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Advances in infrared GRIN: a review of novel materials towards components and devices

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ABSTRACT

Novel optical materials capable of advanced functionality in the infrared will enable optical designs that can offer light-weight or small footprint solutions in both planar and bulk optical systems. UCF's *Glass Processing and Characterization Laboratory (GPCL)* with our collaborators have been evaluating compositional design and processing protocols for both bulk and film strategies employing multi-component chalcogenide glasses (ChGs). These materials can be processed with broad compositional flexibility that allows tailoring of their transmission window, physical and optical properties, which allows them to be engineered for compatibility with other homogeneous amorphous or crystalline optical components. This paper reviews progress in forming ChG-based GRIN materials from diverse processing methodologies, including solution-derived ChG layers, poled ChGs with gradient compositional and surface reactivity behavior, nanocomposite bulk ChGs and glass ceramics, and meta-lens structures realized through multiphoton lithography (MPL).

Keywords: chalcogenide glass, GRIN, multiphoton lithography, poled chalcogenide glass, optical nanocomposites, glass ceramics, integrated photonics

1. INTRODUCTION

Multi-component chalcogenide glass (ChG) compounds suitable for use in planar or bulk form have been prepared with the goal of creating advanced optical functionality beyond those of currently available materials. Recent advances have demonstrated the ability to compositionally tune not only optical properties (spectral window, coefficient of thermal expansion (CTE), refractive index, dispersion, dn/dT [1-6]) but also properties important to their bulk, planar or fiber optical fabrication (such as thermal and chemical stability [7-9], microhardness, toughness, post-molding relaxation behavior [10-12], compatibility with AR coating protocols [13]). Some of these attributes are especially important if the material is to be deployed in planar photonic systems where stability (to thermal decomposition, phase separation, scattering) can define suitability or limit the material's use in an optical design. Over the past decade, CREOL's *Glass Processing and Characterization Laboratory* (GPCL) team members and our collaborators, have made notable advances in developing new material systems, demonstrating they can be scaled up beyond the laboratory scale with commercial

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partners [14], and most importantly, highlighting the flexibility in optical function enabled by the creation of low loss, manufacturing-process compatible compositions [15]. These compositions and their applications are presented and reviewed here, with the key aspects and suitability for diverse use environments, highlighted. Most specifically, examples whereby this process know-how has been applied to the creation of gradient refractive index (GRIN) applications in the infrared (IR) spectral window are discussed. We include for completeness of our review, reference to other advances in materials for IR GRIN. High-level details related to composition, process methodology and optical performance flexibility along with fabrication limitations based are presented.

2. IR GRIN MATERIALS

Over the course of the last decade, advances in materials research resulting in gradients in refractive index (GRIN) as well as gradients in other physical properties, have been extended to the infrared. These materials are attractive in areas such as color- or aberration correction and offer possible advantages as compared to other diffractive or refractive optical approaches [16]. Strategies developed for visible materials (glasses and polymers) such as ion exchange and lamination/inter-diffusion [17-24] have been attempted in the infrared with varying levels of success. These technologies differ in their approaches and compatibility to large scale manufacturability and are at varying levels of progress towards commercialization. Clearly, the interest in developing next generation devices for commercial or defense applications will benefit from an ability to integrate optical function into smaller, more compact packages. This process, enhancing SWAP (size, weight and performance/power) is the goal towards making lighter weight, smaller footprint systems. Most activities to date are examining use of GRIN materials for passive (un-doped) applications such as lenses or windows that do not require high (laser) power transmission where it is known that ChGs (typically evaluated in fiber form) do not perform well due to modest laser damage resistance and high optical nonlinearities [25-31].

Development of promising candidate materials and technologies in the infrared have been limited, but have seen recent interest from funding agencies and programs (such as DARPA's M-GRIN program) which ran from 2010-2016 [32]). However, many advances that resulted from this program remain at the laboratory-scale, or have advanced to prototype level in their production, still awaiting further investment for design-specific development. That said, such technologies are aggressively sought after, as legacy crystalline materials cannot easily be manipulated in the same way that glass and glass ceramic materials can, to offer tailorable/tunable optical properties. Following a short summary of the state of the art, we discuss some of the key attributes and possible limitations of ChG-based GRIN material investigated by our team. Highlighted are key areas where these materials could benefit with further improvements possible with additional development.

Table 1 reviews the current state of the art for IR GRIN, and summarizes each technology's suitability to bulk and/or planar applications. Not discussed here but contained in the references shown are specifics as to the gradient in refractive index and dispersion, over defined spectral ranges. As is known, precise design tools and characterization methodologies for GRIN materials in the infrared are a technical challenge as metrology tools for this spectral region have often not been optimized for such components [33,34]. Included are key attributes that define possible limitations or opportunities unique to the technologies. Here, data is reported based on published aspects/values of performance for comparison.

Table 1. Infrared gradient refractive index (GRIN) technologies, attributes and possible limitations or opportunities.

