribution inside the growing droplet with a radius of 50 nm to 500 µm obtained from the (a) dynamic growth, (b) pure conduction, and (c) static convection models. Every slice of color represents a temperature increase of 0.25°C. Consistent results of the three models were found when the radius of the droplet is smaller than 500 nm where energy transports through conduction. Effects of convection appear ((a) and (c)) when the droplet radius is larger than 5 µm. Convection dominates the energy transport inside the droplet when the radius becomes larger than 200 µm.](image)

To quantitatively evaluate the overall enhancement in heat transfer attributed to convection, we calculated the heat transfer rate and heat flux across the liquid-vapor interface and compared them with results obtained by the pure conduction model. Figure 3.10(a) shows the heat transfer rate $Q$ of a single droplet with a radius from 20 nm to 500 µm at two different subcooling temperatures (1 K and 5 K). Generally, the heat transfer
rate increases with the droplet radius due to the increase of interfacial area to exchange heat, and a larger subcooling temperature always leads to a larger heat transfer rate. For the subcooling temperature of 5 K, the results computed by the pure conduction model coincides with that calculated by the dynamic growth model very well when the radius is smaller than 1 µm as the droplet is in the conduction dominated stage. Differences in the predicted heat transfer rate were observed when the radius is larger than 5 µm (inset of Figure 3.10 (a)), which agrees with the results from the temperature distribution. As expected, the heat transfer rate of the 500 µm radius droplet predicted by the dynamic growth model is much higher than that given by the pure conduction model (0.24 W for dynamic growth model versus 0.05 W for pure conduction model). A similar trend for the heat transfer can be seen when the subcooling temperature decreases to 1 K. The difference between the two models is smaller for a 1 K subcooling compared to a 5 K subcooling because convection effects are weaker at a lower heat flux. The simulation results demonstrate that the traditional conduction-based model underestimates the heat transfer performance of large scale droplets (~100 µm) because the energy transport in such droplets is significant enhanced by convection.

The energy transport can be further interpreted by the average heat flux $q''$ through the contact area. Figure 3.10(b) shows the heat flux varying with the droplet radius at different subcooling temperatures. When the droplet is in the conduction dominated stage, the average heat flux severely degrades at a large radius, because the conductive thermal resistance increases with the growth of droplet. However, when the droplet is in the transition and convection dominated stages, the average heat flux can be steadily maintained at $\sim 4 \times 10^4$ W/m² (for a 5 K subcooling) due to the enhancement of convection. For 500 µm radius droplets, the average heat flux predicted by the dynamic growth model becomes 4.7 times larger than that estimated by its conduction counterpart, indicating the importance of considering convective energy transport for microscale droplets. There is a minimum in heat flux (at $\sim 100$ µm) calculated by the dynamic growth model when the subcooling temperature is 5 K. The minimum appears when the convection inside the droplet develops strong enough to compensate for the loss of heat flux due to the decrease in the effects from conduction. For a 1 K subcooling temperature, as shown in Figure 3.10(a), the general trend of the heat transfer performance varying with the droplet radius is similar to the 5 K subcooling situation. The increase of average heat flux when droplet radius is smaller than 0.1 µm at 1 K subcooling condition shown in Figure 3.10(b) is attributed to the dramatic decrease of the temperature drop associated with the droplet curvature (see Equations. (3.10) and (3.11)).
Figure 3.10. Heat transfer performance predicted by two droplet growth models. (a) Heat transfer rate $Q$ during droplets growth. Inset: the region where the results from two models start to deviate. (b) Average heat flux $q'$ varying with droplet radius. The pure conduction model underestimates the heat transfer when the radius of droplet is larger than 5 $\mu$m. The dynamic growth model predicts 4.7 times enhancement attributed to convection.

We also studied the local effects of convection by calculating the local heat flux across the liquid-vapor interface using different models. Numerical results show that the local effects of convection can be observed when the droplet grows to 5 $\mu$m. The local flux at the top region of the droplet increases due to convection (compared with the pure conduction model), leading to a better predicted heat transfer performance. To quantify the contribution of convective heat transfer at different stages, we calculated the volumetric heat fluxes by conduction and convection, respectively. The contribution of convection increases steadily but conduction decreases as the growth of the droplet.

We have demonstrated the heat transfer modes of condensing droplets in different stages and highlighted the importance of convection to enhance heat transfer of large scale droplets, but the mechanism of convection has not been explained yet. Several possible factors can lead to the convection effects, including interfacial mass flow and continuous growth, the Marangoni effect, gravity driven flow, and the dynamic contact angle.

We first considered the effect of interfacial mass flow and continuous growth. We investigated the interfacial mass flow by evaluating the differences in fluid flow and heat transfer with or without condensing mass on the interface. Since the only difference between the dynamic growth and static convection model is the absence of the interfacial mass flow and corresponding time-dependent growth in the static convection model, the results of the dynamic growth model to that of the static convection model
is compared to understand the role of interfacial mass flow. Figure 4 (a) shows the average heat flux at different radii from the dynamic growth model and the static convection model. The heat fluxes predicted by the two models are almost the same when the radius is smaller than 1 μm, with a relative difference of 0.8% at 1 μm. This result is due to conduction dominating the heat transfer. When the droplet grows to 5 μm, the relative difference in heat flux between the two models is 3.0%. This relative difference is smaller than that between the dynamic growth and pure conduction models, because the convection at this initial stage is beginning to develop slowly and can be treated as a quasi-static state, which is well-described by the static convection model. However, as shown in Figures 4(a) and (b), this discrepancy becomes much larger with droplet growth since the transient effects become important. At a droplet radius of 200 μm, for example, the heat flux from the dynamic growth model is 1.78 times of that from the static growth model, indicating the interfacial mass flow and corresponding dynamic growth are the key factors of the convection dominated stage.

