Kinetics of Photosensitivity in Ge-Sb-Se Thin Films

M. Olivier[1], R. Boidin[1], P. Hawlová[1], P. Němec[1] and V. Nazabal[2,1]
[1]*Department of Graphic Arts and Photophysics, Faculty of Chemical Technology, University of Pardubice, Studenská 573, 53210 Pardubice, Czech Republic*
[2]*Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, Equipe Verres et Céramiques, Université de Rennes1, 35042 Rennes, France*

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Abstract: Chalcogenide $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ thin films obtained using pulsed laser deposition are exposed to light with energy close to band gap energy, in order to investigate kinetics of photoinduced phenomena. It appears that a reversible transient photodarkening is observed. The metastable part of photodarkening, which seems to be slower, is followed by photobleaching. A modelling of the evolution of transmission during illumination suggests that each process has an independent effective time constant, and that magnitude of photoinduced phenomena depends on various parameters, such as laser's fluency, absorption coefficient and composition.

1 INTRODUCTION

Photoinduced phenomena (appearing when the material is illuminated with a light with energy close to band gap energy) are among the most known properties of amorphous chalcogenides. Photoinduced phenomena in thin films are typically linked with the changes of optical parameters, mainly the refractive index (Kolobov, 2006; Němec and Frumar, 2009; Petkov and Ewen, 1999; Todorov et al., 2010) and the band gap energy (Němec and Frumar, 2009; Petkov and Ewen, 1999). These variations depend on composition (Kumar et al., 2013; Todorov et al., 2010). The most notable effect, observed in Ge-based amorphous thin films is photo-bleaching (PB) (Yan et al., 2011). Photo-darkening (PD) is also observed, mainly in As-based layers (Antoine et al., 2009; Ganjoo et al., 2002). These changes can be reversible or irreversible. Reversible phenomena are observed in well annealed films whereas irreversible phenomena are observed in as-deposited films (Kolobov, 2006; Němec and Frumar, 2009).

PD, which is the most studied effect, is known to presents a transient part (TPD) and a metastable part (Antoine et al., 2009; Flaxer et al., 2009; Ganjoo et al., 2002). TPD occurs only during illumination and disappears when pump beam is switched off, whereas metastable part can only be reversed by annealing around glass transition temperature. Yan recently studied photosensitivity in $GeSe_2$ films and showed that PB and TPD can be observed for this film (Yan et al., 2011). PB was linked to intrinsic structural changes in the vitreous matrix, i.e. the increase of Ge-Se bond density, and thus the increase of the ordering of the local structure. The most popular theory to explain the mechanism of transient PD is the bond switching and atom movement under illumination (Barik et al., 2013; Kumar et al., 2013; Yan et al., 2011). This transient state is present because of the existence of an intermediate state of electron transitions between ground and photoexcited state.

Kinetics of photosensitivity in more complicated ternary systems are poorly studied and mainly concern Ge-As-Se compositions (Barik et al., 2011; Khan et al., 2012). Khan recently reported coexistence of fast PD (presenting a transient part and a metastable part), and slow PB in $Ge_{19}As_{21}Se_{60}$ and $Ge_xAs_{35-x}Se_{65}$ glasses (Khan et al., 2014, 2012). Khan reported that the light-induced response depends on the Ge:As ratio and of the rigidity of the glassy network (Khan et al., 2014). In this paper, we report on kinetics of photosensitivity of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ thin film for x=5 to 40. Previous study showed, for these compositions, a PB effect after irradiation of as-deposited films. Furthermore, it was observed that when x increases, thin films were less sensitive to irradiation.

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2 EXPERIMENTAL PART

Thin films are obtained using pulsed laser deposition (PLD). Targets are 25 mm diameter chalcogenide glasses from $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ system, where x is varying from 5 to 40. Their synthesis was reported elsewhere (Olivier et al., 2014). Targets were ablated with a KrF excimer laser emitting at 248 nm. Output pulse energy was 300±3 mJ with a pulse duration of 30 ns and a repetition rate of 20 Hz. Laser fluency is set at 2.6 $J.cm^{-2}$. Pressure in the vacuum chamber at the beginning of deposition is about $3\text{-}4.10^{-4}$ Pa. In order to obtain films with uniform thickness, off axis PLD technique with rotating substrates and targets was used. Substrates were microscope glass (10 mm x 15 mm) and were positioned parallel to the target at a distance of 5 cm.

The study of kinetics was carried out on as-deposited films so in irreversible regime. Photosensitivity was studied for exposures with laser light in band gap region during 2 hours, with power density of 160 $mW.cm^{-2}$ and a laser-sample distance of 50 cm. The probe beam is a low intensity white light operating in the 400 -1000 nm wavelength range. The two beams were directed such as they cross each other at the sample surface with the pumping light completely overlapping the probe light.

