Properties and limitations of chalcogenide films

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Two chalcogenide films with composition Ge_{25}-xSb_{10}+xS_{65} (x = 0, 10) and $Te_{20}As_{30}Se_{50}$, called 2S1G and TAS, respectively, are studied. These materials have high linear and nonlinear refractive indices and present interesting photosensitive behavior toward bandgap light. Further, these chalcogenides glasses can be deposited in an amorphous thin film for optical coatings or waveguides. Their properties and limitations, including their photoinduction effects, nonlinear Kerr effect, photodiffusion of silver, and aging, are discussed.

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Chalcogenide glasses are based on the chalcogen elements S, Se, and Te. These glasses are formed by the addition of other elements such as Ge, As, Sb, and Ga, among others. They present low phonon energies and are generally transparent from visible up to infrared spectral range. Photoinduced phenomena have also been observed in amorphous chalcogenides. Chalcogenide glasses are sensitive to the absorption of electromagnetic radiation (EMR) and show different photoinduced effects as a result of illumination. Their absorption edge can shift either toward longer or shorter wavelengths (like photodarkening and photobleaching effects, respectively), and a modification of their refractive indices can be obtained under light irradiation of appropriate energy and intensity. When they are exposed to short laser pulses with high peak power, large Kerr-type nonlinearity can be induced[1,2].

In this letter, two types of compositions for chalcogenide films were examined, $Ge_{25-x}Sb_{10+x}S_{65}$ (x = 0, 10), called 2S1G, and $Te_{20}As_{30}Se_{50}$, called TAS, which were prepared in the form of rods. These compositions were selected because of their remarkable properties such as large optical window, covering the spectral region from 0.5 to 11 μm for 2S1G and from 1.3 to 18 μm for TAS, excellent resistance to devitrification, good durability in water, and solvent corrosion[3]. Some observations on the photoinduced effects on optical coatings like nonlinear effects, silver photodiffusion in 2S1G glass, and aging of single layers were described.

In the deposition process, two techniques were used. First, for the electron beam deposition (EBD) method, the equipment used was Balzers BAK 600 evaporation plant. It is a typical EBD equipment used for the preparation of coatings associated with optical monitoring in transmission[3] in order to control the manufacture of single layers and passband filters. For all coatings, color filters were used to avoid the influence of light absorption during deposition due to the bandgap energy of the materials located in the visible spectral range (Schott OG 550 and RG 830 for 2S1G and TAS, respectively). For photodiffusion phenomena, a silver target of 99.99% purity was used, and the deposition rate employed to manufacture the silver layer was 0.1 nm/s with an order pressure of 1×10^{-6} mbar. For the second deposition method, 2S1G single layers manufactured by R. F. Magnetron Sputtering (RFMS) were prepared in Ar gas at 13.56 MHz. The base pressure was varied within the range 5×10^{-3} to 5×10^{-2} mbar, the R. F. sputtering power was between 10 and 50 W, and the deposition rate was about 10 to 15 nm/min. The target to substrate distance was about 5 to 10 cm with rotating substrates.

For optical coatings, three types were considered: single chalcogenide layers (TAS, 2S1G), also known as optical planar waveguides, passband Fabry-Pérot filters, and metallochalcogenide filters. A narrow band-pass filter centered at 1550 nm could be described by the following formula: substrate – $(\text{H-L})^n$ – pCh – $(\text{L-H})^n$ – Air, where L (cryolite) and H (ZnS or Ch) carried a low-index and high quarter wavelength layer, and the notation Ch is 2S1G or the TAS high index layer[3–5]. The charac-

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terization methods for determining optical properties, refractive index, chemical composition, structure, topography, and morphology have been investigated for single films deposited by the EBD and RFMS techniques. Both methods gave film structural organizations and chemical compositions that were very close to the bulk glass target as confirmed by Raman scattering analysis and energy dispersive spectroscopy measurements[3]. For the photoinduced characterization of single layers and pass-band filters, spectrophotometry methods have been used within the spectral range of 400 to 1700 nm[3,5]. Certainly, the band-pass filter with a median chalcogenide layer (spacer) is more complicated to implement than a single layer but more appropriate to use in observing the response and measuring the peak wavelength shift of the Fabry-Perot filter as a function of light exposure (halogen lamp 300 W). It could easily reveal the increase or decrease in optical thickness for both TAS (photodarkening) and 2S1G (photobleaching) film spacers. The following refractive index values were obtained for the TAS and 2S1G films: $n_{\rm TAS} = 2.9$, $\Delta n_{\rm TAS} = +\ 0.05$ at 1.55 μm, and $n_{\rm 2S1G} = 2.4$, $\Delta n_{\rm 2S1G} = -0.02$ at 1.3 μm[4,5].