To illustrate the physics between the interfacial mass flow and internal convection in droplets, it is necessary to examine the fluid dynamics during droplet growing. Figure 3.11(c) shows the streamlines of a 200 μm radius droplet. The left side represents the flow field given by the dynamic growth model whereas the right side is the result from the static convection model. For the flow field shown in the left side of Figure 3.11(c), it has been demonstrated that a majority of heat enters the liquid phase from the contact line due to the low thermal resistance. Accordingly, as expressed in Equation (2.15), most of the mass, which carries the heat in phase change, will also flow into the droplet from the contact line. The mass flow not only brings thermal energy but also carries momentum into the liquid phase, which is the source of internal convection. The high flow velocity near the contact line (depicted as the dense streamlines) arises from the high mass flux associated with the high interfacial heat flux. When the mass flow enters the droplets, it has to be redistributed to maintain the spherical shape of the droplets. Here, the driving force of the mass redistribution is the surface tension. Therefore, the incoming mass from the contact line region immediately flows up to ensure uniform expansion of the droplet everywhere along the interface. When the liquid flows along the interface to the top region, it moves reversely to the bottom due to the constraint of the spherical interface. Horizontal flow can be found at the bottom of the droplet to advance the contact line. Consequently, internal circulation driven by the interfacial mass flow develops as shown in Figure 3.11(c). Based on the flow field described above, we can explain the temperature distribution shown in Figure 3.9(a). The elevation of the cold fluid near the contact line is carried by the upwards flow along the interface. The expansion and mixing of the high-temperature fluid at the top center of the droplet arise from the internal circulation. The compressed thin low-temperature layer is attributed to the vertical downwards flow and horizontal flow at the bottom.
Compared to the results from static convection model shown in Figures 3.11(b) and (c), similar flow circulations were found (right side of Figure 3.11(c)), but the circulation direction is opposite to the direction predicted by the dynamic growth model. This is because the circulation occurring in the static droplet is driven by the Marangoni effect rather than interfacial mass flow. Explicitly, the gradient of temperature dependent surface tension drives the liquid near the interface to flow away from the low surface tension regions, i.e., from high-temperature top to low-temperature contact line, to develop a circulation. Thus, the convection effect in the static convection model shown in Figure 3.11(b) can be explained as the cold liquid at the bottom center is carried upwards by the circulation while the hot liquid near the top interface is dragged to the contact line. Since the interfacial mass flow induced circulation can be much stronger than that caused by the Marangoni effect (where the maximum flow velocity is 0.755 m/s for interfacial mass flow compared to the 0.394 m/s with the Marangoni effect at a droplet radius of 200 μm), the interfacial mass flow is the dominant factor responsible for internal convection of the condensing droplet.

Figure 3.11. Comparisons between simulation prediction with (dynamic growth model) and without (static convection model) interfacial mass flow when the subcooling temperature is 5 K. (a) Average heat flux at different droplet radii. (b) Temperature distribution of a 200 μm radius droplet, left side: using the dynamic growth model, and right side: using static convection model. (c) Flow field of 200 μm radius droplet, left side: using the dynamic growth model with maximum flow velocity of 0.755 m/s, and right side: using the static convection model with maximum flow velocity of 0.394 m/s.

As discussed in the last paragraph, the interfacial mass flow and Marangoni flow act in opposing directions on the internal circulation. It is of great interest to study the physics when those two flows coexist in an
individual droplet. For condensing droplets, the temperature gradient along the interface is responsible for
the gradient of surface tension. Figure 3.12 shows the results of the dynamic growth model with and without
including the Marangoni flow function. According to Figure 3.12(a), there are two observations: (1) the
Marangoni effect is significant in the transition stage and then decreases in the convection dominated stage;
(2) the Marangoni effect adversely affects the heat transfer performance. We will explain those two points
in order. The magnitude of Marangoni effect is qualitatively depicted by the Marangoni number given by,

\[
Ma = \frac{-d\sigma R\Delta T}{dT \mu \alpha}
\]

where \(\Delta T\) is the temperature difference along the interface, \(\mu\) is the dynamic viscosity of the liquid and \(\alpha\) is
the thermal diffusivity of the liquid. When the droplet is in the conduction dominated stage \((R < 5 \mu m)\),
both the radius and temperature difference along the interface are small, so the Marangoni effect is
negligible. When the droplet grows to the transition stage \((5 \mu m < R < 200 \mu m)\), both the radius and
temperature difference increase steadily, leading to strong Marangoni effect as shown in Figure 3.12(a).
When the radius increases further \((R > 200 \mu m)\), either the Marangoni induced convection or the interfacial
mass flow induced convection tend to make the temperature along the interface more uniform. The
temperature gradient is only at the contact line. For this reason, the Marangoni effect is only active near the
contact line and the effective temperature difference responsible for the Marangoni effect is small. As a
result, although the radius of the droplet continuously increases, decrease of the effective temperature
difference leads to a weak Marangoni effect in the convection dominated stage.

