Chalcogenide glass thin-film optics for infrared applications

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ABSTRACT

Chalcogenide glasses are increasingly used in infrared-transparent optical systems for space applications due to their relatively low density (compared to Ge or ZnSe), tunable spectral and thermo-mechanical properties, and molding capability. Remaining challenges include their application to thin-film optics and coatings. The high refractive indices of chalcogenide glasses ($n > 2.7$) suggest the possibility for high reflecting coatings based on few periods of alternating layers with high index contrast. As_2Se_3 thin film deposited by thermal evaporation is investigated using ellipsometry which show optical properties consistent with bulk material. Also we demonstrate a novel method for fabrication of anti-reflection coating using porous chalcogenide. Possibility of negligible extinction coefficient and low refractive index of this porous coating promises broadband suppression of undesired Fresnel reflections at the interface from infrared optics.
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Keywords: Chalcogenide glass, photonic crystal, Bragg's mirror, dielectric mirror, quarter wave stack, anti reflection coatings, porous chalcogenide

1. INTRODUCTION

Chalcogenide glasses are transparent over a wide range of the infrared electromagnetic spectrum, making them excellent material candidates for laboratory-based applications including infrared detectors and optics such as lenses and optical fibers. In addition, chalcogenide glasses have been studied extensively for next-generation optical applications, such as Raman gain [1], super-continuum generation [2], and for use as micro-structured fiber [3]. Chalcogenide glasses have comparatively high refractive indices, which is critical for photonic crystal applications. They also exhibit low density, as compared to ZnSe crystals, making them particularly well suited for space optics and especially remote sensing. The high transparency of these glasses in the infrared makes them promising materials for molecular sensing systems, as most organic substances and functional groups have signature absorptions in this spectral region.

In this report we experimentally demonstrate a high reflectivity Bragg mirror formed from alternating quarter-wavelength-thick layers of infrared glass and aluminum oxide. For instance, a quarter wave Bragg stack with 84% reflection in the wavelength range 4.0-5.5 microns requires just 3 periods of As_2Se_3 glass alternating with Al_2O_3 on silicon substrate. We are developing these mirrors for a Fabry-Perot spectrometer, which is part of a trace gas sensor based on quantum cascade lasers and intended for space applications [4-5].

In this report, we also explore fabrication of antireflection (AR) coating on silicon substrate using chalcogenide thin films. In infrared devices, AR coating is a key for suppression of undesired Fresnel reflections [6]. While graded index materials promise broadband suppression of reflection at the interface, this method demands smooth gradient of refractive indices from silicon substrate ($n = 3.42$) to the air ($n = 1$). Stacking of different bulk quarter wave films such as TiO_2, Al_2O_3 and SiO_2 only partially satisfies the conditions for graded index material [7], because availability of existing materials with suitable refractive indices is limited. In particular, bulk materials with refractive index below 1.20 are not found in nature. Novel nano structures such as nano-rodes [8] and pyramid shapes [9] have shown formation of refractive index gradient, but lithographic fabrication of such nano-structure is not compatible with roll-to-roll fabrication or application to curved surfaces.

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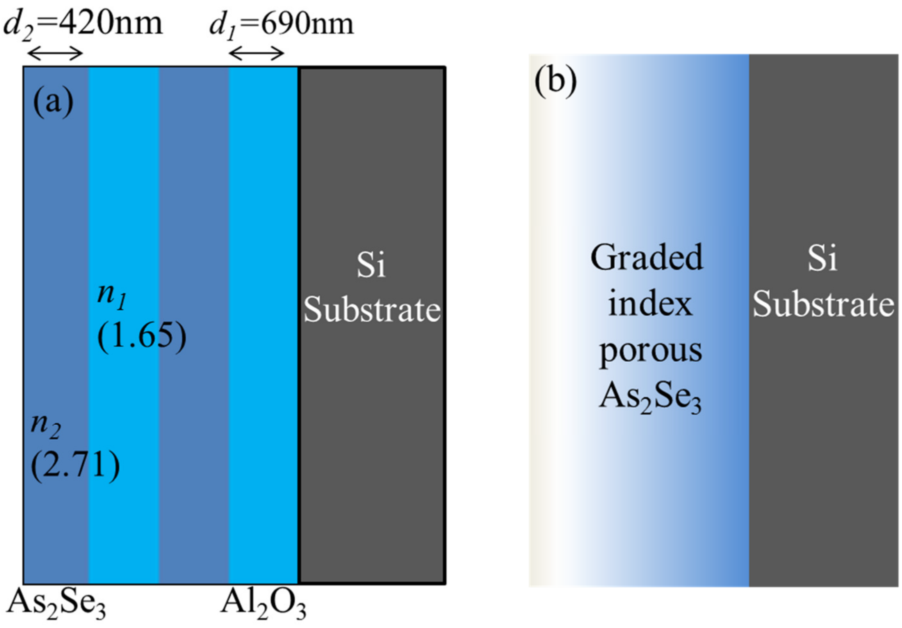