To determine the Kerr nonlinear coefficient, Z-scan methods and the nonlinear image technique with phase object (NIT-PO) were applied to characterize the third-order response of the chalcogenide glasses. These two methods are necessary since the Z-scan method is a single beam method that requires several laser shots with high-intensity lasers to produce one measured value of the complex nonlinear index coefficient. This method could mask completely photoinduced effects. Nonlinear experiments were performed using a Nd:YAG laser (1064 nm, 15 ps, 10 Hz). Recently, temporal variations in the phase contrast (NIT- PO) of TAS films for intensities above 1.2 GW/cm^2 have been demonstrated to reveal the presence of cumulative photoinduced effects. These effects change the refractive index and lead to an ablation threshold between 1.2 and 2 GW/cm^2, masking the nonlinear response of the sample in picosecond regime[6].

In examining bright Kerr solitons in 2S1G chalcogenide waveguides, an experimental setup was used, which was composed of either a laser source Nd:YAG, a 700-ps pulse duration microchip laser at 1.06 μm, or a 5-ps amplified fiber laser operated at 1.53 μm. The nonlinear refractive index n_2 (10^{-18} m^2/W) and nonlinear absorption β (cm/W) obtained at 1.06 μm were $n_2 = 4.5$ and $\beta < 0.05$ for $Ge_{15}Sb_{20}S_{65}$ bulk glass and film, $n_2 = 3.1$ and $\beta = 0.2$ for $Ge_{25}Sb_{10}S_{65}$ film, and $n_2 = 900$ and $\beta = 425$ for TAS film . Another limitation caused by photoinduction was noted during the propagation of Kerr solitons in 2S1G waveguides[7]. Aside from the observation of spatial solitons, how glass photosensitivity could affect the evolution of self-focused laser beams for long illumination times was investigated. For the initial soliton regime, photosensitivity was revealed by broadening the output intensity profile. The perturbation of soliton propagation became significant after more than 1 min of exposure. For the glass compositions used, the influence of the Kerr effect and photosensititivity could be easily dissociated since they induced fast focusing and slow defocusing effects, respectively. Initially, the photosensitivity tended to broaden the output beam, then divided it in such a way that a low-intensity region appeared, where the maximum of soliton intensity was previously seen.

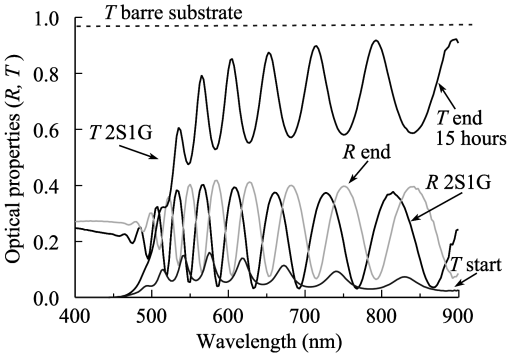

Fig. 1. Measured transmittance and reflectance curves of silica-2S1G-Ag (20 nm)-air filter before (T start) and after illumination (T final 15 h) with a halogen-quartz light.

For the photodiffusion of silver, two metal/chalcogenide structures were examined by using EBD. These were defined by substrate-pCh-M-air and silica-(HL)^{2}2Ch-Ag-2Ch (HL)^2-air, where Ch and M are 2S1G and silver (silver thickness is up to 20 nm), respectively. At room temperature, a KG3 Schott filter and a quartz-halogen lamp (280 W) were used to illuminate the sample across a pinhole for several hours[8]. Evolution of the optical properties of the filter was monitored (Fig. 1).

The rate of Ag dissolution was adapted to the Ge-Sb-S glass system. As compared to the raw 2S1G film, the optical transmittance of doped parts was decreased, and the absorption edge was shifted toward the long wavelengths of the spectrum. After 15 h of illumination, photodoping seemed to have been completed, forming a new single inhomogeneous layer with more absorption in the visible range than the initial 2S1G film. The experimental curves of the optical properties reveal that the homogeneous layer model could not be used to identify the optical constants of the 2S1G doped Ag layer. These observations were confirmed by scanning electron microscope (SEM), which showed the presence of silver nanograins on the surface of the sample after exposure (Fig. 2). Electronic data system analysis of the 2S1G (Ge_{15}-Sb_{20}-S_{65}) film photodoped with silver identified the chemical composition of the film (Ge : Sb : S : Ag = 16 : 23 : 56.6 : 4.4) after 15 h of illumination, which was compatible with the theoretical composition.

This photodoped technique could also be used for a lo-

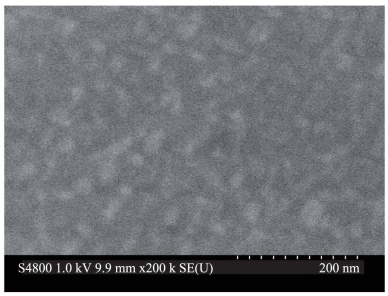

Fig. 2. SEM image of the photodiffusion effect of silver through the 2S1G film deposited on silicon after 15 h of illumination, with a residual silver layer on the sample surface still visible.

