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Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

FY 2004 Infrared Photonics

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Research done by the Infrared Photonics team at Pacific Northwest National Laboratory (PNNL) is focused on developing miniaturized integrated optics for mid-wave infrared (MWIR) and long-wave infrared (LWIR) sensing applications by exploiting the unique optical and material properties of chalcogenide glass. PNNL has developed thin-film deposition capabilities, direct laser writing techniques, infrared photonic device demonstration, holographic optical element design and fabrication, photonic device modeling, and advanced optical metrology—all specific to chalcogenide glass. Chalcogenide infrared photonics provides a pathway to quantum cascade laser (QCL) transmitter miniaturization. QCLs provide a viable infrared laser source for a new class of laser transmitters capable of meeting the performance requirements for a variety of national security sensing applications. The high output power, small size, and superb stability and modulation characteristics of QCLs make them amenable for integration as transmitters into ultra-sensitive, ultra-selective point sampling and remote short-range chemical sensors that are particularly useful for nuclear nonproliferation missions.

During FY 2004, PNNL's Infrared Photonics research team made outstanding progress exploiting the extraordinary optical and material properties of chalcogenide glass. The team published three papers, gave five conference presentations, and submitted four invention reports. We developed a unique capability to fabricate and characterize bulk and thin-film custom chalcogenide glass. Key research was performed to understand and control the photomodification properties. This research was then used to demonstrate several essential infrared photonic devices, including LWIR single-mode waveguide devices, holographic diffraction gratings, and white light holograms. Anti-reflection coatings for MWIR and LWIR applications as well as protective barrier layers to prevent degradation were developed.

The Infrared Photonics research is positioned to develop chalcogenide-based photonic components such as waveguides, beam splitters, multiplexers, couplers, beam shapers, Bragg reflectors, long-period gratings, hybrid lenses, and polarizers. The integration of these guided-wave photonic components on a single substrate along with the QCLs, all in a single package, provides a compact solution that meets the goals of infrared sensing missions.

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1.0 Introduction

Chalcogenide glasses are attractive materials for fabricating mid-wave infrared (MWIR) and long-wave infrared (LWIR) photonic components because they combine relatively low transmission losses with the unique photomodification phenomenon. Amorphous semiconductors such as chalcogenide glasses exhibit a number of effects that are unique to the amorphous phase. They can undergo various transformations between different phases while being illuminated by a given photon energy. One of these transformations is photodarkening, which corresponds to a photo-induced red shift of the absorption spectrum. For photon energy below the band-gap energy, this shift leads to an increase of the refractive index. It is thus possible to use this effect in a controlled manner to create waveguides, and any structure can be patterned in the glass by either moving a focused beam in or on the glass or exposing the glass through an amplitude or phase mask. Chalcogenide glasses exposed with band-gap energy light can undergo a large refractive index change in the infrared spectrum, and values approaching 0.1 have been reported. With proper characterization of the photodarkening effect in thin films, which can differ from that in bulk samples, laser writing of waveguides, couplers, cavities, and other complex optical devices for the infrared sensing application can therefore be achieved in chalcogenide glasses.

In recent years, the property of chalcogenide glass that has attracted the most attention is certainly its large optical Kerr effect, which is caused by the nonlinearity of the refractive index. When submitted to high-intensity laser light away from the absorption edge, the refractive index undergoes an ultra-fast nonlinear modification that can lead to spectrum modulation and beam self-focusing. The nonlinear refractive index of the different chalcogenide glasses can be as high as 1000 times that of silica, which is very promising for the development of nonlinear devices such as all-optical switches, and provides the opportunity for designing compact, ultra-fast active components.

By exploiting the unique and exciting properties of the chalcogenide glass family, Pacific Northwest National Laboratory (PNNL) is developing the photonic optical components needed to miniaturize infrared sensing systems. This research will create a pathway toward efficient, compact, field-deployable systems that will meet the sensing needs of national security missions.

In this report we provide a summary of the FY 2004 research progress for the Infrared Photonics project. In Section 2, we summarize the advances made in chalcogenide glass research. In Section 3, we summarize measurements of photodarkening in both bulk and thin-film chalcogenide glass.
In Section 4, we provide an update on computer generate holography and in Section 5, we discuss the nonlinear optical properties of chalcogenide glass. In Section 6, we discuss the precise optical index measurements provided by the newly procured Metricon prism coupler. Section 7 provides a development update on antireflection and barrier layer coatings and Section 8 summarizes progress in photonic device fabrication.

2.0 Chalcogenide Glass Research and Development

Chalcogenide glass research capabilities were advanced in fiscal year 2004 through the acquisition and design of several critical pieces of equipment and experimental procedures that are required to synthesize high-purity, low-loss infrared (IR) photonic materials. Specifically, five areas were addressed:

- glass processing safety
- custom-designed rocking furnace
- high-vacuum capability
- advanced chemical purification
- anodic anhydrous environmental processing.

Work in each of these five areas during FY 2004 is described in the following sections.

2.1 Glass Processing Safety

Advancements were made through the design and development of a containment device used while melting and reacting the elemental constituents of chalcogenide glass. Certain glass compositions require challenging processing conditions that could possibly result in a failure of the glass ampoules used to seal and contain the reactants. Consequently, a secondary containment device (Figure 2.1) was designed and implemented to provide an additional measure of safety in the event of an ampoule failure at elevated temperatures. The added weight of the containment structure necessitated a modification of the mechanism used to rock the furnace (to promote mixing and homogenization of the glass) during glass processing.