Technology: ***B- Bulk or P-Planar***	**Key material and manufacturability attributes**	**Possible Limitations or Opportunities**	**Reference**
B: Laminated/inter-diffused chalcogenide glasses	Multi-component/index materials are laminated and thermal inter-diffusion results in a composition and refractive index profile associated with chemical mixing of glass constituents; no hard interface results; axial index modifications to $\Delta n=+0.4$ (as measured in the NIR) have been demonstrated.	*Arbitrary* 3-D profiles may not be possible due to intrinsic shape of diffusion profiles; stacking (for axial GRIN) is much easier than rod-in-tube for radial GRIN designs; post-diffusion molding (slumping) could be used to further change the bulk optic's shape and performance.	[35-38]
B: Thermally Poled-diffractive or refractive optics	Mobile ion-containing bulk glass is subjected to a thermal poling process (applied electric field and temperatures near T_g) to create a composition gradient between electrodes; electrode patterning imparts gradient to composition profile with arbitrary shape (grating, micro-lens, etc) without transmission degradation. Index changes (Δn) to +0.05 in ChG shown with long-lived (>1.5 year) stability.	Index modification occurs within near-surface anode region (typically 5 - 10 μm) within the volume; difficult to realize 2π phase shift. Same mechanism (space charge formation with ion migration) leads to creation of a $\chi 2$ and measurable second harmonic generation (SHG) within the amorphous glass. Surfaces are flat (< 100 nm RMS roughening)	[39,40]
B and P: Thermally-induced (furnace or laser-induced) crystallization to form glass ceramics	Glasses (wide composition space available) which can undergo spatially-controlled nucleation and growth result in formation of a high index, nanocrystalline phase within a low(er) index glassy matrix; Gradient in volume fraction of crystallite leads to an effective refractive index change related to the volume fraction of crystal and its identify (refractive index). Nanocomposite GRIN structures (radial and/or axial) can be formed within a (linear) thermal gradient, via spatially-defined nucleation and homogeneous (temperature) growth, or through homogeneous nucleation and spatially varying (laser-induced) growth.	Initial material must be low loss (high optical homogeneity) to realize index modification beyond that of base material. Formation of a glass ceramic results in intermediate thermal/mechanical properties. Tailoring the crystal phase (and its index) as well as the volume fraction defines the magnitude of index change (Δn); observed Δn is base composition dependent but ranges to ~ 0.2 in the MWIR/LWIR. 2π phase shift possible with high index base glass and large (film or bulk layer) thickness. Thick films must be CTE matched to substrate to avoid delamination.	[41-43]
B and P: Laser-induced vitrification (LIV)	Glasses which have undergone controlled crystallization (nanocrystalline phase formation) are subjected to direct laser writing (DLW) which under specific irradiation conditions, leads to re-amorphization; return of localized regions to the glassy state leads to patterns of index variation.	Laser writing parameters are material specific. Within bulk or near-surface re-amorphization is possible. Correlation of loss levels to irradiation conditions have not to date been optimized for all materials studied; diffractive elements have been fabrication but efficiency has not been quantified.	[42,44,45]
P: Solution-derived (SD) printing	ChG powder dissolved in amine solutions are 'inks' which can be 'printed' onto substrates via spin coating (for axial GRIN) or via electrospray (for arbitrary film profile GRIN). Index profile limited by parent glass index and ability to coat to desired thickness	Intermediate ChG layers must be heat treated to remove IR absorbing solvent; adjacent layer must not be soluble in target layer solvent; solvent choice, heat treatment protocol and solution viscosity requires optimization for optical quality film formation;	[46]
P: Chemical Vapor Deposition (CVD)	Layer-by-layer deposition process (with varying gas fractions) creates refractive index variation proportional to fraction of parent crystal phase in an IR transmissive multiphase polycrystalline material. Processing resulted in thick films (up to) t ~ 4 mm thick with a Δn ranging from 0.2 - 0.6 (measured at $\lambda = 0.647$ μm).	CVD co-deposition of ZnS and ZnSe to form a ZnSSe material with a near-linear axial gradient. Physical property variation observed, with hardness (related to grain size), intermediate between the two end-points. Transmission was inferior to parent crystalline end points (ZnS and ZnSe) but improved following hot isostatic press (HIP) processing.	[18]
P: Laser induced photo-polymerization	Photo-sensitive ChGs (select compositions) are exposed to near-bandgap light inducing modification to cross-linking within glass film network. This enables etch selectivity between exposed and unexposed regions.	Limited to ChG compositions which possess bonds that can undergo spatially-selective cross-linking (or de-polymerization) upon exposure enabling patterning which becomes etch selective. Post-exposure pattern fidelity stability is composition specific.	[47-49]

Specific attributes of key technologies developed by GPCL team members and collaborators are discussed in more detail below.

2.1 Bulk GRIN materials

2.1.1 GRIN by thermal poling

Thermal poling of glass is a technology that has been known since the early 1990's [50-52]. The process involves the application of an electric field across a specimen held at high temperature whereby mobile ions in the glass, usually alkali ions, can migrate in directions related to the induced field lines through the glass volume. This migration leads to the establishment of not only a localized depletion of alkali species, but the freezing in of an induced space charge. The structural re-organization of the poled glass leads to the formation of a material that is not only chemically modified, but also modified in its linear and nonlinear optical properties. Whether this re-organization and the physical properties it imparts to the post-poled material is permanent or prone to relaxation, depends on how the now moved mobile cation can be 'stabilized' or locked in, to the now 'modified' glass structure.

Thermal poling of ChG materials has been known since the late 1990's as a means to induce optical property modification [53,54] but has suffered from short term stability due to the low glass transition temperatures of these glasses and the relaxation of the post-poled structure with time, when aged near room temperature. Recently, we have demonstrated the ability to engineer the parent glass' network structure to enable long-lived post-poling induced index change with tailorable magnitude and gradient shape through a nanoimprinting process [55]. This result enables the use of surface-modified bulk chalcogenide glasses as well as a variety of oxide glasses [55-60] to realize induced second harmonic generation (SHG), linear refractive index changes, as well as modification to surface chemical reactivity.

