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Photo-induced effects of the virgin $Ge_{24.9}Sb_{11.6}S_{63.5}$ film

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ABSTRACT

Amorphous $Ge_{24.9}Sb_{11.6}S_{63.5}$ film was prepared through thermal evaporation. A blue shift of the optical band gap by approximately 100 meV was observed as a result of self-bleaching process of protected film aged for two years. The magnitude of the light induced blue shift of the optical band of the virgin film is primarily dependent on the light penetration depth and on the light intensity. The kinetics of photo-bleaching follows the stretch exponential function with a formal rate of bleaching depending on the light intensity while the saturated state is independent from the light intensity. The far infrared spectra indicate that ageing, illumination by over-band gap-photons and annealing of the virgin film are mainly accompanied by the film network ordering. Illumination by UV light photons led to a blue shift accompanied by the significant oxidation as evidenced by the results of the far infrared spectra and the energy dispersive analysis.

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1. Introduction

Chalcogenide glasses are known as materials with various interesting properties and applications such as high optical transmission in the mid to far infrared spectral region, light emission, non-linear optics, memory, sensor applications, and photo-induced phenomena. Renewed attention has been dedicated to Ge–Sb–S glasses and thin films in recent years, see e.g. [1–7]. The reason for the increasing attention is the large glass-forming region [8], the stability of the prepared glasses and the absence of any dangerous element such as the commonly used As. Among the various properties studied, the research is also focused on the interaction of the thin Ge–Sb–S films with light and the ageing of Ge–Sb–S glasses and amorphous films. Charpentier et al. also recently studied photo-sensitivity and protected ageing in $Ge_{15}Sb_{20}S_{65}$ chalcogenide films. The results obtained can be briefly summarized as follows: (i) after six months of exposure of $Ge_{15}Sb_{20}S_{65}$ chalcogenide film to natural light and humidity a blue shift of the optical band gap was observed by approximately 170 meV, while in the case of the sample aged for sixth months, but protected against humidity and natural light, a blue shift in the gap was observed at only approximately 50 meV. (ii) The considerable blue shift (≈170 meV) is attributed to a diffusion of the oxygen into the film and to subsequent formation of Ge oxysulfides. This result seems to be in agreement with the role of oxygen in photo-bleaching of amorphous $Ge_{30}S_{70}$ films [6]. Kawaguchi et al. [9] with their measurements of the oxygen depth profiles with electron spectroscopy for chemical analysis demonstrated, however, that only a fairly thin layer (≈200 Å) of the Ge–S film is oxidized, even under prolonged illumination. It was consequently suggested that photo-oxidation enhances photo-bleaching although it is not the only origin of the blue shift in the optical band gap. It should also be noted that photo-oxidation would be sensitive to the photon energy and photon flux used for the illumination. In this paper we summarize the results of our relatively extensive experimental examination of ageing and photo-induced bleaching of $Ge_{24.9}Sb_{11.6}S_{63.5}$ amorphous film. We selected this chemical composition because the average coordination number is 2.58, assuming that the coordination numbers for Ge, Sb and S are 4, 3 and 2, respectively. We thereby expect by following Phillips–Thorpe [10] approach that the network of this film is over-constrained and that the natural ageing due to network relaxation will proceed quite slowly. In addition, the $Ge_{24.9}Sb_{11.6}S_{63.5}$ film is stoichiometric film hence we expect the absence of the wrong homopolar (Ge—Ge, Sb—Sb, S—S) bonds and the ageing or relaxation will not be significantly influenced by the presence of regular homo bonds as it could be in the case of sulphur under-stoichiometric films and glasses. Finally, the chemical composition of bulk $((GeS_2)_{0.8}(Sb_2S_3)_{0.2})$ ranks, in our experience, with relatively stable glasses which can be used for the preparation of thin amorphous films by simple thermal evaporation with reasonably conserved chemical composition. We examined (i) the

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role of the wavelength and intensity of the excitation light on photo-bleaching, (ii) the role of the film thickness on photo-bleaching, (iii) protected ageing and its role on photo-bleaching, (iv) the possible origin of the photo-bleaching observed and (v) photo-bleaching induced by high intensity illumination.