Fig 1. (a) Schematic diagram of a high reflection (HR) coating quarter-wave-stack Bragg's mirror, (b) Anti-reflection (AR) coating on Si substrate using graded index porous chalcogenide glass films.

Here we present the possibility of utilizing porosity to achieve low indices in an infrared transparent material, chalcogenide glass. We use method of Harris, developed to fabricate porous "gold-black" coatings, to introduce high degree of porosity in Chalcogenide thin films [10-11]. This method has been widely utilized for fabrication of metal black absorber coatings for bolometers [12-13]. The porous Chalcogenide films we produced resemble the metal black coatings in morphology. We successfully fabricated an AR coating in *single run* thermal evaporation process.

2. THEORETICAL CONSIDERATIONS

Fig. 1(a) presents a schematic of the quarter wave stack (QWS) on a Si substrate. The periodic stacks consist of alternating layers of Al_2O_3 and As_2Se_3. The refractive index for Al_2O_3 is taken from ref [14]. The refractive index of As_2Se_3 is measured using ellispometry. The individual thicknesses of the dielectrics are calculated according to the QWS conditions $d_i = \lambda_0/4n_i$, where i=1, 2 stands for dielectrics Al_2O_3 and As_2Se_3, respectively. The values determined for the thicknesses are indicated in Fig. 1(a).

The reflectance for Bragg's distributed mirror is given by,

$$R = \left(\frac{n_0 (n_2)^{2N} - n_s (n_1)^{2N}}{n_0 (n_2)^{2N} + n_s (n_1)^{2N}} \right)^2 \qquad (1)$$

where n_0 and n_s are refractive index of the air and the substrate Si respectively. N is the number of periodic stacks of Al_2O_3 and As_2Se_3. The reflectance increases with increasing number of periods. The theoretical reflectance maxima for 1, 2, 3 and 4 periods are 65%, 85%, 94% and 97% at 4.55 microns, respectively. The bandwidth is given by,

$$\lambda_0 = \frac{4\lambda_0}{\pi} \sin^{-1}\left(\frac{n_1 - n_2}{n_1 + n_2} \right) \qquad (2)$$

The calculated bandwidth is 1.4 microns according to eq(2).

3. EXPERIMENTAL METHODS

As_2Se_3 is melted in a rocking furnace at 650 C in a sealed quartz ampoule for 12 hours. The ampoule is removed and the glass is quenched in blowing air, following which it is annealed below its glass transition temperature to release thermal stress. The glass is then cut into circular substrates and ground into fine powder for thermal evaporation. HR coating is produced by three periods of Al_2O_3 and As_2Se_3 quarter-wave layers. A significant problem encountered with these coatings was that Al_2O_3 cracked or peeled-off from As_2Se_3 surface. In literature it is suggested that thermal expansion coefficient of chalcogenide films is much larger than that of Al_2O_3, which is responsible for large stress storage in these films. However, we found that annealing the film at 50 C for three hours and lower deposition rate minimized this problem.

In order to produce AR coating on silicon substrate, 1.5 micron thick bulk As_2Se_3 was evaporated as the first stack in a standard 10^{-5} Torr vacuum condition. For formation of porous stack, with refractive index lower than 2.7, the chamber was isolated by closing the high-vacuum valve. Then chamber was back-filled with 100 mTorr of N_2 pressure, which was followed by the 40 seconds of evaporation. After the first porous layer was completed, the high-vacuum valve was again opened for a few minutes in order to bring the chamber pressure to 10^{-3} Torr. This was followed by formation of a third layer with similar method at 300 mTorr pressure. This entire process was concluded in a single run without venting the chamber.