The adverse effect of Marangoni flow on heat transfer performance can be interpreted by considering the
interaction between the Marangoni flow and interfacial mass flow. As shown in Figure 3.11(c), the direction
of the circulation induced by the Marangoni effect opposes that induced by the interfacial mass flow. When
these two circulations coexist inside the droplets during the transition stage, they can counteract each other.
By comparing the left side (with Marangoni effect) and right side (without Marangoni effect) of Figure
3.12(c), the interfacial mass flow induced circulation is severely weakened by the Marangoni flow near the
interface and is compressed to the bottom region close to the center of the droplet. In such a situation, the
high-temperature liquid at the top of the droplet is not affected by the circulation and the discrete-layer
temperature distribution is still maintained as shown in the left side of Figure 3.12(b). The Marangoni effect
acts as a retardant of the fully expanded circulation and suppresses the interfacial mass flow induced
convection in the transition stage.
Figure 3.12. Comparisons between the dynamic growth model with and without temperature dependent surface tension when the subcooling temperature is 5 K. (a) Average heat flux at different droplets radii. (b) Temperature distribution of a 100 μm radius droplet, left side: with Marangoni effect, and right side: without Marangoni effect. (c) Fluid field of 100 μm radius droplet, left side: results considering Marangoni effect with maximum velocity of 0.764 m/s, and right side: results considering constant surface tension with maximum velocity of 0.769 m/s.

The effect of gravity driven flow was studied by comparing the dynamic growth model with and without gravity. Our results show that gravity has a negligible influence on the energy transport of condensing droplet as the Bond number is very small. The effects of the contact line movement are studied by considering the dynamic contact angle and contact line velocity. The dynamic contact angle is estimated by the following equations [176],

$$Ca = \frac{\mu v_{CL}}{\sigma} \tag{3.17}$$

$$\frac{\cos \theta_0 - \cos \theta}{\cos \theta_0 + 1} = 4.47Ca^{0.42} \tag{3.18}$$

where $Ca$ is the capillary number, and $\theta_0$ is the static contact angle, respectively. The contact line velocity is solved by the proposed dynamic growth model. The maximum contact line velocity is 1385 μm/s at a radius of 39 nm, corresponding to a capillary number $Ca$ of $1.04 \times 10^{-5}$. When the droplet radius is larger than 1 μm, the largest contact line velocity is 509 μm/s, corresponding to a capillary number $Ca$ of $3.83 \times 10^{-6}$. The capillary number is small such that the difference between the dynamic contact angle and static
contact angle is within 1°. Therefore, the effects of the dynamic contact angle on heat transfer through condensing droplet can be neglected.

At this point, we have demonstrated the energy transport process and corresponding mechanisms during the growth of the condensing droplet. To be clear, we summarized the key features regarding the temperature distribution, flow field and heat transfer modes in different stages during droplet growth in Table 3.1.

Table 3.1. Summary of condensing droplet growth

<table>
<thead>
<tr>
<th>Temperature distribution</th>
<th>Stages</th>
<th>Radii</th>
<th>Features</th>
</tr>
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</table>
|                          | Conduction dominant | <~5µm | - Discrete-layer temperature distribution.  
  - Negligible fluid flows  
  - No convection enhancement |
| 60°C                     | Transition | ~5 to 200µm | - Discrete-layer temperature distribution  
  - Strong interaction between Marangoni flow and interfacial mass flow induced circulation  
  - Convection enhanced heat transfer in the center of droplet bottom |
| 55°C                     | Convection dominant | >~200µm | - Uniform temperature at upper part and compressed thin cold fluid layer  
  - Disappearance of Marangoni flow and complete expansion of interfacial mass flow induced circulation to entire droplets  
  - Significant convection enhanced heat transfer in entire droplets |

To determine the condition where the convection effects in the droplet can never be neglected, we performed simulations of condensing droplets with different subcooling temperatures and static contact angles. In this work, we defined the critical radius as the radius of droplet at which the heat transfer rate given by the pure conduction model deviates 5% from that predicted by dynamic growth model. We calculated the critical radius under different conditions.

Figure 3.13 shows the dependence of the critical radius on subcooling temperatures and contact angles. Figure 3.13(a) shows that the critical radius decreases as the subcooling temperature increases because larger heat and mass fluxes enter the droplet driven by the larger temperature difference, leading to stronger convection at an earlier stage. A similar trend can be seen between the critical radius and contact angle
shown in Figure 3.13(b). The significant convection occurring at small droplet radius can be attributed to the small contact area resulting from the large contact angle. For practical considerations, it is of great importance to take the effects of dynamic growth into account especially for large subcooled condensation on a superhydrophobic surface. As shown in Figure 3.13, the critical radius can be as small as 1-2 µm, a scale at which the pure conduction model works well. Our proposed dynamic growth model provides guidelines on scenarios by which transient convection needs to be carefully considered in condensation studies.