Poling induces changes in physical properties to the local glass network, as shown in a sample specification sheet compiled for one glass composition following a specific (singular) set of poling conditions [Fig. 1]. Not discussed here, is that these conditions can be varied to change the shape of the post-poled alkali ion compositional profile, as well as the gradient in physical properties that results from the poling properties. Key attributes for the modification correlate with a partial depletion of mobile alkali ions from the anode surface which can be quantified through secondary ion mass spectrometry (SIMS) analysis (as shown in Fig. 2a). Figure 2b illustrates the optical transmission of the material through the infrared. Most impressive is the fact that through compositional tuning of the parent glass believed to yield defective bonding configurations with a net negative charge, these species serve to stabilize the post-poling mobility of the Na^+ thereby 'locking in' the induced properties over time. This provides needed charge compensation to the network and allows the resulting compositional gradient to be stable. The gradient in composition translates to a refractive index gradient which varies with the magnitude of alkali ion doping level, but is long-lived upon aging at room temperature. The induced Δn is stable over temperature excursions (-40 - +80°C). By patterning the electrode associated with the poling process (i.e., to form circles or lines), this compositional profile can be imparted with shapes (i.e., microlenses or gratings) that can imprint optical function into the glass surface. The magnitude and gradient shape of the refractive index profile can be changed with variation in the electrode pattern shape and size. Shown in Fig. 3a, is the measured refractive index stability (at λ = 4.5 μm) in a sample poled with unpatterned, homogeneous ITO anode and cathode coatings. As can be seen, the stability imparted by the compositional tailoring of the glass matrix leads to formation of a robust, index gradient. This can be used to create spatially varying composition and index gradients as shown for the micro-lens array (MLA) depicted in Fig. 3b.

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ChG μ-GRIN3

(B3-P6) is a broadband chalcogenide glass (ChG) that when thermally poled results in a compositional modification that yields a stable (> 6 mo @ RT) local refractive index change. By controlling the gradient of refractive index, micro-optics can be created with geometrically specific profiles, on-demand. The glass has properties and manufacturing behavior similar to other commercially available chalcogenide glass materials.

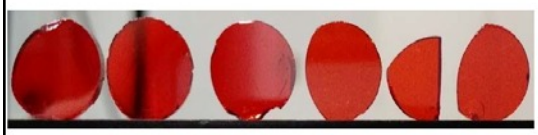
Product Information

The melting process involves heating the glass through a melting/homogenization protocol, followed by a controlled cooling to the quenching temperature to minimize inhomogeneity within the glass. The glass was then finely annealed to ensure refractive index homogeneity. The mass of the melt was 30 grams. The diameter of the bulk sample was 10 mm. Composition reported as batched unless marked as "Measured".

Special Symbols and Measurement Information

Density is determined by Archimedes method at room temperature. Specific heat and thermal conductivity are determined (at 24°C) by the transient planar method. Transition temperature (T_g) and crystallization onset (T_x) measured by DSC (rate 10°C /min). Hardness measured with load of 100mN. Refractive index and dn/dT measured at wavelength shown using an infrared prism coupler at 30°C unless otherwise noted. Thickness of the GRIN layer measured by SIMS.

* values defined by poling conditions used



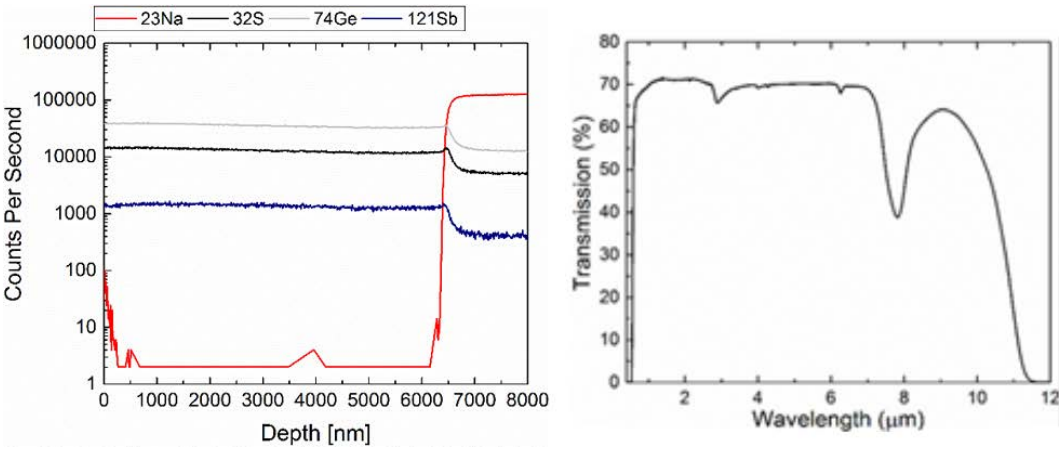
Picture of representative samples (diameter of discs ~ 10mm)

Product-specific properties

As-Batched Composition	GeSbS - 3 mol% Na_2S
Density	3.059 ± 0.009 g/cm^3
Thermal Expansion	---
Specific Heat	0.407 ± 0.01 J/gK
Thermal Conductivity	0.275 ± 0.0032 W/mK
Transition Temperature	264°C
Crystallization Temperature [peak]	490°C
Hardness (Vickers)	2032 ± 32 MPa
Dispersion	*Abbe number:* SWIR: 84 MWIR: 133 LWIR: 21
Refractive index homogeneity of base glass (at 4.5 μm)	$\pm 4.10^{-4}$
Refractive index change induced by thermal poling * (measured at 4.5 μm)	-0.046
Thickness of the GRIN layer (SIMS) *	t ≈ 6.5 μm
Thermal Change dn/dT	*Measurement in process*
@ λ = 4.515 μm;	---
ΔT = X°C (30-90°C)	*To be defined*
Transmission window	0.6 – 10 μm