The infrared transmittance is measurement using a vacuum-bench BOMEM DA8 Fourier spectrometer with 77 K HgCdTe detector, KBr beam splitter, and globar source. Reflectance is measured using a mirror assembly. The initially focused incident beam of the spectrometer is collimated by a concave mirror and is incident on the sample at an angle of 8 deg. Reflected light is finally diverged at the appropriate acceptance angle to the detector collection optic by another concave mirror.

The optical constants n and k for the glass films were determined using a J. A. Woollam V-Vase ellipsometer. For these measurements, the substrate was coated with 200 nm of gold before depositing the glass. The WVASE32 modeling software accounted for all layers.

4. RESULTS

4.1 High Reflection Coating

Fig. 2 (left) presents the transmission spectra of As_2Se_3 chalcogenide glass. The thickness of the glass is ~4 mm. Fig. 2 (right) presents the fitted value of refractive index for 1.22 micron thick As_2Se_3 chalcogenide glass on 200 nm gold on Si substrate. The film was deposited by thermal evaporation. Refractive index of As_2Se_3 remains more or less constant with the value $n = 2.71$ for a wide range of wavelength range from 2-20 microns. Transmission Fig. 2 (left) is reduced beyond 15 microns wavelength due to absorption. Since the sample for transmission is thick, the loss here is significant, though the extinction coefficient κ measured by ellipsometry is smaller than the uncertainty.

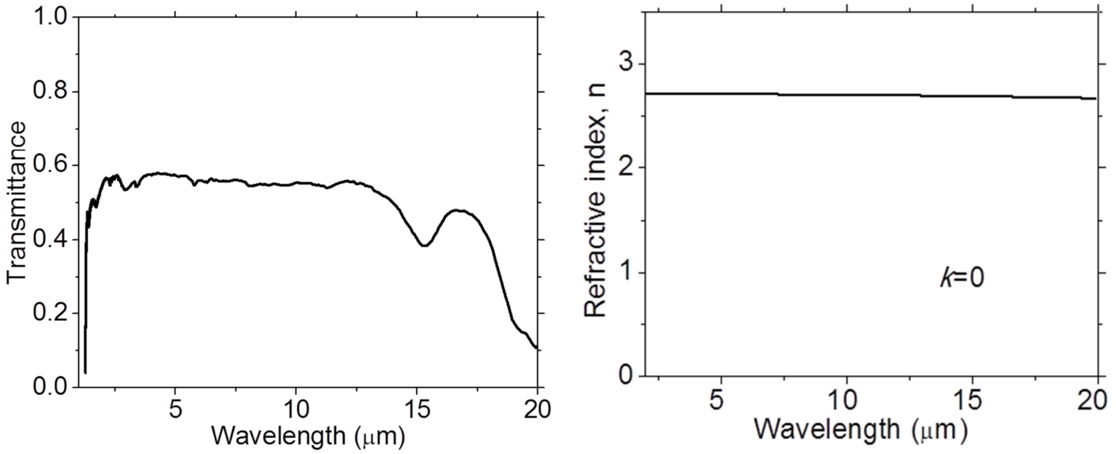


Fig. 2: (left) Transmission spectra through As_2Se_3. (right) refractive index of As_2Se_3 thin film measured by ellisometry (k~ 10^{-16}).

In fig. 3, red and black lines represent experimental reflectance spectra from a one and two period stack of Al_2O_3 and As_2Se_3, respectively, on a double sided polished Si wafer. The measured thicknesses of the Al_2O_3 and As_2Se_3 films are 690 nm and 420 nm respectively. We achieved 88% reflectance is achieved at 4.55 microns with bandwidth of ~1.4 micorns. However, deposition of Al_2O_3 on As_2O_3 remains a challenge because of high thermal expansion of As_2O_3. During evaporation of Al_2O_3 on As_2O_3 heats up and expands because of which the layers crack and peel off.