2. Experimental section

Thin films were prepared by thermal evaporation ($p \approx 10^{-3}$ Pa, rate of evaporation ≈2–2.5 nm/s) onto microscope glass and Si substrate from the stoichiometric bulk $(GeS_2)_{0.8}(Sb_2S_3)_{0.2}$ ($Ge_{23.5}Sb_{11.8}S_{64.7}$ in atomic fraction). For more details about the bulk preparation see [11]. Special shielding of the substrates was used in order to prepare the samples with different thicknesses: 1000–1130 nm, 420–450 nm, 140–160 nm and 40–50 nm, respectively. The chemical composition of the films was determined by an Energy Dispersive X-ray Spectroscopy (EDX) employing a Jeol JSM 5500 LV Scanning Electron Microscope (SEM) and it was found to be $Ge_{24.9}Sb_{11.6}S_{63.5}$ in atomic fraction with a precision better than ±0.5 at.% for all studied thin films.

The samples were stored in the dark and in a dry atmosphere. The samples measured or treated over a period shorter than 100 h after preparation were further marked as "virgin" samples, the samples measured or treated over a period longer than 100 h after preparation were marked as "aged" samples and the samples annealed for 2 h in the dry argon at a temperature T = 272 °C were marked as "annealed" samples. The illumination was performed in a sample holder allowing the protection of the sample surface against photo-oxidation and light induced overheating [12,13] for employed illumination intensity typically ≈150 mW/cm^2. The films were illuminated by the following light sources: i) the monochromatic light from a Xenon lamp (1000 W, Newport) equipped with IR cut-off filter and interference Melles Griot band-pass filters with a band-half-width 10 nm with a peak transmission at the wavelength λ_{ill} in nm (for the corresponding photon energy E_{ph} in eV mentioned, see the brackets) 400 (3.10), 450 (2.76), 500 (2.48), 550 (2.25), 600 (2.07) and 650 (1.91) with the average light intensity 150 mW/cm^2 [14]; ii) the 250 nm enhanced Mercury-Xenon lamp (200 W), housed in a LC-08 (Hamamatsu). The UV photons were generated in the wavelengths (photons energy/band-half-width) regions: λ_{ill} = 360 nm, (3.44 eV/7 nm) and λ_{ill} = 310 nm, (4 eV/20 nm) which cover >75% of the light energy output of the lamp with the low (I = 150 mW/cm^2 equipped with 360 nm band-pass filter) and the high (10 W/cm^2) photon intensity [14,15]; iii) the continuous-wave (CW) green laser (λ_{ill} = 532 nm) with an unfocused macro-spot (diameter of the illuminated spot >5 mm; photon intensity in a range 75–1000 mW/cm^2) or with a focused laser beam (diameter of the illuminated spot 300 μm, I ≈ 20 W/cm^2) [16].

The optical transmission of the studied films in the region of the short wavelength absorption edge (SWAE) was measured employing a Perkin Elmer Lambda 12 spectrophotometer. The classical Swanepoel method [17] was used for determination of the as deposited film thickness (d). The thickness was controlled with the scratch method for the film with the thickness 40–50 nm [18]. The optical band gap (E_g^{opt}) of the film was determined using Tauc's model [19] assuming that the non-direct interband transitions are responsible for the SWAE. The values of the single oscillator energy (E_0) and the dispersion energy (E_d) were calculated according to the Wemple–DiDomenico model [20].

The infrared spectra of the illuminated spot (3 mm aperture) were measured using the Fourier–Transform Infrared Nexus spectrometer (Thermo Nicolet, USA) against the Si substrate [21]. Raman scattering spectra excited with a laser operating at 785 nm were measured with a Dimension P2 setup (Lambda Solution, USA) [7]. The topology of the surface, film thickness and the map of the mechanical behaviour were studied employing an Atomic Force Microscopy (AFM) Solver Pro-M (NT-MDT, Russia) in contact, semi-contact or AFAM modes [18,21].

