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All-chalcogenide middle infrared dielectric reflector and filter

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ABSTRACT

We have fabricated a dielectric reflector and a passband filter, both with first order photonic bandgaps in the middle-infrared region around $\lambda = 4$ μm. The devices were made from alternating amorphous $Ge_{25}S_{75}$ and $Ge_{15}Te_{85}$ chalcogenide films with high transparency in the middle infrared region stacked in multilayers. Due to high thickness accuracy and periodicity of prepared multilayers we also observed second order photonic bandgaps at $\lambda \sim 1.4$ μm. The experimental data were in good agreement with theoretical predictions. The work focused on investigation of compositional homogeneity, surface roughness, thermal and optical properties of individual amorphous $Ge_{25}S_{75}$ and $Ge_{15}Te_{85}$ films. We confirmed chalcogenide materials as being of suitable choice for designing middle-infrared quarter wave stack devices. FT-IR reflectance spectra confirmed occurrence of 99.4% stopband near $\lambda = 4$ μm for fabricated reflector and narrow ~50% passband of prepared filter near $\lambda = 3.934$ μm.

1. Introduction

Optical elements based on multilayer quarter wave stacks (QWS) [1,2] play an important role in current optical devices. Application of QWS devices bears the advantages in high-efficiency of reflectance ($R > 99\%$), reduced optical losses (in units of dB) and possibility to tailor optical properties from ultraviolet to infrared frequencies depending on materials composition and multilayer design. Good optical quality of dielectric films, high refractive index difference, materials compatibility, chemical stability and reproducible deposition are demanded to achieve the high quality QWS elements [3,4].

Variety of dielectric materials can be used for fabrication of QWS (AlInN/GaN, Si/SiO_2, SiO_2/TiO_2, etc.) [5–7] including the multilayers of chalcogenide and polymer films (As_2Se_3/PEI, $Ge_{33}As_{12}Se_{55}$/PAI, $Ge_{20}Se_{80}$/PS) [8–10] ranging photonic bandgaps from ultraviolet, visible to near infrared regions. The utilization of traditional materials in designing middle-infrared QWS devices is limited by presence of either long wavelength absorption edges (nitrides, oxides) or significant absorption bands (oxides, polymers), e.g. –OH, $–CH_x$, $–NH_x$, –CN groups etc. The middle-infrared QWS devices could be made from multilayers based on Ge/SiO_x films designed for night vision band $\lambda = 3$–5 μm [11], Te/Polystyrene system used for laser band $\lambda = 8$–12 μm [12] or crystalline halides and chalcogenides, i.e., YF_3/ZnS multilayers with meteorology applications in $\lambda = 3$–16 μm range [13] and CdTe, HgTe systems used for far infrared wavelengths $\lambda = 15$–70 μm (applications in astronomy) [14]. Chalcogenide bulk glasses and thin films [15] are well known as materials having high transparency in the infrared range of $\lambda = 0.5$–20 μm depending on chalcogenide composition, see Fig. 1. Binary glasses based on compounds of sulfur, selenium and tellurium have broad range of refractive indices, i.e., $n = 2$–3.6 in IR region.

In this study, we report fabrication of an all-chalcogenide dielectric reflector and a passband filter with photonic bandgaps around $\lambda = 4$ μm. Demanded contrast in the refractive index of 17-layer all-chalcogenide reflector and filter was achieved by alternating amorphous $Ge_{25}S_{75}$ and $Ge_{15}Te_{85}$ films, where $\Delta n = 1.35$ at 4 μm. The occurrence of photonic bandgaps was confirmed by IR reflectance measurement. We also quantified compositional homogeneity, surface roughness, and thermal properties of chalcogenide films. This work is based on our previous study, where we demonstrated preparation and optical performance of the all-chalcogenide near infrared QWS devices [16–18].

2. Experimental techniques

The all-chalcogenide dielectric reflector and filter were deposited by vacuum evaporation technique. The chalcogenide $Ge_{25}S_{75}$ ($n \sim 2.07$ at $\lambda = 4$ μm, $d = 485$ nm) films were thermally evaporated from corundum crucible placed in Mo boat using $Ge_{25}S_{75}$ bulk glass as source at residual pressure ~10^{-4} Pa and deposition rate ~1 nm/s. The $Ge_{15}Te_{85}$ films ($n \sim 3.43$ at $\lambda = 4$ μm, $d = 119$ nm) were deposited by flash evaporation from powdered bulk material (particle size < 0.4 mm) at ~10^{-4} Pa and deposition rate ~0.3 nm/s. The flash evaporation has been developed in our labs and helps avoiding phase separation in vapors, which is well pronounced during conventional thermal evaporation, if materials with high differences in partial pressures are used [19]. The reflector and filter were deposited on polished IR transparent Si wafers. In both devices the multilayer sequence started with $Ge_{25}S_{75}$ film at bottom. The filters