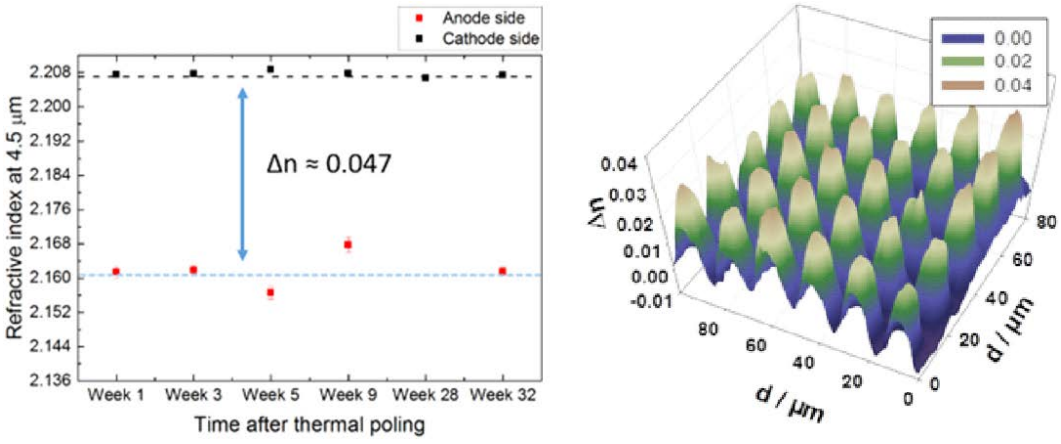
μm	Transmission %	Index
0.98	72	2.2629
1.88	72	2.225
2.9	67	2.2155
4.515	72	2.2089
7.968	42	2.1879
9.294	66	2.1756

Figure 1. Sample specification sheet for ChG μ-GRIN3 GeSbS (3 mol% Na_2S) glass summarizing characteristic material properties



(a) (b)

Figure 2. (a) SIMS profile of the compositional variation induced by thermal poling. The signal decrease of Ge, Sb and S at t = 6.5 μm is due to charging of the sample during the measurement, but illustrates the near-surface depletion of Na after poling. (b) Transmission spectrum (not corrected for Fresnel loss); sample thickness = 1.04 mm, sample diameter = 10 mm (as shown in figure 1 above).



(a) (b)

Figure 3. (a) post-poling refractive index stability measured over 32 weeks. The observed stability has now been documented beyond 1.5 years with no degradation to the magnitude of the compositional and refractive index change (Δn), or the material's surface quality. (b) Qualitative measurements of the Δn profile of a μ-lens array (MLA), using phase imaging (Phasics SID4BIO) on B-3_P glass. Target dimensions of the MLA's pitch was ~ 17 μm.

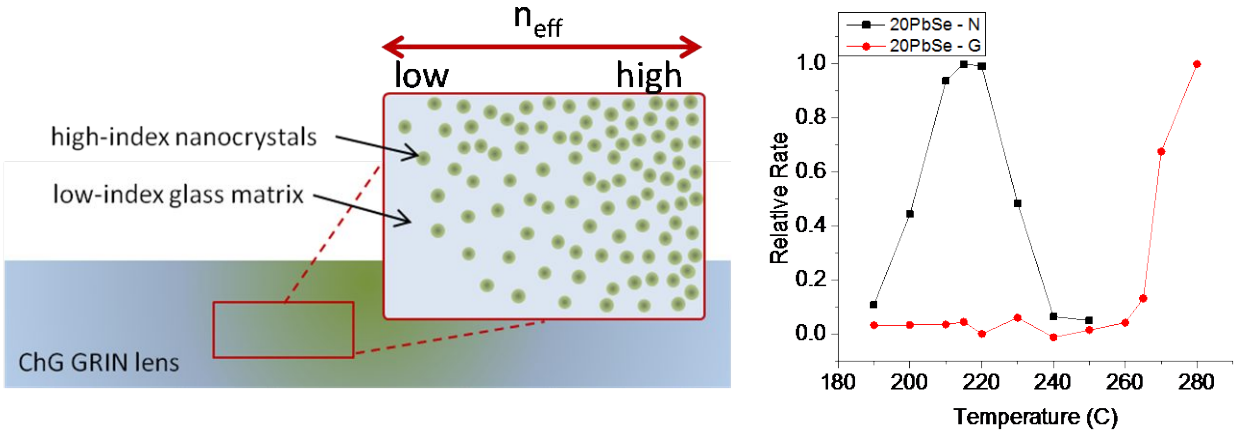
2.1.2 Nanocomposite (glass ceramics) via spatially controlled nucleation and growth

As part of DARPA's MGRIN program initiated in 2010 and introduced by the Penn State-led team in our first presentation made at SPIE in 2016 [61], we have demonstrated the ability to compositionally tailor multi-component chalcogenide glasses (ChGs) to create multiple glasses with varying refractive indices which are amenable to controlled nucleation and growth of high index crystals within a low index matrix to create optical nanocomposites. The DARPA funded effort has focused on optimization of a $GeSe_2$ – As_2Se_3 – PbSe (GAP-Se) glass material for use in the mid-infrared (MIR).

Creation of an effective index, approximated by the refractive indices (n) and volume fractions (V) of the glass and crystalline phases, respectively, as shown in equation 1:

$$n_{eff} \approx (V_{glass})(n_{glass}) + (V_{crystal})(n_{crystal}) \quad (1)$$

suggests that by simply controlling the volume fraction of the respective phase(s) in the monolithic solid, it's refractive index can be modified, to realize an effective refractive index, n_{eff}. If the secondary (crystalline) phase(s) have a higher index than the initial parent glass phase, this results in an increase in index. Controlling the spatial distribution of the nanocrystalline particles as depicted in the illustration shown in Fig. 4a along with strict control of their size and absorption, one can create a low loss optical nanocomposite. Such control over the desired low loss crystalline phase requires knowledge of the crystal phase's nucleation rate (I) and growth rate (U) behavior, as illustrated in Fig. 4b for a 20 mol% PbSe material. Knowledge of each glass' I-U behavior, discussed in detail for small experimental melts [62] and as a function of melt size [43], is critical to selecting an optimal time and temperature to create the desired crystalline phase.