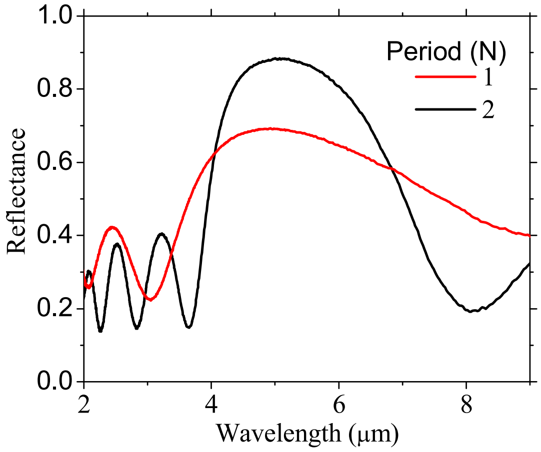
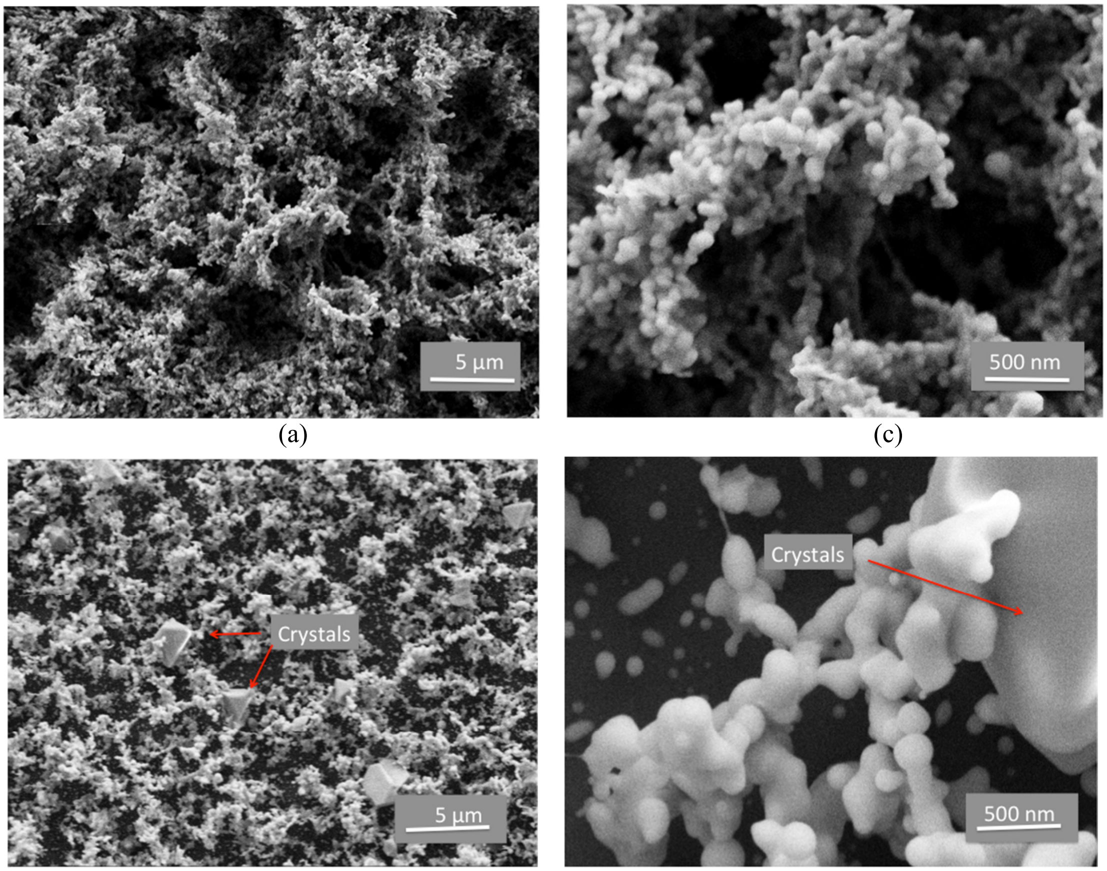


Fig. 3: Experimental reflectance spectra of 2 period of the Bragg mirror structure on double sided polished Si.