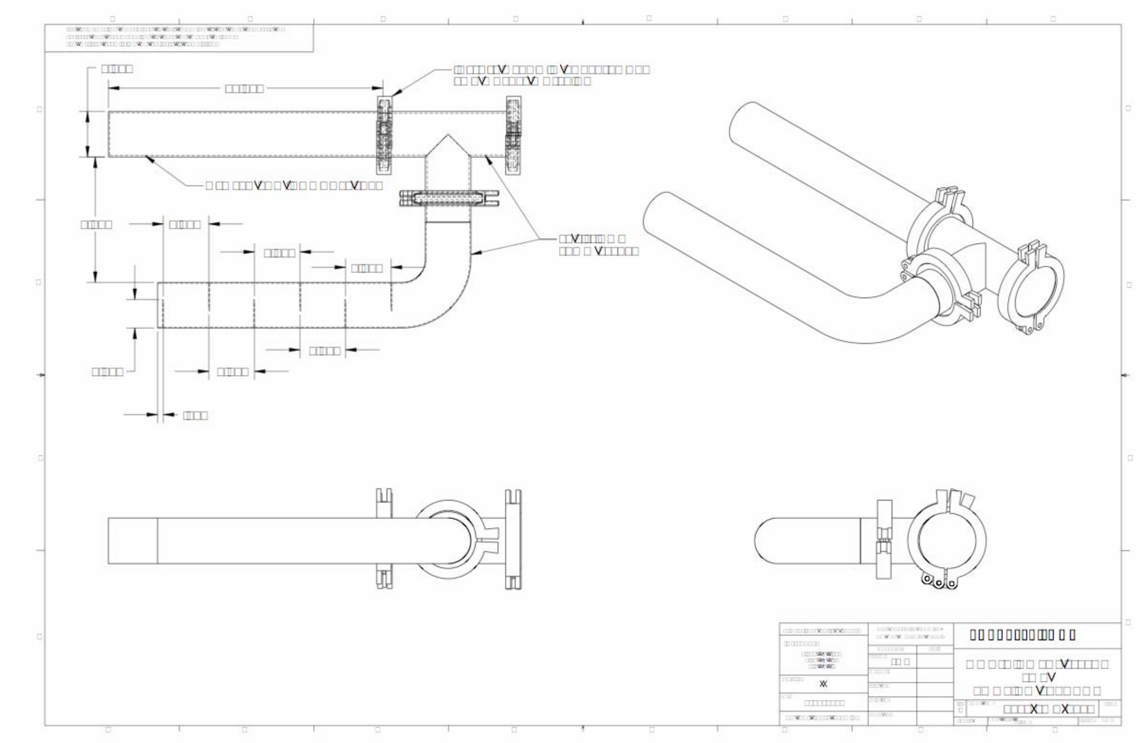


Figure 2.1. Secondary Containment Device Used for Processing Molten Chalcogenide Materials.

2.2 Custom-Designed Rocking Furnace

A second-generation, custom-designed rocking mechanism for a rocking furnace was developed and built. Chalcogenide glasses need to be agitated to promote mixing and homogeneity during melt-based processing. This typically involves the use of a rocking furnace to agitate the melt as the elemental constituents react to form a glass. However, these materials have very high viscosities at the temperatures used to process them, such that the liquid does not flow readily. Although the viscosity decreases with increasing temperature, higher processing temperatures create additional safety concerns in the event of an ampoule failure. Due to the high viscosities, homogenization can be improved by increasing the centrifugal force on the liquid when the rocking furnace is moving but then pausing at each end point to allow the melt to flow to its equilibrium position before reversing direction. Consequently, a new type of rocking mechanism was engineered (Figure 2.2) to allow adjustment of the swing arc, pendulum distance, swing speed, and variable time control at each end point.

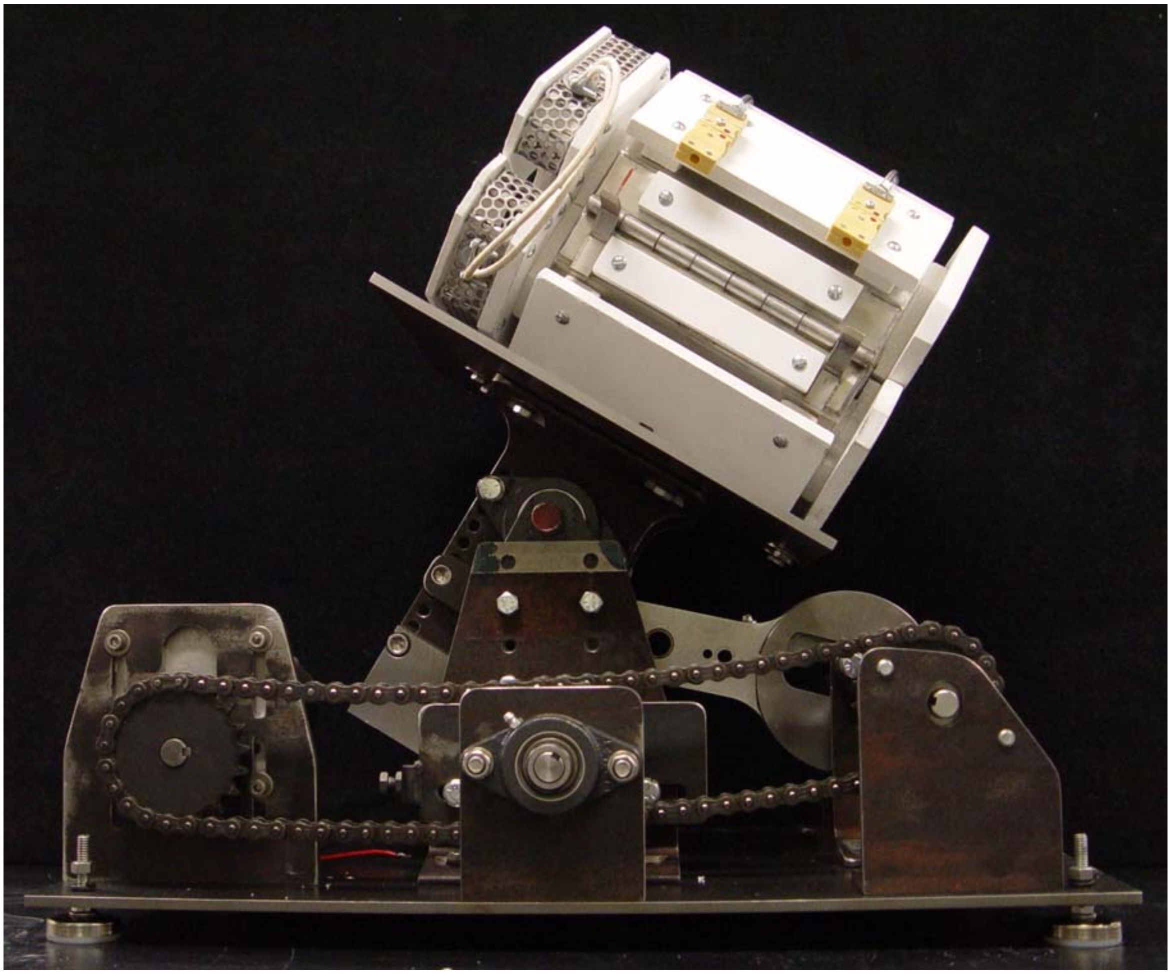


Figure 2.2. Custom-Designed Rocking Furnace for Processing Chalcogenide Materials.

2.3 High-Vacuum Capability

A portable turbo molecular pumping station (Figure 2.3) was acquired to facilitate high-vacuum processing during chalcogenide glass ampoule assembly. High-vacuum processing is crucial during the ampoule assembly, since oxygen and water are deleterious contaminants to chalcogenide IR materials. Even small traces of these contaminants produce significant IR absorption losses. Consequently, diligent effort is required to eliminate these contaminants. High-vacuum pumping capability is essential to this effort. The portable pumping station was connected to the updated piping and valving system (Figure 2.4) to enable us to evacuated fused quartz ampoules at pressures as low as 10^{-6} torr.

Figure 2.3. Portable Turbo Molecular Pumping Cart Used To Make Fused Silica Ampoules for Processing Chalcogenide Glasses.

Figure 2.4. High-Vacuum Piping and Valving Station Used To Fabricate Chalcogenide Ampoules.