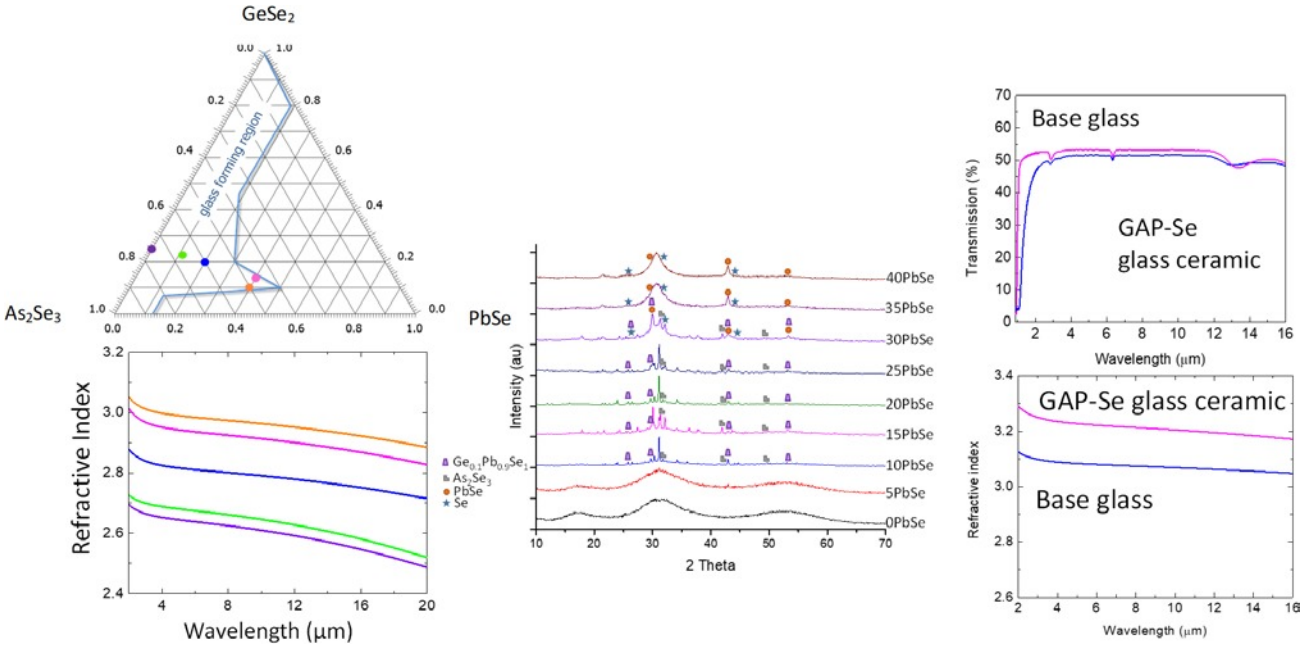


(a) (b)

Figure 4. Chalcogenide glass (ChG) GRIN lens where a gradient index is created through the spatial control of high refractive index particles embedded in a lower refractive index glass matrix [61].

Varying the high index ingredient (in this case the Pb content) in the parent glass, in itself, leads to a modification in the base material's index and dispersion behavior. Shown for the five (5) compositions depicted in the $GeSe_2$–As_2Se_3–PbSe ternary phase diagram in Fig. 5a (top), unique glasses with defined dispersion [Fig. 5a (bottom)] can be realized prior to any further heat treatment (HT). This variation in starting glass composition, defines what possible crystal phases can be realized following heat treatment. Figure 5b shows the possible crystal phases which can form across the Pb-series, following a single, unoptimized HT schedule. As is shown in the legend, the key crystalline phases which form (the volume fractions of which are defined by the precise time and temperatures used in the HT step) can include PbSe, As_2Se_3, Se and other AsSe and GeAsSe phases. As predicted by equation 1, the constituents in the glass are converted with heat treatment to form these crystal phases, thus depleting the glass (and changing its refractive index and volume fraction in the composite). This formation of crystal phases in the glass matrix, gives rise to a modification in the material's transmission as depicted in Fig. 5c (top) as well as its refractive index and dispersion (Fig. 5c, bottom). Shown here for a fixed composition and heat treatment protocol, these specific conditions are variable enabling the tailoring of the composite to fit specific optical design needs.

Recent efforts have demonstrated the ability to engineer the index and dispersion behavior in bulk and thin film forms [63] of GAP-Se materials with precision, including the ability to not only use laser-induced nucleation and/or growth to spatially control the localized crystal phase formation [42], but also the ability to locally induce vitrification (or re-amorphization) of previously formed glass ceramics, to create a drop in refractive index by converting previously formed nanocrystals, back towards its initial, glassy state [45]. Such flexibility in both compositional design and processing routes will enable a wide variety of materials which can be tailored to fit applications across the infrared.



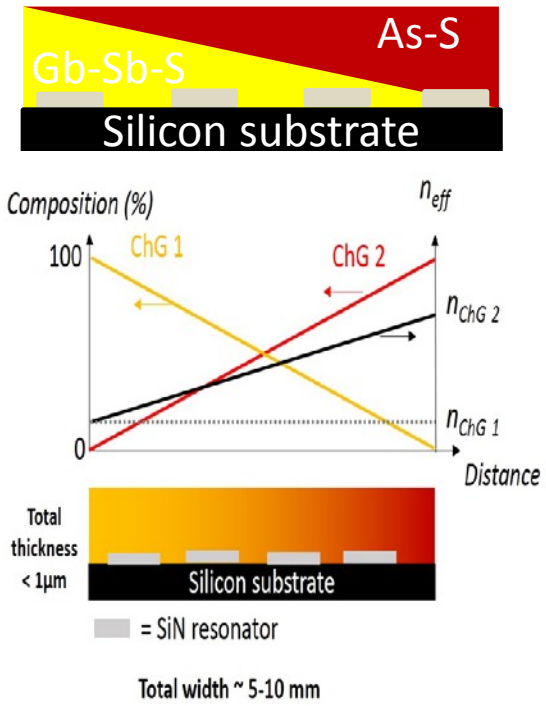
(a) (b) (c)

Figure 5. (a) compositional glass forming within the $GeSe_2$ – As_2Se_3 – PbSe (GAP-Se) material system (top) and corresponding MWIR-LWIR dispersion of the corresponding (color coded) compositions [from 61]. (b) crystal phase evolution upon heat treatment for GAP-Se glasses with various PbSe content (mol%) [44,61] (c) transmission of parent glass (pink) and post-heat treated glass ceramic (blue) of nanocomposite after defined heat treatment protocol; sample thickness, t = 2 mm, not corrected for Fresnel loss (top); pre- and post-heat treatment dispersion of glass and glass ceramic for the same composition as determined by spectroscopic ellipsometry.