4.2 Antireflection coating

Figs. 4(a) & (b) present scanning electron microscope (SEM) images in top view of chalcogenide films produced at 100 & 300 mTorr pressure, respectively. The porosity increases with pressure and the structures in both the films appear formed of nanowires. The higher magnification images of both films in Fig 4 (b) & (d) clearly show that these nanowires consist of adjoining nanoparticles. Interestingly in film produced at higher pressure in Fig 4 (d) the particle size appears to be more than 200 nm, which is far larger than what is observed in Fig 4 (c). Films produced at 300 mTorr also have 0.5-1 micron size crystals, which can be responsible for scattering of light. However, for the longer IR wavelengths, light scattered from these structures will be negligible.



(a) (c)

(b) (d)

Fig. 4: SEM top view of porous chalcogenide film produced at 100 mTorr pressure at 30 µm (a,b) & 3 µm field of view (c,d).

Fig. 5 presents the cross section SEM image of graded index material. The refractive indices of silicon & bulk are As_2Se_3 3.42 and 2.7, respectively. Although the refractive index of porous stacks of As_2Se_3 remains unknown, it should be lower than the bulk value due to porosity. The refractive index of the chalcogenide layers produced in presence of N_2 pressure should be lower. The functional dependence of refractive index on porosity needs to be investigated through more experiments.

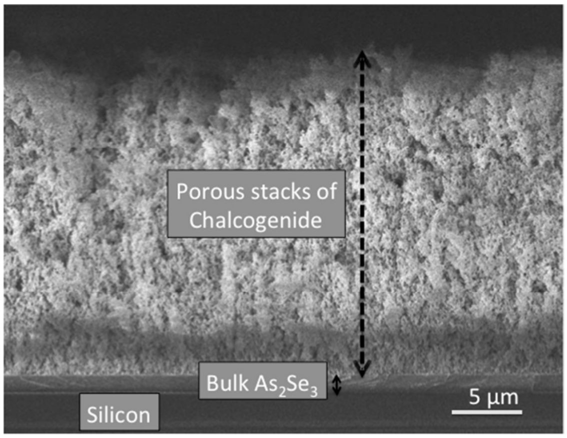


Fig 5: Cross section SEM image of graded index material

Figure 6 (left) and (right) present reflectance and transmittance measurements, respectively, of silicon substrate without and with graded index coating. It is evident that after formation of graded index material there is broadband suppression of reflection. At 15 micron wavelength the total transmittance is increased by 25% from its initial value.

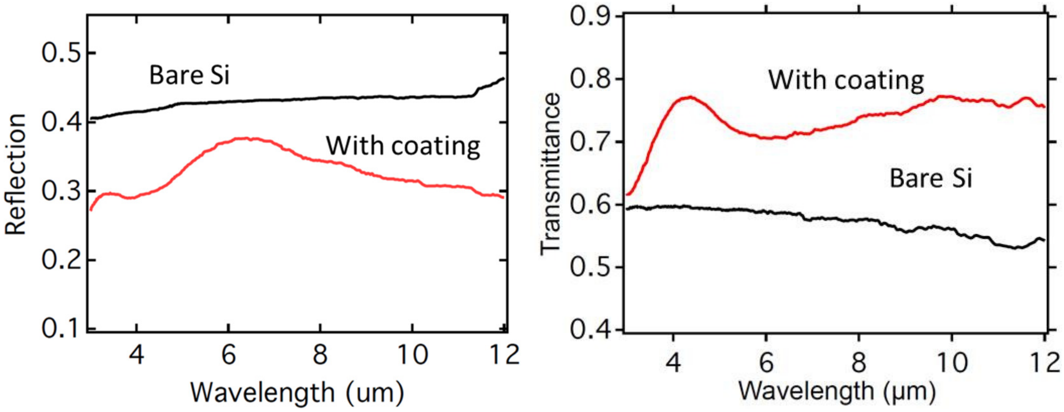


Fig 6: Reflectance and transmittance spectra of AR coating on Si. Black and red lines show reflectance/transmittance spectra for bare Si and AR coating on Si, respectively.