2.4 Advanced Chemical Purification

Chemical purification of elemental constituent (e.g., sulfur, arsenic) is required to produce high-quality, low-loss chalcogenide glasses. Source chemicals as received from chemical vendors contain significant amounts of hydrocarbon contamination and thus are insufficiently pure for IR photonic glass synthesis (Adamchik *et al*. 2000, 2001). This is particularly problematic for sulfur. A literature survey was conducted, and based on those results, an advanced sulfur purification process has been developed. To date, a safe operating procedure (SOP) has been developed, reviewed, and approved by technical experts, health and safety personnel, and environmental compliance specialists. The experimental apparatus and safety, control, and monitoring equipment have been procured and are being assembled in accordance with the SOP (Figure 2.5). The experimental work will commence upon final review. Additionally, purification procedures for the other elemental constituents such as arsenic and selenium have been identified and will be implemented in the near future.

Figure 2.5. Apparatus Used for Purifying Elemental Sulfur.

2.5 Anodic Anhydrous Environmental Processing

An atmospherically controlled glovebox (O_2 < 1 ppm, H_2O < 1 ppm) was designed, procured, and installed (Figure 2.6). The addition of this capability to the workflow was a significant step toward high-purity chalcogenide processing. Based on our experience in non-oxide glass research, we have determined that atmospheric oxygen and moisture present a substantial source of contamination. The addition of this atmospherically controlled glovebox will enable us to eliminate these deleterious contaminants during purification and handling of the elemental constituents. Additionally, the glovebox was designed to accommodate a furnace and a wide variety of feed-throughs (electrical, gas, vacuum, thermocouple), so it is equipped with a chiller, two antechambers, and a solvent removal and extraction system. This glovebox will facilitate both the synthesis of ultra-high-purity non-oxide materials (e.g., chalcogenide glasses, heavy-metal fluoride glasses, nitrides, carbides) as well as manipulation of these materials into high value-added components for advanced photonic applications (e.g., molded lenses, custom antireflective (AR) coating materials, aspheres).

Figure 2.6. Custom-Designed Atmospherically Controlled Glovebox for Processing and Purifying Chalcogenide Materials.

2.6 Summary of FY 2004 Accomplishments

The team achieved three key accomplishments in chalcogenide glass research and development during the year:

1. Chalcogenide ampoule loading now performed at high vacuum.

2. Rocking furnace redesign significantly improves safety and glass mixing.

3. Advanced chemical purification methods and newly installed atmospherically controlled glovebox improves chalcogenide glass optical quality

3.0 Photodarkening in Chalcogenide Glass

Photodarkening is an important photomodification process present in chalcogenide glass. Illumination of the glass using light near the bandgap energy results in a shift of the band edge toward the longer wavelengths and a corresponding increase in the optical index of refraction in the infrared spectrum. The capacity to controllably alter the index of refraction forms the basis of infrared photonics component fabrication by direct laser writing processes. It is important to develop a method of monitoring the photodarkening process during the laser writing process so that controllable index adjustments can be achieved. It was anticipated that by measuring either the writing laser transmission through the chalcogenide glass or the reflection from the surface might provide an indirect assessment of the change in index.

3.1 Photodarkening in Bulk Glass

The time dynamics and laser exposure dependencies of photodarkening in bulk chalcogenide glass were investigated using the optical setup described in Figure 3.1. Here a collimated helium-neon (HeNe) laser beam with a wavelength of 633 nm was used as the photomodification source. This laser wavelength is ideal for such experiments because it is moderately absorbed, thus leading to refractive index changes deep below the surface of the glass. As shown in Figure 3.1, a quartz plate was inserted in the beam path with an extremely small tilt angle to monitor any laser power fluctuations. The monitor was used as the reference level channel. The laser beam impinged on a 2-mm-thick chalcogenide glass sample at a small off-normal angle to facilitate the monitoring of both transmitted and reflected laser powers, measured by Photodetectors 1 and 2, respectively. The overall background illumination level due to stray reflections was suppressed using appropriately located beam blocks and irises. Photodarkening measurements were performed at a maximum laser power of 40 mW corresponding to an incident power density of 5 W/cm^2 where an increased exposure leads to increased absorption until saturation is reached. Synchronized power measurements from the three detectors were acquired simultaneously using custom LabVIEW software, and the data were made available for further analysis.

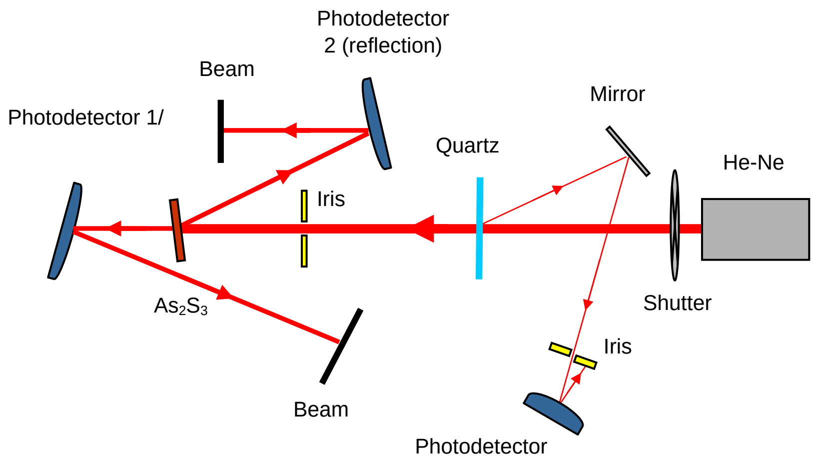


Figure 3.1. Experimental Apparatus for Characterizing Photodarkening in Chalcogenide Glass.

A series of photodarkening experiments were conducted. Simultaneous measurements of the transmitted and reflected powers as a function of illumination time were acquired and then normalized (Figure 3.2). It can be seen that the transmission and reflection measurements both displayed oscillatory behavior in the first 10 minutes (~6000s) of the photodarkening process. Summation of the transmitted and reflected powers showed an unexpected oscillatory behavior indicating that the reflection peaks did not completely correspond with the transmission dips. The cause of this behavior remains unclear and is subject to further investigation.

The overall trend of the recorded total power shows significant absorption as a function of time, as anticipated, since glass photodarkening is occurring. The glass photodarkening resulted in attenuation of the incident beam by ~45%. The chalcogenide glass window forms a Fabry-Perot cavity structure, whose transmission properties are dependent on the optical index of refraction. The time-varying refractive index, produced by the continuous laser exposure, generates the oscillations in the transmitted and reflected laser power. It is also apparent that the oscillations are damped as time evolves, consistent with the saturation of the refractive index change.

Additional experiments were conducted in which the angles of incidence and illuminating powers were varied. The photodarkening exhibited similar data trends except that the oscillatory behavior was slower when the incident angle was changed. This is also consistent with Fabry-Perot cavity transmission properties. Finally, lower incident laser power densities resulted in smaller attenuation values that required longer exposure times to achieve saturation.