2.2 Planar GRIN materials

2.2.1 3D printing of solution-derived ChG glasses

Spatial control and variation of physical properties in IR transparent glasses is a desirable attribute that not only is useful in bulk optics but also in thin films which are compatible with other on-chip materials and components. Efforts by our team and others over the past decade have shown that ChGs are soluble in a variety of amine-based solvents [64]. First demonstrated by teams lead by co-authors Richardson [65-67] and Hu [68,69] with Craig Arnold at Princeton [68,70-72], we showed that solution-derived ChG films could be processed with physical properties closely matching that of the parent bulk material. These efforts, largely focused on chipscale integration of ChGs for sensing applications, and formed the basis of further activities aimed at doping with nanoparticles or quantum dots whereby luminescent behavior could extend the optical functionality of the films [73,74]. To aid in the physical dispersion of such particles to create tailorable optical function without quenching, coating techniques were further optimized to develop an electrospray (ES) technique [75,76] whereby particles could be contained within aerosol droplets which upon evaporation of solvent during deposition, particles would not undergo the typical agglomeration realized in spin coating and other coating techniques. Once optimized, ES was shown to be suitable for depositing multiple composition of ChG and enabled the systematic creation of multi-layer films. By altering the thickness of each film, with knowledge of the ES spot film profile and resulting post-heat treated film thickness, effective index gradient layers were created [46]. These direct print structures can be tailored for thickness, index and thus resulting effective index profile defined by the path of the three dimensional (3D) printing profile. Depicted in Fig. 6a are multiple solutions of various ChG compositions following dispersion in amine solvents. Figure 6b (top) illustrates the gradient film deposition profile of a bi-layer of GeSbS and AsS glasses (on Si) and the variation in effective index, n_{eff}, calculated based on the layer thickness and parent glass refractive indices, as deposited on a SiN resonator array. Such deposition requires an electrically conductive substrate (i.e., Si) but is amenable to plano and other shaped substrtes. Additionally, the magnitude of the resulting index gradient is only defined by the film thickness and the excursion (Δn) between the candidate glasses used.



(a) (b)

Figure 6. (a) multiple solutions of various chalcogenide glass materials [77] dissolved in amine solvents. Bilayer design of a GeSbS and AsS gradient profile (top) and actual effective index profile (bottom) of the measured gradient layer, as a function of position across a SiN resonator array. [46]

2.2.2 Photo-induced polymerization of ChG glasses

Since the first efforts to write optical functionality into oxide glasses with lasers, glasses have been evaluated for their use as waveguides [78], 2D waveguide arrays [79], resonators, and other refractive or diffractive optical elements [80]. Such structures have been realized by laser-writing, usually using fs laser pulses or by lithographic processing of glassy layers deposited by a range of film deposition techniques. Planar thin films based on chalcogenide glasses have been long known to be photo-sensitive, as evidenced by their use in Xerographic processes [81] and as resists for lithographic applications [82]. This photosensitivity has been found to arise from defect 'tail' states associated with normal and abnormal (over or under-coordinated electron- or hole- containing) bonds within the chalcogen-containing amorphous semiconductor network. Extension of laser-writing approaches to non-oxide materials specifically to write on-chip optical structures and to understand the fundamental differences in properties between bulk and thin films [83,84] and the mechanisms of photo-structural modification [85], was initiated by our team in conjunction with collaborators at Laval University, in the mid- to late 1990's. Figure 7 illustrates the variation in as-formed structural units within glasses of As_2S_3 in bulk, thin film and fiber form, highlighting the presence of 'abnormal' bonds in ChG films, as quantified by Raman spectroscopy. Note especially the presence of homopolar As-As and S-S bonds which impart higher photosensitivity in as-deposited films or waveguides, as compared to bulk glass.

Using the device fabrication and optical characterization tools from the Laval team in conjunction with the glass processing and characterization tools at UCF, we were able to quantify for the first time, variations in optical and physical properties as a result of forming processes and extension of bulk glasses to film form. As discussed in the literature, most as-deposited ChGs (bulk glass targets or crystalline alloy targets are typically amorphous following film deposition [88]), exhibit photo-sensitivity, specifically the ability to change their optical properties (bandgap or refractive index) through the thermal or photonic modification of localized bonds. Modification of such materials with varying types of radiation, can lead to the creation of unique optical functionality, including enhanced nonlinearities. The photo-sensitivity of ChGs in laser-written

structures has been well studied (see the review contained in [89]) and the optical function and stability of gratings, waveguides have been shown to be a function of glass' composition, the wavelength of light used to write the structure and the environment where post-formation aging takes place [90-96].