In this work, we developed a multi-scale dynamic growth model for condensing droplets which accounts for the continuous growth of droplets from the nucleation size to hundreds of microns. The energy and mass transport process at different length scales during condensation were investigated. The simulations showed internal circulation arises from interfacial mass flow near the contact line and then expands to the entire droplet at the micron size scale. Our dynamic model, which considered the strong convection effect driven by this internal circulation, shows the heat transfer rate of a 500 µm radius droplet is 4.7 times larger than that predicted by the pure conduction model. The complete growth process of a condensing droplet can be classified as three stages, i.e., the conduction dominated, transition, and convection dominated stage. The range of each stage can vary with subcooling temperature and contact angle. We also determined the radius where convection begins to impact the results, which can be as small as 1 µm at a large subcooling and contact angle. By capturing the multi-scale time-dependent condensation process directly, we anticipate
that this model can be used to enhance the understanding of the transient energy transport and thermal-fluidic coupling effects in condensing droplet, as well as to provide design guidelines. This proposed modeling methodology can be either combined with droplet distribution theory to predict the overall heat transfer performance of condensation or further extended to investigate a variety of phase change phenomena such as pool boiling and thin film evaporation.

3.3.2 Using Enhanced ESEM to Study Condensing Droplets Dynamics

Vapor condensation is a common phenomenon in nature and has been widely applied to engineering applications such as power generation [177], energy conversion [153-155], water harvesting [142], anti-frosting [156-158], as well as high heat flux thermal management [154]. A mechanistic understanding of the dynamics of condensing droplets is necessary to advance high-performance phase change technologies. A number of experimental and theoretical efforts have been made to analyze condensation of droplets, among which ESEM has been of particular interest [178].

The unique ability to deal with a wide range of wet and insulated materials in their natural states highlights the significance of ESEM [179-181]. Different from conventional scanning electron microscopy (SEM), ESEM is capable of detecting the secondary and/or backscattered electrons from ionized gas molecules (typically water vapor molecules) around the samples [179]. The charging artifacts arising from nonconductive samples are effectively suppressed by the positive ions accumulating on the sample surface [179]. Consequently, the necessity to maintain a high vacuum environment and coat insulators with a conductive layer is avoided when using ESEM. Thanks to these properties, ESEM can provide physical insights into the phase change of matter [179, 181], and was widely applied to study nano-to-microscale droplet condensation [178].

However, the presence of gas in the ESEM chamber also leads to degradation of image quality. As depicted in Figure 3.14, when the pressure is elevated, incident electrons have a larger possibility to be scattered by gas molecules. This scattering of electrons spreads the focused electron beam (e-beam) outside the area of interest (see the inset of Figure 3.14), thereby degrading the resolution and contrast of images. For this reason, the pressure of an ESEM chamber should be controlled within \(\approx 1000 \text{ Pa}\) in practice [179], which limits the broad application to droplet condensation analysis at high-pressure conditions.
Here, we developed a technique to improve the imaging quality of ESEM, which enables ESEM to be operated at higher pressures up to 2500 Pa. It has been proven that the phase of an optical field is a sensitive agent to image weak perturbation. For this reason, phase probing using either interferometry or depth scanning were extensively used to extract weak signals from noisy background in biological and nanoscale research [108-111]. Similarly, if we consider there is also a “phase” associated with the electron wave, it is reasonable to expect that high contrast information embodied in the phase can be reconstructed. Although the phase of an electron wave is hard to measure directly, it is possible to retrieve the phase from scattering intensity through the transport of intensity equation. If we assume conventional wave interpretation is still valid to describe the behavior of an electron wave, the relation between the phase and intensity of an electron wave is expressed as,

\[ \nabla_{xy}^2 \psi(x, y; z_0) = -k \frac{\partial I(x, y, z)}{\partial z}_{z_0} \] (3.19)

where \( \nabla_{xy} \psi = I \nabla_{xy} \phi \), and \( I \) and \( \phi \) are the two-dimensional intensity and phase of the scattered field at position \( z = z_0 \). Here, the electron wave propagates along \( z \) direction with a wave vector \( k \). Equation (3.19) is a Poisson equation as the right-hand side is known from the intensity field captured by ESEM, and the left-hand side containing the information of phase needs to be solved.

To obtain the phase field, it is necessary to compute the gradient of intensity along the propagation direction. In optical microscopy, the depth scanning technique is typically used to collect the out-of-focus information [139, 140]. In the study of condensing droplets using e-beam, however, the out-of-focus information can...
be directly obtained without moving the sample stage along optical axis. As depicted in Figure 3.14, the focal plane where the e-beam is concentrated on is fixed (see the dashed line of Figure 3.14), but the best focal plane of the droplet (typically crossing the center of the droplet) is rising continuously with the growth of this droplet. Consequently, except for the moment when the best focal plane coincides with the preset focal plane, images captured at any other time intervals are de-focused. As depicted in Figure 3.14, in the droplet coordinate, to construct the gradient field at \( z_0 \), we need out-of-focus information at planes \( z_0 - \Delta z \) and \( z_0 + \Delta z \). It should be noticed that at the moments \( t_0 - \Delta t \) and \( t_0 + \Delta t \), the preset focal plane coincides with planes \( z_0 - \Delta z \) and \( z_0 + \Delta z \) respectively. When the scanning rate of e-beam is much faster than the droplet growth rate, i.e. \( \Delta t \) is small enough that the droplet does not expand too much, the out-of-plane \((z_0 - \Delta z \text{ and } z_0 + \Delta z)\) information at moment \( t_0 \) can be approximated by the images taken at moment \( t_0 - \Delta t \) and \( t_0 + \Delta t \) respectively. Therefore, the correlation between the spatial gradient and the temporal gradient of the intensity field can be formulated as,