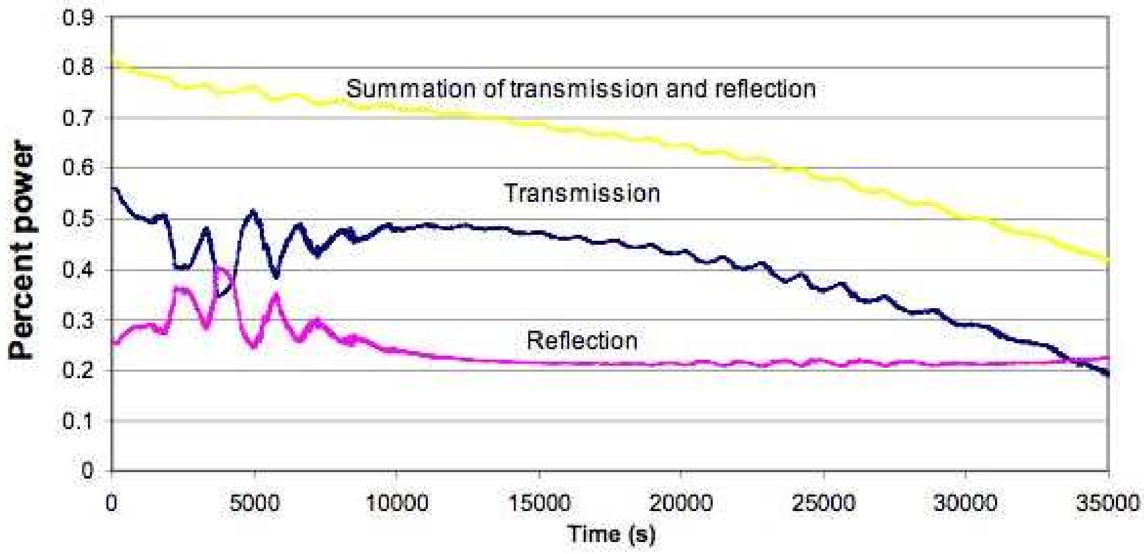


Figure 3.2. Normalized Transmitted and Reflected Powers as a Function of Laser Exposure Time or Photodarkening Time. Power fluctuations of the source were subtracted from both transmission and reflection data. The cause of the oscillations in the summation remains unclear and is subject to further investigation.

Although the experimental results did not produce a practical photodarkening monitoring method for the chalcogenide glass laser writing process, it is interesting to realize that this oscillatory behavior could be used for characterizing refractive index changes in thin films. Because in this case the films are only a few microns thick, the refractive index change will be constant throughout their depth. The Fabry-Perot cavity with a time-varying refractive index change then can be properly modeled and the time dynamics of the photodarkening can be deduced. Performing that experiment will enable the determination of many important parameters of the direct laser writing process, such as the necessary dose to reach a given refractive index change and also the maximum index change that can be induced in the material.

3.2 Photodarkening in Thin-Film Glass

Another avenue to monitor photodarkening is to measure the band edge shift. Photomodification of thin-film (2-µm) chalcogenide glass was performed using the 514.5-nm line of the argon-ion laser. The penetration depth of the laser at this wavelength is approximately 30 µm, so the film could be fully photodarkened through its thickness. The time required to reach photodarkening saturation was greatly reduced due to the increase absorption at this wavelength. A fiber-coupled spectrometer was used to characterize the shift in absorption band edge due to photodarkening. Figure 3.3 shows the transmission spectra of an annealed As_2S_3 film with a thickness of approximately 3 µm under exposure times ranging from 0 sec to 180 sec in steps of 30 sec. It can be seen that the absorption band edge shifts toward longer wavelengths with increased exposure. Also, differential shift in the absorption band edge reduces with increased exposure, saturating at around 180 sec. In addition, annealed chalcogenide thin films produced a smaller absorption band edge shift compared to unannealed films. This is not unexpected and in accordance with previously published data because the thermal vacuum deposition process produces a nonrelaxed metastable glass matrix. Annealing is required to stabilize the glass and the subsequent photonic device.

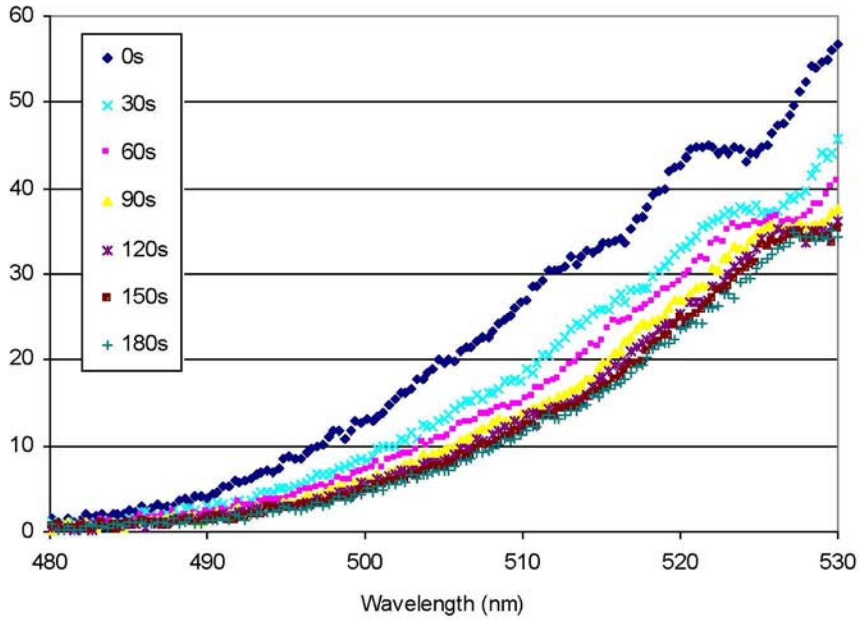


Figure 3.3. Normalized Transmitted Power as a Function of Wavelength for an Unannealed As_2S_3 Thin Film Exposed to an Argon-Ion Laser Beam for Various Exposure Times.

3.3 Summary of FY 2004 Accomplishments

Photodarkening research during FY 2004 resulted in three key accomplishments:

1. The initial photodarkening experiments enabled the identification of several variables that are responsible for the photodarkening.
2. The photodarkening transmission measurements uncovered the formation a Fabry-Perot cavity structure in the chalcogenide window. It was found that the time-varying refractive index, produced by the continuous laser exposure, generated oscillations in the transmitted and reflected laser power.
3. The band edge shift measurements have demonstrated a potential method with which to indirectly measure index change during direct laser writing. Further insight into these parameters would provide greater control of the photomodification and laser writing processes in chalcogenide glass. To better understand the contributions of the individual parameters, future efforts will include the following:

    - Perform a controlled set of experiments to determine the contributions of the individual parameters responsible for photodarkening.

- Measure refractive index changes due to photomodification using the newly acquired Metricon Prism Coupler.

- Develop a model with which to predict refractive index changes based on various illumination parameters.

- Conduct experiments on annealed, bulk, and thin-film chalcogenide glasses with different stoichiometries.

- Optimize laser-writing parameters for the fabrication of specialized optics.