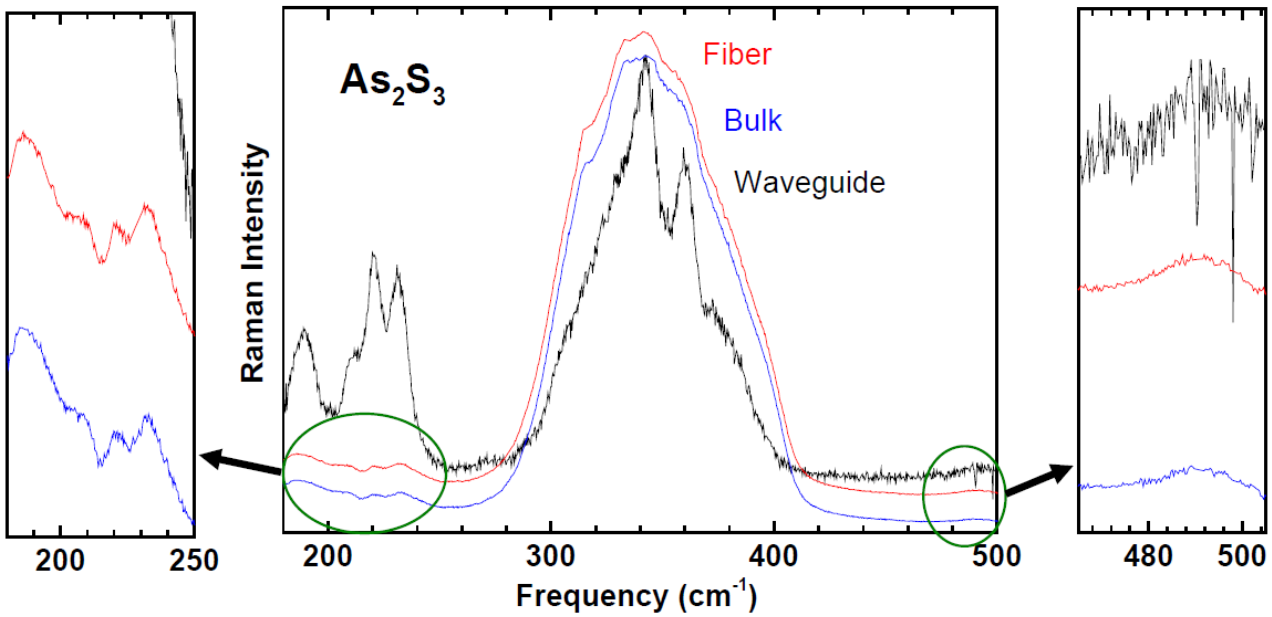


Figure 7. MicroRaman spectra illustrating heteropoloar (As-S) and homopolar bonds (As-As and S-S) in As_2S_3 (λ_{exc} = 840nm) measured with 1.5 cm^{-1} spectral resolution. Highlighted in the circled areas are the higher concentration of homopolar (As-As and S-S) bonds found in films/waveguides (features in the 200-250 and 490 cm^{-1} region, respectively) as compared to bulk and fiber forms of the material. Theoretically, stoichiometric material should only possess heteropolar (As-S) bonds. These abnormal, homopolar bonds not present to the same extent in the bulk and fiber forms, and render films much more photosensitive [86,87].

Most studied by our team [97,98] and others is As_2S_3 whereby planar films can be doped or locally altered to realize gratings and waveguides. While responsive, these as-written structures and their optical property stability are sometimes short-lived, in that light-induced bond-reorganization may lead to localized crystallization or post-exposed modification which anneals out at room temperature due to the glass' low glass transition temperature (T_g). Recent efforts have exploited the ease of glass network re-organization imparted by photo-induced bond modification, to realize structures which exhibit etch selectivity between bonds contained in the modified region, as compared to un-irradiated material. This processing has been employed to realize two- and three-dimensional structures with a wide range of optical functionality. Defined by our team as multi-photon lithography (MPL), we have carried out systematic dose dependent material modification studies to most recently realize meta-structures.

Figure 8a illustrates the pillar pattern realized in a 2D array in As_2S_3 over a 250 x 250 μm region [49]. Similar irradiation conditions were used to realize gratings which could be tuned (Figs. 8b, 8c and 8d) to realize diffractive features which exhibited spectral-specific response [47]. These structures exhibit good optical functionality but suffer from limited stability due to the crystallization tendency of these ChGs films. Recently, we have shown that modifying the glass network with a constituent known to enhance cross-linking, Ge, the long-term stability can be enhanced. While still exhibiting etch selectivity (albeit, reduced as compared to the binary As-S glass films), the aging stability of such structures remain after times up to four years [99]. A post-aged array of a GeAsSe structure is shown after 4 years in Fig. 9a. By tailoring the