3. Results and discussion

The typical spectral dependence of the absorption coefficient for the virgin films for a thickness in a range 50 < d (nm) < 1100 is shown in Fig. 1A. The optical band gap was determined to be 2.20 ± 0.03 independent of the film thickness. Nearly independent values of the E_g^{opt} the film thickness were in fact recently reported by Todorov et al. for GeS_2 films: E_g^{opt} = 2.63, 2.56, 2.61 and 2.60 for the film thickness 34, 583, 859 and 1296 nm, respectively (E_g^{opt} values we calculated from Fig. 5a in Ref. [22] according to Tauc's model).

Typical changes in SWAE induced by the illumination and annealing are illustrated in Fig. 1B and the values of certain optical parameters are summarized in Table 1 for the film thickness ≈1050–1100 nm. The illumination of the virgin state of the film led to considerable photo-bleaching ($\Delta E_g^{opt} = E_g^{opt}(\text{illuminated}) - E_g^{opt}(\text{virgin}) = 196$ meV; e.g. $\Delta E_g^{opt}/E_g^{opt}(\text{virgin}) = 9\%$) and to a decrease in the disorder (parameter $B^{1/2}$ increases by almost 14%). The photo-induced changes of the parameters E_g^{opt} and $B^{1/2}$ can be classified as "giant" since both exceed 9 rel. % with respect to the virgin state [23]. In contrast to E_g^{opt} and $B^{1/2}$ changes, the changes in the refractive index (n), the thickness (d), the single oscillator energy (E_0) and the dispersion energy (E_d) were found to be negligible. The change induced by annealing (272 °C, 2 h, dry argon) of the virgin film was much more pronounced: $\Delta E_g^{opt} > 300$ meV with respect to the photo-induced bleaching.

3.1. Spectral and intensity dependencies of the photo-bleaching

The magnitude of the photo-bleaching (ΔE_g^{opt}) induced by light with a similar intensity (I = 150 mW/cm^2; time of illumination 150 min up to the steady state) appeared to be strongly spectral dependent, Fig. 2. The maximal ΔE_g^{opt} values were obtained for the slightly over-band-gap photons with energy: $E_{ph} > E_g^{opt}$: $\Delta E_g^{opt} = 196$ meV ($E_{ph} = 2.33$ eV/λ_{ill} =

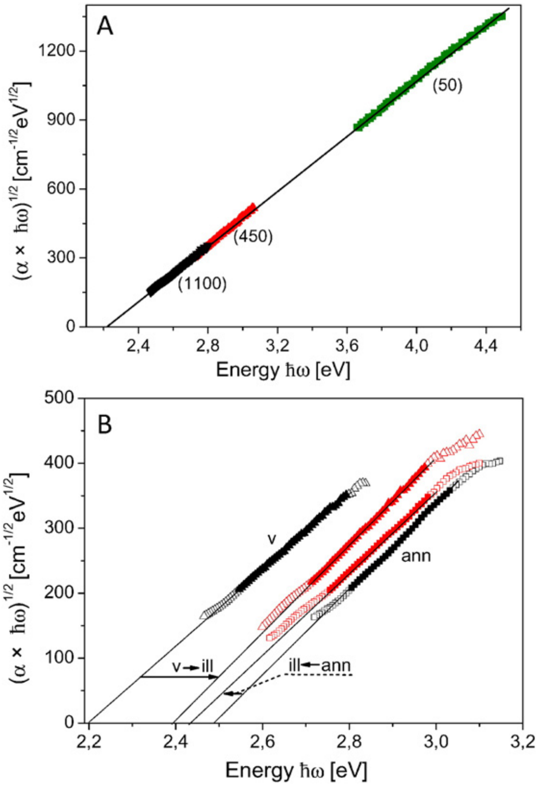

Fig. 1. A — Spectral dependencies of the absorption coefficient $(\alpha \times \hbar\omega)^{1/2}$ for virgin films with a different thickness; the numbers in parentheses are the film thickness in nanometers; B — Typical spectral dependencies of the absorption coefficient for the virgin (v), annealed (ann) or illuminated (ill) by monochromatic light λ_{ill} = 532 nm (v → ill and ann → ill) films.

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