4.0 Computer Generated Hologram Design and Fabrication

Diffractive optical elements (DOEs) can be designed to perform a variety of functions through the use of diffraction. This design generally involves a modification of the phase transmission profile of material, although modification of the amplitude transmission also can be used but with a lower efficiency. Within this project, DOEs are being investigated as elements that perform 1) traditional lens operations including focus and defocus, 2) aberration correction for refractive optical elements, 3) optical functions in combination with refractive optical elements (hybrid designs), and 4) holographic photonic functions like optical waveguide coupling. DOEs can be made through both optical and numerical methods. A numerically derived DOE is often called a computer-generated hologram (CGH).

Synthesis of CGHs requires modeling of diffraction through an optical element. The CGH element design then is iteratively optimized to achieve the desired optical element performance. A variety of CGH synthesis methods exists, depending on the functionality of the DOE and its desired response (e.g., accuracy, diffraction efficiency, manufacturability). For diffraction modeling, CGH algorithms can use far-field scalar diffraction theory based on Fourier analysis, near-field scalar diffraction theory based on Fresnel analysis, full scalar diffraction theory based on Kirchhoff analysis, or rigorous diffraction theory based on complete electromagnetic theory. There is a significant computational burden for more rigorous approaches. CGH synthesis requires establishing a pattern within the CGH element that will produce a desired diffraction pattern. Often iterative techniques are employed to optimize the desired output of the DOE within the constraints of its CGH. For simple diffractive elements, the phase profile of the CGH can be made deterministically. For example, a DOE that encodes a spherical lens could be made as a step-height phase mask that produces a wavefront phase shift equivalent to the desired spherical wavefront.

A range of methods exists to fabricate CGH-based DOEs. For chalcogenide glass, photomodification of the material allows direct laser writing of the CGH phase profile into the material. It also allows the use of a grayscale mask to represent the phase profile. This grayscale mask can be imaged onto the chalcogenide glass to form the DOE, or it can be a contact transfer of the mask onto the glass. All three of these techniques employ the photomodification properties of chalcogenide glass. Photomodification permanently changes the refractive index profile of the glass based on illumination laser fluence. When the CGH is used as an optical element, the previously recorded photomodification results in a phase modulation of the incident optical wavefront.

Direct laser writing and contact imaging methods are being investigated for recording desired phase profile, encoded using a grayscale mask, into the chalcogenide glass. To implement any of these photomodification methods in CGH fabrication, we need to understand the relationship between photomodification exposure time and energy to the refractive index change, depth of change, and the resulting phase shift. To explore this relationship, holographic diffraction gratings were recorded into chalcogenide glass substrates. By varying the holographic exposure duration and energy density and then comparing the ratio of the zeroth diffracted order to the first diffracted orders, a relationship between phase shift and exposure time can be determined.

To achieve the required optical performance from a DOE, the hologram recording media must be capable of producing up to a full wavelength phase shift. Without this capacity, a portion of the incident light will not be diffracted and will become an optical loss. A full wavelength shift within the chalcogenide glass likely will require a fairly thick modulation depth (product of the index change and the thickness of altered index region). The phase difference, φ, in the photomodified region is given by

$$\varphi = 2\pi/\lambda \ast \text{path difference}$$

where the path difference is given by the product of the physical thickness, t, and the index change. For example, if a 0.024 (1%) index change results from photomodification, then the required thickness at a wavelength of 10 μm is 417 μm (t = (10μm)/(0.024)) for a 2π phase shift. This becomes a considerable thickness requirement for a thin film. Obviously larger optical index changes, due to photomodification, will reduce the film thickness requirements.

Other fabrication methods include lithographic/etching approaches. In these methods, a profile representing the phase modulation is encoded in a lithographic mask (e.g., electron beam lithography). This is followed by either a direct contact or imaging transfer into a photoresist layer coated onto the chalcogenide glass. Next, an etch process (e.g., chemical, ion beam) is used to remove portions of the glass. This can be a multi-step process where phase is encoded in several binary masks. At mid-infrared wavelengths, it is also possible to produce diffraction patterns of high accuracy onto the glass with a diamond turning system. In this method, the CGH phase mask is used to control the diamond turning process. In both approaches, the depth profile etched into the glass encodes the phase modulation.

To design a corrective DOE, geometric optical ray-tracing software (e.g., OSLO®) is used to determine the wavefront error in the system. A custom software routine was developed to sample the wavefront error across the aperture and then generate the corresponding phase error mask. To generate this phase mask, the relationship between the refractive index change produced by photomodification and the laser writing parameter must be well understood. A major part of the current research is to relate phase modulation to laser exposure. This phase mask is then recorded into the chalcogenide glass, ultimately creating the corrective optical element.

4.1 Summary of FY 2004 Accomplishments

Accomplishments in holography research during FY 2004 included the following:

1. Modeled simple optical system with commercial ray-tracing software (OSLO).

2. Developed methods to sample wavefront error within OSLO ray-tracing software and then generate the phase mask.

3. Devised holographic diffraction grating mask test for determining relationship between photomodification and the resulting phase shift. This technique has not yet been tested.

4. Surveyed commercially available CGH software.

5. Held discussions with Richard Rallison (Ralcon Development Lab) a world-renowned expert on the fabrication of computer-generated holograms, and his Utah State University colleague, Professor Stephen Bialkowski. These discussions involved setting up collaborations on developing computer-generated holograms in chalcogenide glass.

5.0 Nonlinear Optical Properties of Chalcogenide Glass

To achieve an electrically controllable device requires the discovery and exploitation of nonlinear properties of chalcogenide glass. The first-order Pockels effect occurs in amorphous material, but no observation of it has been reported for chalcogenide glass. The second-order nonlinear susceptibility ($\chi^{(2)}$) requires a centrosymmetric structure not usually found in the amorphous state, unless poling is performed on the material. To date, much of the research into nonlinear optical effects in chalcogenide glass has centered on its well-known third-order nonlinear susceptibility ($\chi^{(3)}$). This property relates to the optical Kerr effect and the two-photon absorption. Much work has been published on second harmonic generation, third harmonic generation, optical Kerr shutter, self-focusing, and degenerate four-wave mixing.

Quiquempois *et al.* in Canada (2000) described the creation of a second-order nonlinear susceptibility ($\chi^{(2)}$) in As_2S_3. To achieve this second-order nonlinear susceptibility required electrical poling of the material. Private discussions with Professor Alain Villeneuve (formerly with the University of Laval, Quebec) gave us insight into the possibility of poling chalcogenide glasses. Since these glasses have a high $\chi^{(3)}$ it is likely they can be poled to also achieve a large $\chi^{(2)}$. Indeed, the poling results in a frozen built-in electric field due to charge migration and trapping, and the $\chi^{(2)}$ tensor is then proportional to the product of this field and the $\chi^{(3)}$ tensor. Both thermal and optical poling methods have been reported for As_2S_3.

Other approaches to electrical control of chalcogenide properties also are being investigated. Andriesh *et al.* (1976, 1984, 1995) in Russia have demonstrated a method to alter the surface profile of chalcogenide glass through both optical illumination and applied electric field within thin-film structures of chalcogenide glass. Mateleshko *et al.* (2004) in Ukraine have mentioned an electro-optic effect in relation to an electro-luminescence effect in chalcogenide glass. We will investigate these approaches as well to help determine a practical electro-optic effect in chalcogenide glass.