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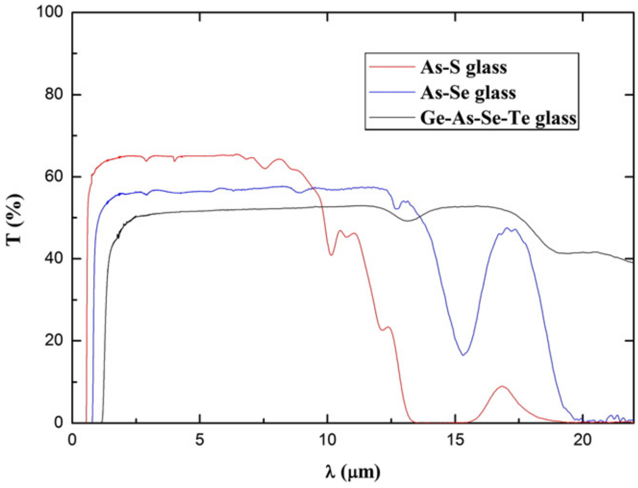

Fig. 1. Chalcogenide glasses are highly transparent in the infrared region. Transparency window is red-shifted with heavier atoms in glassy matrix, i.e., from sulfur to tellurium.

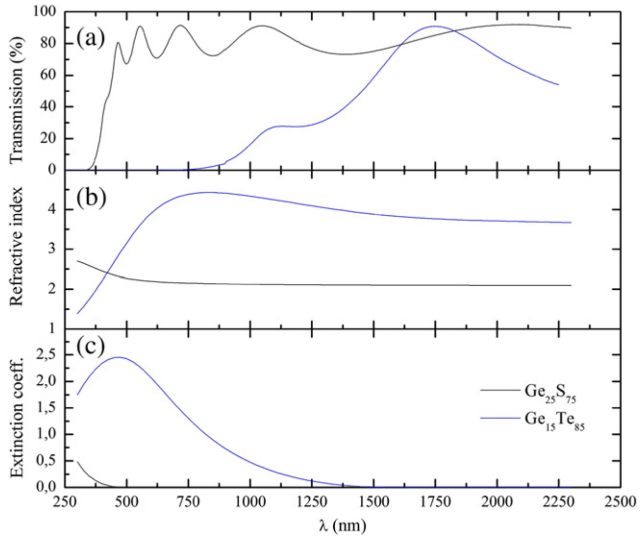

Fig. 2. Optical transmission spectra of the individual $Ge_{25}S_{75}$ and $Ge_{15}Te_{85}$ films are shown after annealing ($T = 110$ °C, 1 h) (a). The optical functions $n(\lambda)$ and $k(\lambda)$ of the films are depicted in (b) and (c), respectively. The refractive index difference was determined from extrapolation of $n(\lambda)$ dependence to $\lambda = 4$ μm.

consisted of a low index spacer sandwiched between two reflectors, i.e., $4\times(Ge_{25}S_{75}/Ge_{15}Te_{85})$ reflector/$Ge_{25}S_{75}$ spacer/$4\times(Ge_{15}Te_{85}/Ge_{25}S_{75})$ reflector. The $Ge_{25}S_{75}$ spacers had thickness $d = 1940$ nm, i.e., four-times thicker than the individual $Ge_{25}S_{75}$ film in the reflectors. After deposition, both the reflector and the filter were annealed at $T = 110$ °C ($0.85\times T_g$ of $Ge_{15}Te_{85}$ films) for 1 h in a vacuum oven at residual pressure ~5 Pa to stabilize the as-deposited chalcogenide films. In the following text, we will always refer properties of the annealed chalcogenide reflectors or the annealed filters.