\[
\frac{\partial I}{\partial z} \bigg|_{z_0,t_0} = \frac{\partial I}{\partial t} \bigg|_{z_0,t_0} \frac{dt}{dzz} \bigg|_{z_0,t_0} \tag{3.20}
\]

where \( \frac{\partial I}{\partial t} \bigg|_{t_0,z_0} \) can be directly obtained from ESEM images, and \( \frac{dt}{dzz} \bigg|_{t_0,z_0} \) is a term related to the growth of the droplet which acts only as a scaler factor and will not affect the relative strength of the phase signal in each frame. We solved the discretized form of Equation (1) numerically using finite difference method.

To assess our concept, we carried out dropwise condensation experiments in an ESEM chamber. The saturation vapor pressure is maintained at 1000 Pa, 1300 Pa, 1500 Pa, 2000 Pa and 2500 Pa respectively, and the sub-cool temperature is set to 1 K. Figures 3.15 (a) and 3.15(b) show the temporal evolution of growing droplets at 1000 Pa and 2500 Pa respectively. Specifically, the time-lapse images in the first row of Figures 3.15 (a) and 2(b) were directly captured from ESEM, whereas the second row of Figures 3.15(a) and 3.15(b) shows corresponding phase images retrieved from Equation (3.19). Examining the experiment at 1000 Pa is helpful to validate the accuracy of the proposed method, because although the contrast of the raw ESEM images becomes very low at such high pressure, the position and size of droplets can still be observed and compared with corresponding phase images. As depicted in Figure 3.15 (a), phase imaging can precisely recover the size and morphology of each droplet, verifying the viability of this method in quantitative analysis. As expected, the image contrast was significantly improved through phase reconstruction. The background noise is successfully suppressed, and the phase shift arising from wave propagation in the liquid phase can be well retrieved. Additionally, it is of great interest to comment on
some dynamics revealed from phase imaging. Growth of an individual droplet with time (see the white-dashed circles of Figure 3.15(a)) can be measured from the retrieved phase. Coalescence of two droplets (see the yellow-dash circles of Figure 3.15(a)) is also captured. As depicted in the last image of Figure 3.15(a), the size and position distribution of small droplets (< 10 μm in radius), which is difficult to be resolved from raw ESEM images, are extracted from background noises (see the red-dash boxes).

When the chamber pressure increased to 2500 Pa, the large-angle scattering of electrons became so severe that the signal from droplets is completely submerged into background noises (see the raw ESEM images in the first row of Figure 3.15(b)). However, surprisingly, the growth and coalescence of multi-droplets can still be seen from the retrieved phase images (see the red-dashed boxes in Figure 3.15(b)). Some detailed information about droplets interactions are revealed. For example, in the red-dashed boxes of Figure 3.15(b), there are two droplets growing initially (from t = 10 s to t = 12 s), and then three more droplets close to those two droplets start to grow at t = 12 s. These five droplets located at the upper side of the images begin to interact with adjacent droplets at t = 23 s. In the moment of t = 35 s, the interfaces of three droplets (two close to the upper boundary and the other one at the center of the red-dash box) approach each other and merge into one larger droplet at t = 52 s.
Figure 3.15. ESEM and corresponding phase images of condensing droplets at (a) 1000 Pa and (b) 2500 Pa respectively. Droplets condense on a smooth silicon wafer coated with 137 nm of Teflon AF with an advancing contact angle of 115.5°. The first row of (a) and (b) depicts the time-lapse ESEM images during droplets condensation. The droplet dynamics, including the growth of single droplet (see the white-dash circles) and droplets coalescence (see the yellow-dash circles) are clearly resolved from the phase images shown in the second row of (a). Distribution of tiny droplets (see the red-dash boxes in the second row of (a)) and droplet interaction at high-pressures (see the red-dash boxes in the second row of (b)) can also be retrieved through phase imaging. (c) Normalized intensity (from raw ESEM images) and (d) phase (from transport of intensity
equation) distribution along the white dashed-line (1) and (2) respectively. The white-dashed lines shown in (a) pass through the center of a droplet (≈ 20 μm in diameter). The diameter of this droplet cannot be determined from the intensity distribution due to high noise level, but it can be estimated from the phase distribution (see the blue band with strong phase signal).