5.1 Summary of FY04 Accomplishments

Accomplishments in nonlinear research during FY 2004 include the following:

1. Reviewed literature associated with nonlinear optical effect in chalcogenide glass.

2. Discussions held with Professor Alain Villeneuve, world-renowned researcher in chalcogenide glass, on the existence of an electro-optic effect in chalcogenide glass.

3. Initiated development of a theoretical model of the electro-optic effect to determine the strength of a possible electro-optic effect in chalcogenide glass through the use of the second-order nonlinear susceptibility.

6.0 Precision Index of Refraction Measurements Using the Metricon Prism Coupler

A customized Metricon Model 2010 prism coupler was procured to rapidly and accurately measure both the refractive index/birefringence and the thickness of amorphous chalcogenide glass bulk and films. The Model 2010 offers unique advantages over conventional instruments based on ellipsometry because the sample's physical parameters need not be known in advance. This instrument features a factory-installed HeNe laser, a prism capable of measuring refractive indices ranging from 2.1 to 2.65, a germanium detector that covers 0.63 μm to 1.55 μm wavelengths, and peripheral optics that all are contained in a lightproof housing. This instrument also was designed to allow measurements at two user-selectable laser wavelengths through two ports at the rear of the main optics module. The optical and mechanical components were customized to allow measurement at both the MWIR and LWIR wavelengths.

Using the HeNe (633-nm) wavelength, simultaneous thickness and index measurement are possible for films that are about 15 μm in thickness. An index resolution ±0.0003 can be routinely achieved for films with a thickness of 0.5 to 1.0 μm. The index resolution can be improved up to ±0.00005 using a high-resolution rotary table. Typical measurement time with the high-resolution table is 15 to 75 sec. For thicker films, however, simultaneous thickness and index measurements are not possible. Accurate measurements of the refractive index can be made without thickness measurements and similarly film thicknesses up to about 100 μm can be measured within 0.3% without obtaining information of its refractive index.

The Metricon prism coupler has been installed and tested in our laboratory using thin-film chalcogenide glass coated at PNNL. Because good coupling between the prism and the glass sample is essential to the measurement process, both surfaces must be extremely clean. For this, a standard cleaning procedure has been developed involving the use of acetone as the solvent in conjunction with a spin-cleaner, lint-free wipes, and a nitrogen blow-drying process. Once the samples are optimally cleaned, the laser beam and the coupling spot are aligned by carefully adjusting the optics inside the instrument.

However, initial experiments on thin-film chalcogenide glasses have shown that the refractive indices obtained from the instrument are close to the measurement limit of the current prism with HeNe illumination. In addition, the thickness measurements of the thin films do not agree with the thickness measurements from other instruments.

The problem we are currently faced with is that there are no commercially available films that have refractive indices in the range of 2.1 to 2.65. This makes it difficult for us to calibrate the system and gain a better understanding of its measurement techniques. Also, there are no calibration standards traceable to the National Institute of Standards and Technology (NIST) for high-index materials. Thus, we have ordered a low-index (<1.8) prism and prism coupler module to enable instrument calibration using NIST-traceable calibration standards.

In addition to the problem just described, the current prism-HeNe combination does not provide a readout of the first few coupled modes, resulting in measurement errors for film thicknesses greater than 3 μm. This problem, however, can be resolved by using a longer-wavelength laser (e.g., 1.55 μm) as the illumination source. For this, an additional chamber with appropriate optics will need to be built.

Once the Metricon system has been adjusted and calibrated for refractive index and thickness measurements in the appropriate region for chalcogenide glasses, the impact of stoichiometry, photomodification, and annealing will be determined. Eventually, refractive indices for the As-S and As-S-Se material will be mapped for varying stoichiometric compositions and photomodification conditions.

7.0 Antireflection and Barrier Layer Coating Research

Thin-film antireflection (AR) coatings greatly reduce the light loss due to Fresnel reflections by making use of phase changes and the dependence of the reflectivity on index of refraction. The simplest AR coating is a quarterwave layer, where the coating optical thickness is one quarter of the design optical light wavelength. A single quarter-wavelength coating, with an index higher than the substrate, can greatly reduce reflection at one wavelength. Multi-layer quarterwave coatings can reduce the loss over a wider wavelength spectrum, but this design requires quarterwave coatings with both high and low refractive indices.

The research goals were to develop 3% reflectance AR coatings both on As_2S_3 for the MWIR (3- to 5-µm) and on As_2Se_3 for the LWIR (8- to 12-µm) wavelengths. A key that makes this research both required and unique is that the AR coating also must function as a barrier coating to prevent surface degradation associated with water and ultraviolet (UV) light exposure.

7.1 Antireflection Coating Designs for Mid-Wave Infrared

A simple two-layer quarterwave stack, tuned for 3.5-µm operation, was designed using zinc sulfide (ZnS) as the high-index layer (n = 2.25) and aluminum oxide (Al_2O_3) as the low-index layer (n = 1.57). For optimum performance, any AR coating needs to be deposited on both sides of the substrate to remove both Fresnel reflections. The design is

$$Al_2O_3/ZnS/\text{bulk substrate}/ZnS/Al_2O_3.$$

All coatings were deposited by magnetron sputtering in a 28-in. box coating chamber in PNNL's thin-film coatings laboratory. A 3-in. ZnS target and 6-in. Al_2O_3 target were used. Both substrates were loaded into the chamber as-received due to concerns regarding wet cleaning. After an overnight pumpdown (7.0×10^{-7} torr), the substrates were ion-cleaned for 5 minutes. Before the source shutter was opened, the ZnS target was conditioned for 2 min to clean the target surface. The ZnS quarterwave deposition time was 1 hr. The Al_2O_3 target was conditioned 1 min prior to the source shutter opening. The Al_2O_3 quarterwave deposition time was 6 hr and 25 min. The substrates were stationary over each target to optimize the deposition rates. The two-layer AR coating was deposited on the As_2S_3 film side of the microscope slide and on both sides of a 1-in.-diameter bulk As_2S_3 substrate.

The reflectance of the bare As_2S_3 substrate (both sides) was approximately 29% in this range (Figure 7.1, red plot). The average design reflectance after applying the two-layer AR coating to one side was 17% (magenta plot). The measured reflectance after applying the coating (Run #AR #1D-M) to one side was slightly better at 16% (lavender plot).

The design, which predicted an average of 1% reflectance at 3.5-µm wavelength, assumes a perfect AR coating is applied to the second surface (yellow plot). The reflectance of the actual coating after deposition to both sides (AR #1D & E-M) measured 5% to 6% (purple plot). This difference may be due to an index variation between actual coating and the values on file that are used by the design software and the assumption of a “perfect” AR on the second substrate side.