5. SUMMARY AND CONCLUSION

In this report, we demonstrate infrared high reflection and anti-reflection thin-film coatings formed from chalcogenide glass. We show that high reflection of 88% can be achieved using just a single stack of Al_2O_3 and As_2Se_3 on a double sided polished Si wafer. Anti- reflection coating is fabricated using porous chalcogenide in a single evaporation on a double sided polished Si wafer and 78% of transmission is achieved. This structure shows transmission enhancement up to 25% at 15 microns as compared to bare Si.

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REFERENCES

[1] R. Stegeman, G. Stegeman, P. Delfyett, L. Petit, N. Carlie, K. Richardson, and M. Couzi, "Raman gain measurements and photo-induced transmission effects of germanium- and arsenic-based chalcogenide glasses," Opt. Express 14, 11702 (2006).
[2] A.B. Seddon, "Chalcogenide glasses - A review of their preparation, properties and applications," J. Non-Cryst. Solids 184, 44 (1995).
[3] O. Fedotova, A. Husakou, and J. Herrmann, "Supercontinuum generation in planar rib waveguides enabled by anomalous dispersion," Opt. Express 14, 1512 (2006).
[4] A. V. Muraviev, D. E. Maukonen, C. J. Fredricksen, Gautam Medhi, and R. E. Peale, "Quantum cascade laser intracavity absorption spectrometer for trace gas sensing,"Appl. Phys. Lett. 103, 091111 (2013).
[5] Douglas Maukonen, Andrey V. Muraviev, Christopher J. Fredricksen, Joshua Colwell, Ammar Alhasan, Robert E. Peale, "High-sensitivity trace gas sensor at 30-km altitude," Proc. SPIE 9113, 25 (2014).
[6] Minfeng Chen, Hung-chun Chang, Allan S. P. Chang, Shawn-Yu Lin,2, J.-Q. Xi, and E. F. Schubert, "Design of optical path for wide-angle gradient-index antireflection coatings." Applied Optics Lett. 46, 6533 (2007).

[7] J.-Q. XI, Martin F. Schubert, Jong Kyu Kim, E. Fred Schubert, Minfeng Chen, Shawn-Yu Lin, W. Liu & J. A. Smart, "Optical thin-film materials with low refractive index for broadband elimination of Fresnel reflection." Nature Photonics 1, 176 (2007).
[8] Silke L. Diedenhofen, Gabriele Vecchi, Rienk E. Algra, Alex Hartsuiker, Otto L. Muskens, George Immink, Erik P. A. M. Bakkers, Willem L. Vos, and Jaime Go´mez Rivas, "Broad-band and Omnidirectional Antireflection Coatings Based on Semiconductor Nanorods." Adv. Mater. 21, 973 (2009).
[9] J. Zhu, Z. Yu, G. F. Burkhard, C. M. Hsu, S. T. Connor, Y. Xu, and Y. Cui, "Optical absorption enhancement in amorphous silicon nanowire and nanocone arrays." Nano letters 9, 279 (2008).
[10] L. Harris, "The transmittance and reflectance of gold black deposits in the 15- to 100 lm region." J. Opt. Soc. Am. 51, 80 (1961).
[11] L. Harris, R.T. McGinnies, B.M. Siegel, "The preparation and optical properties of gold blacks." J. Opt. Soc. Am. 38, 582(1948).
[12] Deep Panjwani, Mehmet Yesiltas, Janardan Nath, D.E. Maukonen, Imen Rezadad, Evan M. Smith, R.E. Peale, Carol Hirschmugl, Julia Sedlmair, Ralf Wehlitz, Miriam Unger, Glenn Boreman, "Patterning of oxide-hardened gold black by photolithography and metal lift-off." Infrared Physics & Technology 62, 94(2014).
[13] M. Hirota, Y. Nakajima, M. Saito, M. Uchiyama, "120 × 90 element thermoelectric infrared focal plane array with precisely patterned Au-black absorber." Sensors & Actuator 135, 146(2007).
[14] I. H. Malitson and M. J. Dodge, "Refractive Index and Birefringence of Synthetic Sapphire."J. Opt. Soc. Am. 62, 1405 (1972).