It is worthwhile to comment on the necessity to image the phase in droplet analysis. We show the intensity and retrieved phase distribution along a line (see lines (1) and (2) in Figure 3.15(a)) crossing the center of a droplet in Figures 3.15(c) and 3.15(d) respectively. As seen from Figure 2(c), the strength of the intensity signal from the droplet is comparable to the amplitude of the background noise level. Although the droplet can be seen from the intensity image (Figure 3.15(a)), it is difficult to distinguish the droplet from the intensity distribution along a single cutline. However, on the contrary, a strong phase signal is found in Figure 3.15(d), which shows the position and size of corresponding droplet. Specifically, the position of the droplet can be estimated by the center of the peak and the size is determined from the width of the peak (see the blue band in Figure 3.15(d) which indicates the diameter of this droplet is ≈ 20 μm). Therefore, counting a large number of droplets as well as measuring their spatial and size distribution can be rapidly achieved by fitting the peaks using a computer program, which cannot be realized from previous ESEM raw images. The practical significance in computer-aided analysis of droplets with this proposed method is demonstrated.

To quantitatively analyze the enhancement in image quality, we compared the contrast of ESEM raw images and corresponding phase images at different chamber pressures. The image contrast in this study is defined as the strength of the peak signal from a droplet over the amplitude of background noise, which can be expressed as,

$$\gamma = \frac{I_p}{\text{max}(I_b) - \text{min}(I_b)}$$  \hspace{1cm} (3.21)

where $I_p$ is the peak signal from a droplet, and $I_b$ is the distribution of the background signal along a reference line. In our computation, we chose a line crossing the center of one droplet (such as dashed line (1) in Figure 3.15(a)) to obtain the peak signal and picked another line as a background reference to calculate the amplitude of noise where there are no droplets. As the situation can be quite different in different images and droplets, the image contrast varies even at the same pressure. We considered the first several frames after the first condensing droplet was observed and averaged the image contrast over different droplets. Figure 3.16 shows the image contrast of ESEM and reconstructed phase varies with
chamber pressure. The image contrast of ESEM always stays at about 1 with small uncertainties, demonstrating the peak signal from droplets is comparable to background noises according to Equation (3.21). The contrast of image can be improved up to about six times through phase reconstruction at 1000 Pa. The contrast of phase decays with pressure rapidly due to electron scattering and falls to about 2 at 2500 Pa. The uncertainty of phase contrast is generally high, because of the choice of different droplets and reference lines in our calculation.

![Graph showing image contrast vs. chamber pressure](image)

*Figure 3.16. A comparison of ESEM and corresponding phase image contrast at different pressure conditions. The contrast of ESEM raw image remains at about 1 steadily, indicating the peak signal is comparable to the amplitude of noise. The image contrast is significantly improved though phase retrieval, which decays as the increase of pressure. The error bar arises from the standard deviation of multiple measurements on different droplets and images at the same pressure.*

We next applied this enhanced ESEM to understand the growth dynamics of condensing droplets. Figure 3.17 shows the growth of individual droplet with different sub-cool temperatures at 1400 Pa. The radius of droplets was measured from the retrieved phase images. The droplet grows almost linearly with time when the radius ranges from 10 μm to 50 μm and has larger growth rate at higher sub-cool temperature. To support our measurements of the droplet radius, we compared experimental results with the time-dependent dynamic growth model (see section 3.3.1 for details of the dynamic growth model). As depicted in Figure 4, simulation results show good agreement with experiments, which proves the capability of our method in droplets analysis.
Figure 3.17. ESEM experimental validation of numerical results of single droplet growth at 1 K and 5 K subcooling temperatures. Temporal evolution of droplet radius on a smooth silicon wafer coated with 137 nm thick teflon AF at 1400 Pa. Inset: Schematic of the droplet morphology. The error bars in the experimental data account for the resolution of ESEM images, as well as the uncertainty from averaging the sizes of five individual droplets.

In summary, we presented an approach to enhance the quality of ESEM imaging for condensing droplets analysis. We extended the concept of phase to e-beam imaging and demonstrated its sensitivity. We retrieved the phase of the electron wave by solving the transport of intensity numerically. We carried out a proof-of-concept study with droplet condensation in high-pressure environments, at which the noise of conventional ESEM becomes comparable to the signal of droplets. Experimental results show that this enhanced ESEM can extend the pressure limit up to 2500 Pa, which doubles the performance of conventional ESEM without any technical changes in the experimental setup. Thanks to the improvement of image contrast, dynamics including droplet growth and coalescence is clearly extracted from low contrast intensity images and computer-aid analysis on large numbers of droplets becomes possible. Finally, we applied this enhanced ESEM to analyze the effect of subcool temperature on individual droplet growth. Experimental results show good agreement with theory. Our study suggests a new direction to interpret ESEM images through phase reconstruction and shows its capability for analyzing droplet condensation. We anticipate the enhanced understanding to phase imaging will be helpful for fully quantitative analysis of e-beam based microscopy. Additionally, the device-level innovation in electron microscopy for direct phase measurement might also be promising for high sensitivity e-beam probing.
4. Discussions: Future Directions