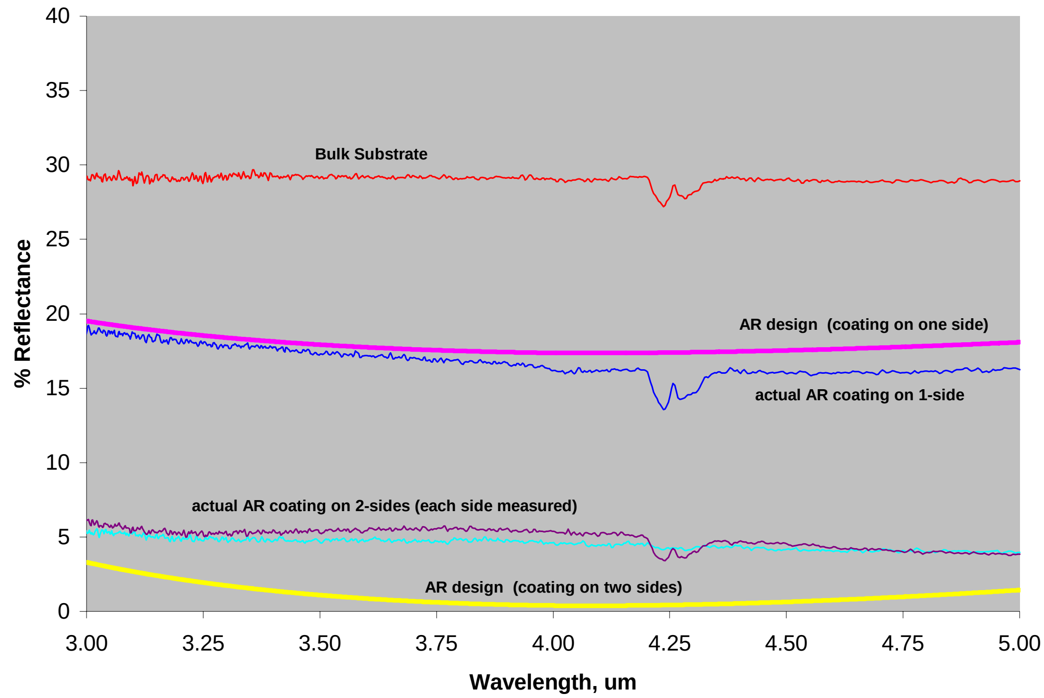


Figure 7.1. Relative Reflectivities for Coated and Uncoated Substrates. The software used for the AR coating designs is FilmStar, available from FTG Associates (http://ftgsoftware.com/).

Ideally, the AR coating should function also as a barrier coating to block both water absorption and UV light because both are needed to initiate the surface oxidation. Research done on a previous project has shown Al_2O_3 to be an effective oxygen and moisture barrier. Successful designs have used an alternating stack comprising several coating layers of 400-Å Al_2O_3/0.5-µm polymer. This design has been tested at ambient and accelerated test conditions of 85°C at 50% relative humidity and 60°C at 90% relative humidity. The purpose of the alternating stack is to provide adequate coverage of surface topography and debris as well as a tortuous path for ingress of both oxygen and moisture.

For our barrier layer experiments, both thick single-layer Al_2O_3 and polymer coatings were deposited over several As_2S_3 thin-film coated microscope slides. These samples were then tested in the accelerated environment exposure experiment.

7.2 Antireflection Coating Designs for Long-Wave Infrared

This work is still in the design phase. Because the As_2S_3 transmission is limited to wavelengths below 8 μm, As_2Se_3 will be used for applications in the 8- to 12-μm. Although many high-index materials are available, the challenge is to find a low-index material that works in this range. Ideally, as well as fulfilling the barrier requirements, the materials will be ones with which we have worked in the past and are familiar with their deposition requirements.

8.0 Photonic Device Fabrication

Excellent progress was made on custom chalcogenide glass research and photomodification studies. This research was followed by demonstrations of several essential infrared photonic devices. A single-mode waveguide was modeled, fabricated, and tested (Figure 8.1). The waveguide structure was designed for wave-guiding at 8.16 μm, a convenient quantum cascade (QC) laser wavelength. This work represents a key milestone for the Infrared Photonics project and the first reported LWIR single-mode waveguide demonstration.

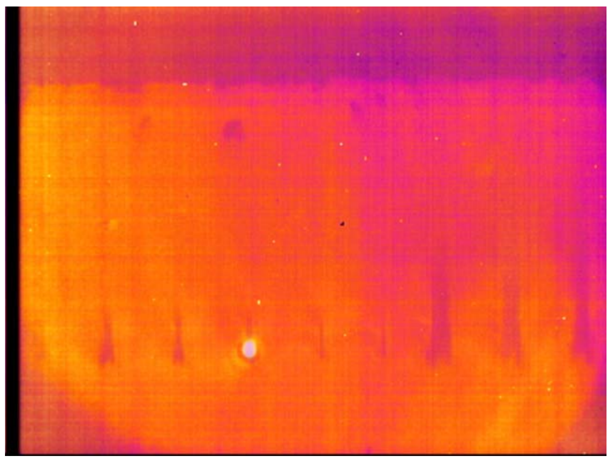
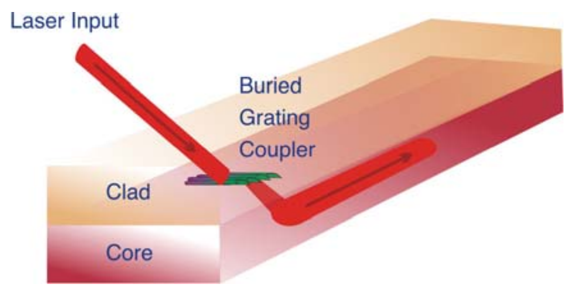


Figure 8.1. Single Mode Wave Guiding at 8.16-μm Laser Wavelength. The image shows laser light exiting the waveguide facet (bottom, left). The waveguides were direct-laser written 600 μm below the surface of the glass.

We also investigated the broadband holographic recording properties of chalcogenide glass. Our studies showed that the chalcogenide photomodification properties provide the basis for a broadly applicable single-step holographic medium that does not require chemicals to develop, stop, or fix the film. This investigation found that the chalcogenide film resolution is comparable to existing holographic media. The film properties have both superior operating temperature and an optical transmission range extending from the visible to about 12 μm wavelength. These findings revealed that holographic optical elements now can be designed and fabricated to function at the mid-wave or long-wave infrared. This is an important breakthrough because, to our knowledge, no other infrared holographic medium is available. To study the holographic properties, holographic diffraction gratings were recorded into thin chalcogenide glass films. Using holographic recording methods, we fabricated high-efficiency diffraction gratings with periodicities from 0.7 to 12.5 μm and film thickness from 0.2 to 8.0 μm. Properly designed, these gratings can function as buried grating couplers that can inject incident laser light efficiently into and out of the thin-film waveguide (Figure 8.2).