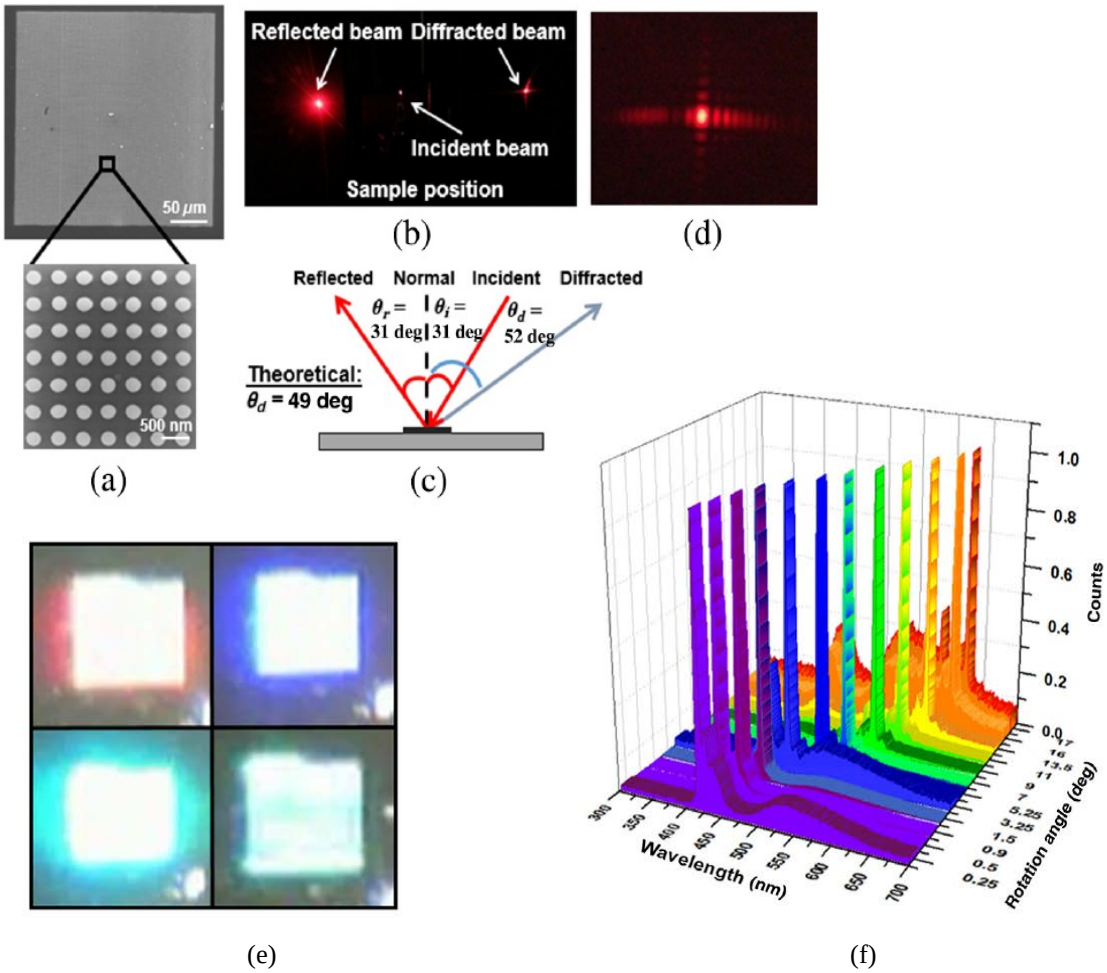
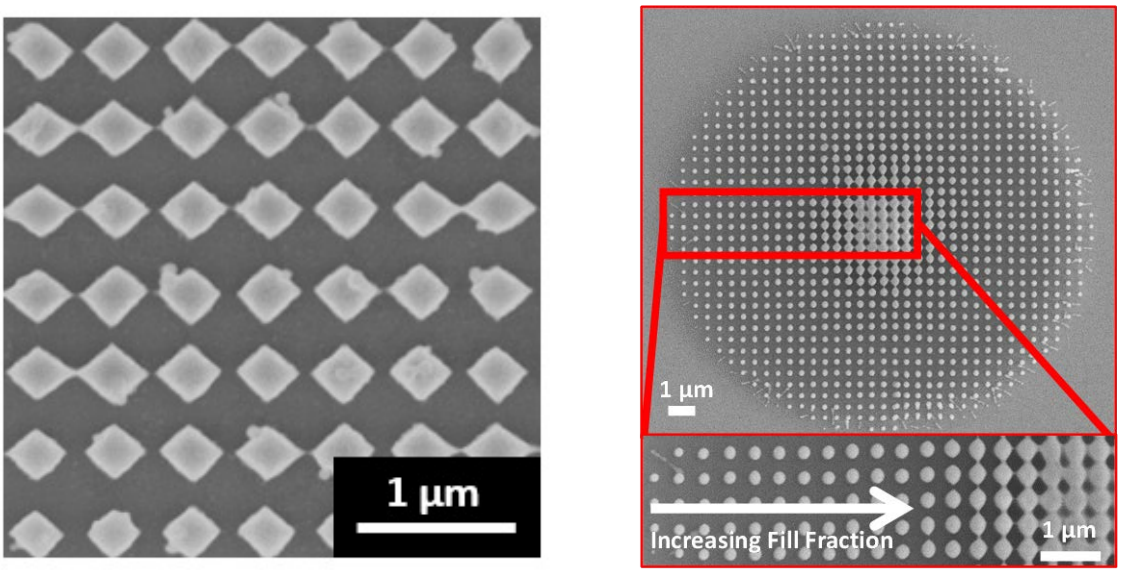


Figure 8. (a) top-down SEM image of the 250 μm x 250 μm nanostructured pillar array (As_2S_3) with a close-up image showing the tops of the individual structures (b) optical image of the incident, reflected and diffracted beams (c) diagram depicting the actual angle for the reflected and diffracted beams and the predicted angle for the diffracted beam (d) close up optical image of the actual refracted beam pattern (e) Optical images of a 250 μm x 250 μm nanostructured pillar array showing that the structure diffracts light of different colors as the angle of incidence is changed. (f) Plot of the diffracted light intensity versus wavelength of white light incident at varying angles [47].

composition (for stability) and filling fraction (of glass pillar material and free volume of air) of an area where such a pattern exists (Fig. 9b), a gradient effective index (here in the form of a metalens structure) can be realized.



(a) (b)

Figure 9. (a) Ge-containing As-Se film array pattern ($Ge_5(As_{40}Se_{60})_{95}$) after t = 4 years of aging. Features show minor deterioration at their edges but retain their as-written lateral dimensions. (b) an As_2S_3 meta-lens created using multi-photon lithography (MPL), as discussed in [47].

3. CONCLUSIONS

The recent history of efforts aimed at realizing gradients in refractive index (GRIN) across a range of infrared-transparent materials is reviewed. The ability to exploit material composition, photosensitivity, processing methodology and resulting optical function, specifically highlighting the trade-offs and scale-ability of solutions, has been presented. Four specific examples of strategies in bulk and thin film ChGs are discussed. The recent efforts by the IR community to evaluate alternate strategies to add optical functionality to elements suitable for use in this important region of the spectrum highlights the promising future of such approaches to reduce the size, weight and power (SWaP) requirements needed for next generation optical components and systems.

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