4.1 FUTURE POSSIBILITY FOR RAMAN THERMOMETRY IN HEAT TRANSFER RESEARCH

In this section, we discuss the future directions of Raman spectroscopy in nanoscale heat transfer. Although we have shown the capability of using gold-silicon nano-Raman sensor to realize in situ nanoscale temperature measurement, the application still relies on accurately positioning the nano-Raman sensor. Instead, the temperature mapping using nano-Raman sensor is still restricted by the diffraction limit, which limits the broader application of this technique. For these reasons, direct nanoscale temperature probe is of great interests. The scanning probe microscopy (SPM) technique, which uses nanoscale physical probe to scan the sample surface, has been widely used to image a variety of nanoscale events. Typical SPM applications include scanning tunneling microscopy (STM), atomic force microscopy (AFM) and optical scanning probe microscopy. In Raman spectroscopy application, the SPM technique named tip enhanced Raman spectroscopy (TERS) has been widely used. As shown in Figure 4.1, a nanoscale metallic tip is placed very close to the sample surface, which acts as a scanning probe. The laser excitation is focused on the tip to excite SPR. It has been reported the enhanced electric field can be confined within a ~10 nm diameter spot [182]. This highly localized field near the sample can excite strong Raman scattering which is then collected by the detector. Although the TERS has widely been used as a nanoscale Raman imaging technique for biological researches and material science, seldom research efforts were found to use the TERS as thermometry. Yue et al. presented a temperature measurement on silicon wafer, which was heated by the probe laser using TERS which achieved sub-10 nm resolution. This experimental work shows great potential of using TERS to realize nanoscale thermometry. Therefore, one possible future direction is to develop nano-Raman based on TERS technique. The key challenging is to remove the heating effect brought by the enhanced field.
4.2 FUTURE POSSIBILITIES FOR PHASE IMAGING IN NANOSCALE FEATURES INSPECTION

In this section, we discuss some possible directions of phase imaging in nanoscale detection. The phase imaging technique which was discussed in this thesis is based on the paraxial approximation. However, this approximation is not valid when the NA of the imaging system is larger than 0.5. To perform quantitative phase imaging for high NA system, the paraxial approximation should be removed. For this reason, one possible direction is to develop the non-paraxial transport of intensity equation which will be discussed in section 4.2.1. On the other hand, although the sensitivity of phase imaging has been demonstrated in this work, the resolution and sectioning ability of the phase have not been well understood before. Compared to conventional imaging technique, we need both in-focus and out-of-focus intensity field to image the phase, which means more information will be included. Therefore, it is worthy to consider whether the phase imaging can have better resolution or sectioning ability than the conventional imaging techniques.

4.2.1 Non-paraxial Transport of Intensity Method

In this section, we present the preliminary investigations in the phase retrieval method using non-paraxial transport of intensity equation (TIE). This proposed method is capable of retrieving the phase from high numerical aperture (NA) imaging system, by eliminating the constraint of paraxial approximation, which is commonly made in traditional TIE method. To prove this concept, we simulated the image field of a red
blood cell (RBC) and retrieved the phase image from simulated intensity using the reported method. By comparing the retrieved phase with the actual simulated phase, the performance of this non-paraxial TIE method is well demonstrated.

The traditional TIE can be derived from the transport equation by assuming paraxial propagation of incident and scattered light. The transport equation governed by conservation of energy is obtained from Helmholtz equation. The transport equation is given by,

$$\nabla^2 \psi = 0$$  \hspace{1cm} (4.1)

where $\nabla \psi = I \nabla \phi$. $I$ and $\phi$ are the intensity and phase of the wave respectively. Assume the incident wave propagates alone the $z$ axis. Without losing generality, we start from the transport equation (4.1). The phase term can be expressed as,

$$\phi = k z + \phi'.$$  \hspace{1cm} (4.2)

Mathematically, any function $\phi$ can be expressed as Equation (4.2). However, in some special cases, for example, if we assume the illumination is a plane wave propagating along z axis, the first term in Equation (4.2) represents the “bulk phase delay” due to free space propagation of incident light. The second term shows the perturbation arising from weak scattering from the object. Plug Equation (4.2) in to Equation (4.1), the transport equation can be simplified as,

$$\nabla^2 \psi' = -k \frac{\partial I}{\partial z},$$  \hspace{1cm} (4.3)

where $\psi'$ is defined as $\nabla \psi' = I \nabla \phi'$. Equation (4.3) is a three-dimension Poison equation without the paraxial approximation. Still, the RHS is directly obtained from imaging system, and the perturbed phase is reconstructed by solving Equation (4.3).

To solve Equation (4.3), boundary conditions are needed. It is reasonable to apply periodic boundary condition on the walls parallel to the optical axis if the size of the image is much larger than the object (which is often true). For the front and back walls perpendicular to the optical axis, the periodic boundary for phase is no longer valid due to the “bulk phase delay” of free space propagation. However, by decoupling the “bulk phase delay” $kz$ term from total phase change as shown in Equation (4.2), the
periodicity can be held by the perturbed phase $\phi'$, if (1) these two wall are symmetric with respect to the image focal plane and (2) weak scattering, i.e., $\phi' \ll k z$ is assumed. Therefore, periodic boundary condition is assumed for all boundaries when solving Equation (4.3). Consider the periodic boundary, we use fast Fourier transform (FFT) to solve the Equation (4.3) in this work.