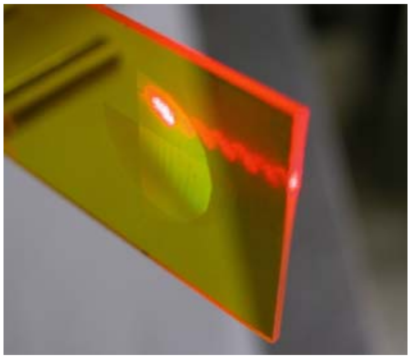
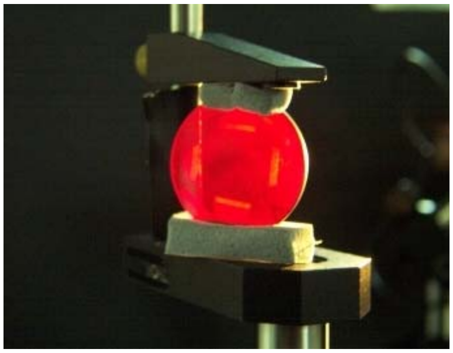


Figure 8.2. Conceptual Waveguide Coupler (left) and Practical Implementation of the Device (right). A microscope slide was coated with a 2-µm-thick chalcogenide glass film. A waveguide coupling grating was holographically recorded into the glass film. HeNe laser light is seen coupled into the slide and then guided to the edge.

Following these successful results, a long-wave infrared waveguide coupler was designed, fabricated, and tested (Figure 8.3). An 8-µm-thick As_2S_3 glass film was evaporated onto a 1.0-mm-thick ZnSe window. Two opposing 12.5-µm gratings were recorded into the film using holographic methods. Laser light (λ = 8.16 µm) was launched into the grating at incident angle such that the beam was diffracted at an angle greater than the critical angle for the ZnSe glass/air interface. After multimode wave guiding through the ZnSe substrate, laser light is seen exiting the second (right) grating coupler. Not only do the holographic gratings function as efficient waveguide couplers, they provide a simple method to significantly improve the quality of QC laser beam wavefront.



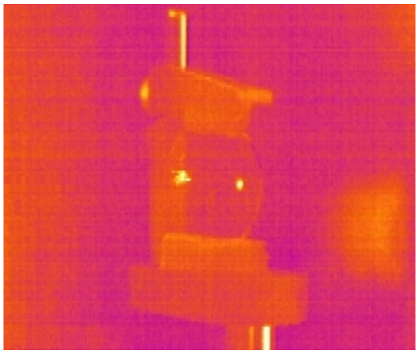


Figure 8.3. Infrared Waveguide Coupler (left) and Infrared Laser Light Coupling into and out of the Waveguide Structure (right). The laser light is seen scattering off the incident grating (left) and exiting the second (right) grating coupler after propagating within the waveguide.

Finally, the remarkable holographic properties of chalcogenide glass were demonstrated further using white light holographic recording methods. These white light holographic exposures, in chalcogenide thin films, demonstrated the superb recording resolution of the chalcogenide recording media (Figure 8.4).

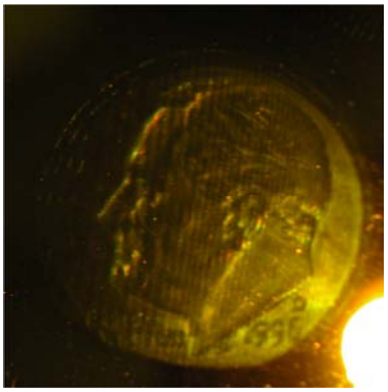


Figure 8.4. White Light Hologram Using Chalcogenide Thin Films. The dime mint letter "D" for Denver is plainly visible in the holographic recording.

9.0 Photonics Progress Summary

In summary, we have developed a unique capability to fabricate and characterize bulk and thin-film custom chalcogenide glass. Key research was performed to understand and control the photomodification properties of this glass. Anti-reflection and barrier layer coatings were developed for both mid-wave and long wave photonic applications. A single-mode waveguide device at LWIR wavelengths was laser written into bulk As_2S_3. Holographic diffraction gratings and white holograms have been recorded and characterized in chalcogenide glass films. The fabrication and demonstration of visible and infrared photonic devices establish the unique broadband holographic properties of chalcogenide glass. This work leverages PNNL's extensive experience with the photomodification properties of chalcogenide glass, along with the availability of a custom vacuum deposition system, extensive experience fabricating and characterizing chalcogenide glasses, and the newly developed holographic single-step recording methods.

Potential high-payoff applications of chalcogenide-based photonic components include telecom, mid–wave infrared, and long-wave infrared components, where traditional optical components are bulky, optically inefficient and require complicated mounting hardware. Chalcogenide-based photonics can be used to fabricate waveguide beam splitters, multiplexers, couplers, beam shaper, Bragg gratings, long-period gratings, mirrors, hybrid lenses, and other complex integrated optics. In many cases, fabrication of these optical elements would be impossible or impractical by any other method.

10.0 Project-Related Publications, Presentations, and Intellectual Property

10.1 Publications

Anheier NC, BR Johnson, and SK Sundaram. 2004. “Laser writing in arsenic trisulfide glass.” Chapter 8 in *Optoelectronic Materials and Devices -- Volume 1, 2004, Non-Crystalline Materials for Optoelectronics*, pp. 259–296, eds. G Lucovsky and M Popescu. INOE Publishing House, Bucharest, Romania (invited book chapter).

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Sundaram SK, BR Johnson, MJ Schweiger, JE Martinez, BJ Riley, LV Saraf, NC Anheier Jr., PJ Allen, and JF Schultz. 2004. “Chalcogenide glasses and structures for quantum sensing.” In *Photonics West 2004: Integrated Optoelectronics Devices, Quantum Sensing and Nanophotonic Devices*, Volume 5359, pp. 234–245. The International Society for Optical Engineering (SPIE), Bellingham, Washington.

10.2 Presentations

Sundaram SK, BR Johnson, MJ Schweiger, BJ Riley, JE Martinez, NC Anheier Jr., PJ Allen, PL Gassman, CE Fay, R Dieken, BG Potter, HJ Barnaby, P Lucas, and SA Macdonald. 2004. “Photo-modification of Chalcogenide Glasses.” Presented to the American Association for the Advancement of Science Annual Meeting, February 12-16, 2004, Seattle, Washington.

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Allen PJ, RT Baran, BE Johnson, MH Engelhard, BT Broocks, NC Anheier Jr., and SK Sundaram. 2004. "Surface Degradation of $As_{40}S_{60}$ Thin Films." Presented to the American Ceramic Society Glass & Optical Materials Division Fall 2004 Meeting, November 8, 2004, Cape Canaveral, Florida.

10.3 Invention Reports, Patents, and Other Intellectual Property

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Anheier NC Jr., SK Sundaram, BR Johnson, PJ Allen, PE Keller, JE Martinez, BJ Riley, F Liau, and A Laforge. November 2003. "Photonic Band Gap Structures Holographically Fabricated Using Chalcogenide Glass." Invention Report 14288-B.

Anheier NC Jr. October 2003. "Broadband Holographic Recordings Using Amorphous Chalcogenide Glass." Invention Report 14269-G.

Anheier NC Jr. and BD Cannon. November 2003. "Hybrid Holographic Optical Lens Assembly." Invention Report 14269-G Addendum.

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