Composition of chalcogenide films was analyzed by scanning electron microscope (JEOL JSM-5500LV, accelerating voltage 20 kV) equipped with Energy-Dispersive X-ray micro-analyzer (IXRF Systems) and detector (GRESHAM Sirius 10). Cross-sectional SEM images were captured by the same facility at accelerating voltage of 10 kV. SEM images were used to confirm periodicity of annealed chalcogenide films in the reflector and the filter. Optical spectra of chalcogenide films were recorded using an UV–VIS-NIR spectrometer (Jasco V-570) in the spectral range of $\lambda = 0.5$–2.3 μm. Experimental ellipsometric data were recorded from $\lambda = 0.3$–2.3 μm at angles of incidence 35–65° with step of 10° using spectroscopic ellipsometer (VASE, J.A. Woollam Co., Inc). The optical functions, i.e., $n(\lambda)$, $k(\lambda)$ and thicknesses of studied chalcogenide films were evaluated by fitting ellipsometric Ψ and Δ spectra using the Tauc–Lorentz dispersion formula in the entire spectral region [20]. The Cauchy formula was used to fit the optical function of studied samples in transparent region [21]. The surface roughness of individual chalcogenide films was evaluated using Bruggeman effective medium approximation (EMA) [22]. The surface roughness, R_q, of films was determined by using atomic force microscopy (Solver Pro M Atomic Force Microscope) in semi-contact mode using method of least squares according to the formula $R_q = [\Sigma(z_i - z_{ave})^2/N]^{1/2}$, where z_i is the height of a given point, z_{ave} is the average height in a given area and N is the number of points in the area. Surface area of 5×5 μm was scanned at scan rates 0.5–1 Hz. Glass transition temperature T_g of chalcogenide films was determined in the range of $T = 30$–450 °C at heating rate $\upsilon = 10$ K min^{-1} by differential scanning calorimetry (DSC 822^e, Mettler–Toledo) under dry nitrogen. Films were peeled off from substrates (10 mg) and encapsulated in aluminium pans. Middle-infrared transmission spectra were recorded against Si substrate under nitrogen atmosphere by using the FT-IR Nicolet Nexus spectrophotometer in the spectral range of $\lambda = 2$–8 μm.

3. Results and discussion

Composition of prepared thin films was confirmed to be $Ge_{24.7}S_{75.3}$ and $Ge_{15.8}Te_{84.2}$ with standard error of ±0.3 at.%. Fig. 2a shows optical transmission spectra of the $Ge_{25}S_{75}$ and the $Ge_{15}Te_{85}$ films after annealing (110 °C, 1 h). Fig. 2b,c depicts optical functions $n(\lambda)$ and $k(\lambda)$ of the chalcogenide films calculated from best model fit to experimental ellipsometric data. The optical functions of chalcogenide films at $\lambda = 4$ μm were determined by extrapolation of best model fit ellipsometric data. Absorption of the $Ge_{25}S_{75}$ films was measured up to $\lambda \sim 500$ nm while $Ge_{15}Te_{85}$ films exhibited absorption up to $\lambda \sim 1500$ nm (Fig. 2c). Absorption of films was far from the middle infrared range ($\lambda = 3$–5 μm) and did not negatively influence position of photonic bandgaps of the reflector and the filter. Thickness values satisfying the QWS condition [4] were calculated to be $d_{Ge25S75} = 485$ nm and $d_{Ge15Te85} = 119$ nm. Maximum deviation in the films thickness was calculated to be ±9 nm (ellipsometric data), i.e., ~1.9% for the $Ge_{25}S_{75}$ films and ~3.1% for the $Ge_{15}Te_{85}$ films. The surface roughness of chalcogenide films was found to be $R_q = 2.73 \pm 0.05$ nm ($Ge_{25}S_{75}$ films) and $R_q = 1.72 \pm 0.05$ nm ($Ge_{15}Te_{85}$ films) according to AFM measurements. The surface roughness of films according to EMA approximation [22] (ellipsometry) was found to be $R_q = 3.47 \pm 0.07$ nm ($Ge_{25}S_{75}$ films) and $R_q = 1.02 \pm 0.07$ nm ($Ge_{15}Te_{85}$ films), respectively. We did not include either some interfacial mixing or surface roughness of individual layers in theoretical reflectance calculation of the multilayers. The prepared chalcogenide reflector, filter and individual $Ge_{15}Te_{85}$ film (T_g values close $T = 130$ °C and crystallization temperature $T_C = 220$ °C) were found to be thermally stable against crystallization at annealing temperature 110 °C. Values of glass transition temperature ($T_g \sim 360$ °C for $Ge_{25}S_{75}$ film) together with optical constants, surface roughness, thickness and composition analysis are summarized in Table 1. Annealing of chalcogenide films provides thermodynamically stable samples due to relaxed structure with lower free energy and the devices become less sensitive to any further structural changes, namely

Table 1

Measured values of glass transition temperature (T_g) of the $Ge_{25}S_{75}$ and the $Ge_{15}Te_{85}$ films, refractive indices ($n_{\lambda=4\mu m}$), thickness (d), surface roughness (R_q, R_{EMA}) and compositions (x) are summarized in the table.

	$Ge_{25}S_{75}$	$Ge_{15}Te_{85}$
x (at.%)	(Ge) 24.7 ± 0.5, S (75.3) ± 0.5	Ge (15.8) ± 0.5, (Te) 84.2 ± 0.5
n ($\lambda = 4$ μm)	2.07 ± 0.01	3.42 ± 0.01
d (nm)	485 ± 7	290 ± 7
T_g (°C)	360 ± 3	130 ± 3
R_q (nm)	2.73 ± 0.05	1.72 ± 0.05
R_{EMA} (nm)	3.47 ± 0.07	1.02 ± 0.07