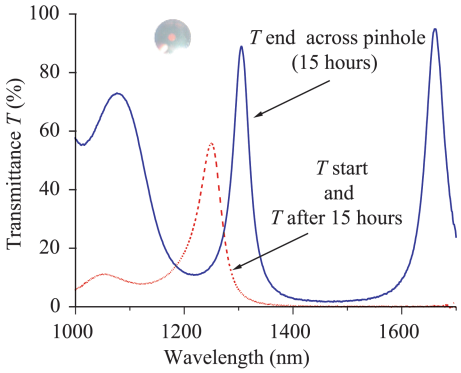

Fig. 3. Photodiffusion effect of silver on optical filter silica-$(HL)^2$ 2Ch-Ag-2Ch $(HL)^2$-air at 1550 nm.

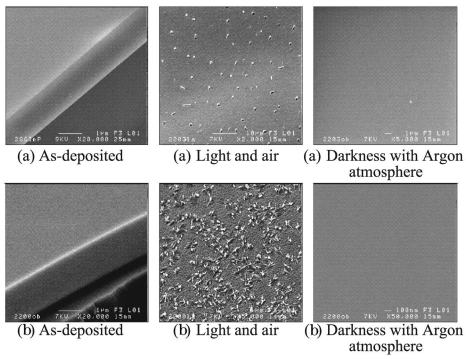

Fig. 4. SEM images of (a) 2S1G and (b) TAS EBD films as deposited and exposed to light with air atmosphere or darkness with Ar atmosphere for 6 months.

cal refractive index change that allows optical waveguide fabrication, as shown in Fig. 3, for a photosensitive band-pass filter. In this structure, the silver layer is placed at the center of the spacer of the band-pass filter. After photodiffusion of silver through its coating structure due to light exposure, a band-pass filter was set up with low residual optical losses.

To conclude, the aging of TAS and 2S1G films was studied in relation with the applications of chalcogenide films as, for example, narrow band-pass filters or optical waveguides. For the composition of chalcogenide films, the influence of exposure to natural light and humidity was considered. Thus, some EBD films were exposed under atmospheric conditions, while other films were protected from light by keeping them in the dark, or from humidity by maintaining them in a glove-box under Ar atmosphere (few ppm of $[H_2O]$). The photosensitivity of both TAS and 2S1G thin films was examined by following the evolution of their bandgap during aging. After six months' exposure to light and air atmosphere, their transmittance curves were found to shift toward shorter and longer wavelengths. Evidence of a photo-oxidation process on the surface of the chalcogenide films was determined by following the evolution of the SEM images (Fig. 4), which showed the growth of microcrystals attributed to arsenic trioxide in the case of the TAS films. For the 2S1G films, degradation due to photosensibility was also observed, but this phenomenon was stronger in the TAS films.

In conclusion, two chalcogenide compositions (TAS and 2S1G) were studied owing to their intrinsic properties which have potential applications in the manufacture of optical components, such as optical waveguides and optical thin film filters. However, several limitations were identified in Kerr soliton propagation in chalcogenide waveguides, film aging, or metal photodiffusion. Photoinduced behaviors were not clearly understood, which warrants further complementary experimental studies on the mechanism of photoinduction in the transparent spectral domain for optical nonlinearity (ONL) properties. Further, choice of chacolgenide composition, deposition method, and thickness of the silver layer, as well as the power and exposure time of the incident light should be considered. Photosensitive chalcogenide films react with environmental conditions catalyzed by light exposure, such as humidity and the presence of oxygen. In order to retain their advantages owing to their photosensibility, film protection or a barrier must be developed to avoid rapid optical coating deterioration. Thus, the wide range of photoinduced phenomena exhibited by chalcogenide glasses make them suitable for a variety of optical applications, such as in the correction of spatial uniformity of filters or the fabrication of integrated optical components and devices like selective optical filters, couplers and modulators, and planar waveguides for soliton Kerr propagation for ultrafast optical application. Overall, the discussions above outline the properties and potential applications of chalcogenide films, as well as their limitations which can be addressed through further research in this field.

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References

1. A. B. Seddon, J. Non-Crystal. Solids **184,** 44 (1995).
2. A. Zakery and S. R. Elliott, J. Non-Crystal. Solids **330,** 1 (2003).
3. V. Nazabal, M. Cathelinaud, W. D. Shen, P. Nemec, F. Charpentier, H. Lhermite, M. L. Anne, J. Capoulade, F. Grasset, A. Moreac, S. Inoue, M. Frumar, J. L. Adam, M. Lequime, and C. Amra, Appl. Opt. **47,** C114 (2008).
4. W. D. Shen, M. Cathelinaud , M. Lequime, V. Nazabal, and X. Liu, Opt. Commun. **281,** 3726 (2008).
5. W. D. Shen, M. Cathelinaud, M. D. Lequime, F. Charpentier, and V. Nazabal, Opt. Express **16,** 373 (2008).
6. K. Fedus, G. Boudebs, Cid B. de Araújo, M. Cathelinaud, F. Charpentier, and V. Nazabal, Appl. Phys. Lett. **94,** 061122 (2009).
7. M. Chauvet, G. Fanjoux, K. P. Huy, V. Nazabal, F. Charpentier, T. Billeton, G. Boudebs, M. Cathelinaud, and S. P. Gorza, Opt. Lett. **34,** 1804 (2009).
8. C. C. Huang and D. W. Hewak, Thin Solid Films **500,** 247 (2006).