To validate the proposed non-paraxial phase retrieval method, a simulation of RBC is carried out. As shown in Figure 4.2, there is a plane wave illumination $U_0(r)$ propagating in a uniform media (water) with index of refraction $n_m (=1.332)$ from the left to the right. The incident light is scattered by the RBC with refractive index of $n (=1.397)$. The total scattered field $U(r)$ is then collected by an optical imaging system with $NA = 1.2$, and finally an image field $U_i(r)$ is formed at the right hand side. Both incident and total scattered field are described by Helmholtz equation as,

$$\nabla^2 U_0(r) + n_m^2 k_0^2 U_0(r) = 0,$$  \hspace{1cm} (4.4)

and,

$$\nabla^2 U(r) + n^2(r) k_0^2 U(r) = 0$$  \hspace{1cm} (4.5)

where $k_0 = \omega/c_0$ is the wave vector in vacuum. As the refractive index of medium (water) is closed to the object (RBC), we apply the weak scattering assumption and pick the first order term from the scattering series. The total scattering field, as a result, is expressed as $U(r) = U_0(r) + U_s(r)$ and $U_s(r)$ is the first order weak scattering term. We assume on-axis plane wave illumination $U_0 = \exp(i \beta z)$. Comparing Equation (4.4) with Equation (4.5) and defining scattering potential $\chi(r) = n(r)^2 - n_m^2$, we have following equation expressing the first order scattered field as,

$$\nabla^2 U_s(r) + n_m^2 k_0^2 U_s(r) = -k_0^2 \chi(r) \exp(i \beta z).$$  \hspace{1cm} (4.6)

The total scatted field $U(r)$ is computed from Equation (4.6) and the image field $U_i(r)$ is then constructed according to the scatted field using propagation theory.
According to the simulation, we can extract the physical phase field around the RBC after scattering. We can also have the intensity of image field. We solve the phase by putting the intensity of the image into non-paraxial TIE. We compare the retrieved phase with the physical phase directly obtained from simulation. Figure 4.3 shows the comparison between paraxial TIE retrieved phase image (Figure 4.3 (a)), non-paraxial TIE retrieved phase (Figure 4.3 (b)) as well as physical phase (Figure 4.3 (c)). All the images are normalized by the maximum phase. It can be observed that phase retrieved from non-paraxial TIE agrees with the physical phase much better than that retrieved from tradition TIE. To be clear, we plot the cross section of the phase images along the center line as shown in Figure 4.3 (d). A large mismatch can be seen when comparing the results retrieved from paraxial TIE and physical phase, indicating the tradition TIE is not valid any more for high NA imaging condition. Phase retrieved by the proposed method provides quantitative agreement with physical phase. The only discrepancy occurs at the center because the NA of the imaging system is not high enough to capture all the large-angle scattering arising from large curvature of RBC at the center. In addition, it is of great interest to comment on the difference between intensity image and phase image by comparing Figure 4.3 (e) with Figure 4.3 (b). The intensity image of RBC has very low contrast because the RBC has high transmission. However, high contrast image is obtained from phase retrieval as the phase is very sensitive to the change of refractive index and geometrical profile of materials. For this reason, phase image is of great importance in visualizing transparent (typically biological) materials in practice.
4.2.2 Comprehensive Investigation on the Resolution, Sensitivity and Sectioning Ability of Transport of Intensity Method

In classic optics, the resolution of image was defined by the size of the diffraction spot in the intensity field. However, this definition of resolution based on intensity distribution might not be valid in the phase field. Additionally, we have shown the capability of phase imaging in detecting nanoscale features and attributed this to the high sensitivity of phase. However, the nanoscale detection ability could also be arising from the improvement of resolution using phase imaging. Therefore, more theoretical analysis should be carried out to understand the resolution of phase image. As the phase imaging relies on depth scanning experiment with small scanning step, the effect of the out-of-focus noise can be effectively removed from phase imaging. For this reason, the sectioning ability of phase imaging might be higher than that of the conventional intensity imaging. If this hypothesis is valid, this computational phase imaging technique will have comparable sectioning performance with the confocal microscopy.
Chapter 5

5. Conclusions

This master thesis has made a number of contributions in the field of Raman spectroscopy, phase imaging and their application in micro-to-nanoscale heat transfer. The major contribution of this work is to present the great potential of Raman spectroscopy in thermal characterization of solid-state materials, phase change heat transfer and nanoscale temperature measurement. Specifically, we provided theoretical frameworks in predicting the dependence of Raman peak positions on multiphysics based on the symmetry of the crystal structures and demonstrated the experimental techniques of measuring the multiphysics and thermophysical properties of semiconductor materials. We developed micro-Raman experimental setup integrated with phase change and radiative heat transfer to measure the temperature rise during thin film evaporation and in the silica aerogel. Finally, the concept of using gold-silicon nano-Raman sensor to realize nanoscale temperature probe was demonstrated. In this thesis, we also explored the possibility of using phase imaging to realize nanoscale detection. We developed a phase imaging technique using transport of intensity equation which has nanoscale sensitivity. The capability of the phase imaging technique was proven by inspecting the deep-subwavelength defect on 9 nm semiconductor wafers. Finally, this developed technique was used to improve the image quality of environmental scanning electron microscopy and study the droplets dynamics during condensation. We anticipate the developed techniques in this thesis will inspire more research efforts in the multidisciplinary field of using micro-Raman spectroscopy and phase imaging for micro-to-nanoscale heat transfer.
6. Bibliography