During illumination, transmission of thin layer is recorded every second using a Stellar Inc EPP 2000 portable spectrophotometer, which can collect the entire optical spectrum in 50 ms.

To avoid the oxidation of the films during irradiation, the samples were maintained under nitrogen flux. For these experiments, 5 different laser wavelengths were available: 532 nm (2.33 eV), 593 nm (2.09 eV), 635 nm (1.95 eV), 690 nm (1.80 eV) and 808 nm (1.53 eV).

Thicknesses of thin films were extracted from the variable angle spectroscopic ellipsometry data measured with an automatic rotating analyzer ellipsometer (VASE, J. A. Woollam Co., Inc.). Measurement parameters were the following: spectral region 300-2300 nm (i.e. 4.13-0.54 eV) with wavelength steps of 10 nm and angles of incidence of 50°, 60°, and 70°.

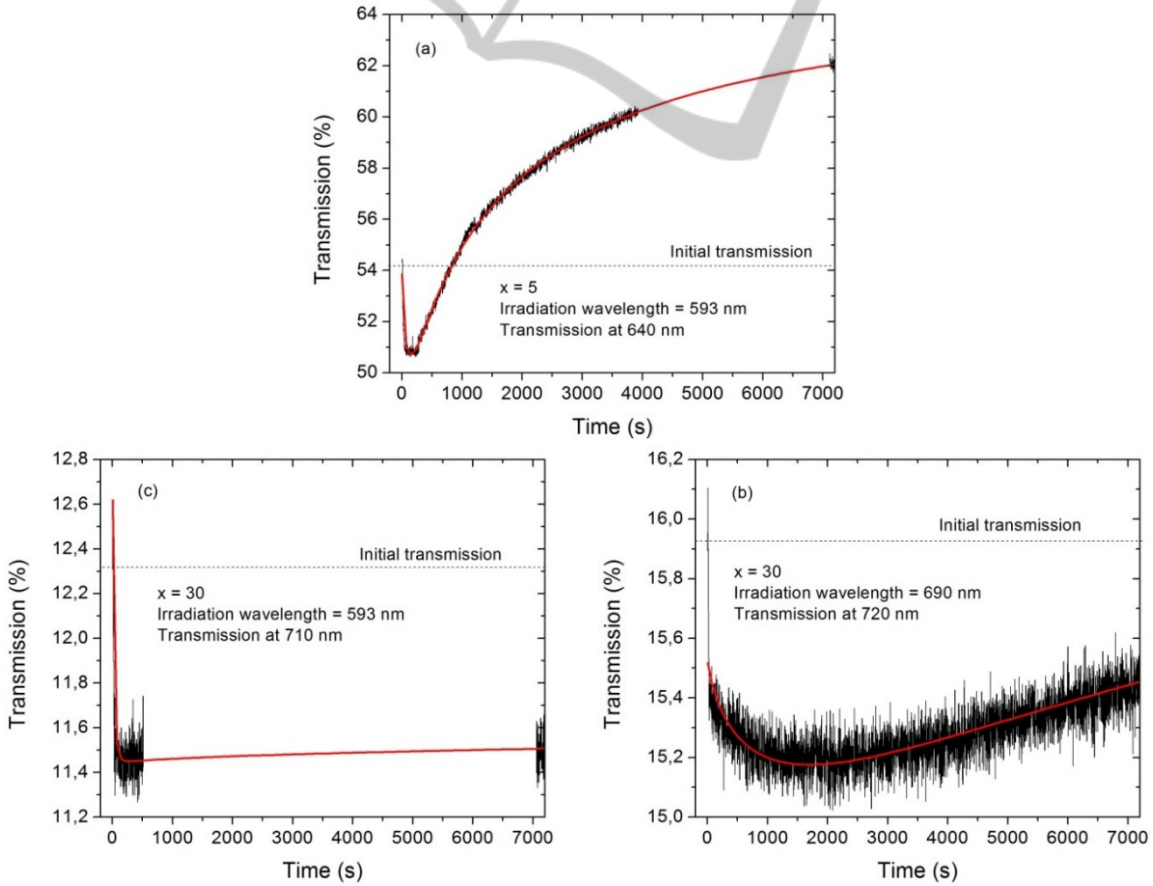

Figure 1: Typical transmission time dependences for $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ as-deposited films under different irradiation wavelengths, (a) x = 5, (b) and (c) x = 30.

3 RESULTS AND DISCUSSION

3.1 Experimental Results

As-deposited $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ thin layers were homogeneous according to SEM observations. The films show a good planarity with a smooth surface and neither cracks nor breaks. Table 1 detailed thicknesses of chalcogenide layers, determined from VASE measurements. To study the effect of pump beam illumination, transmission spectra were previously recorded in dark condition (Initial transmission). Then the pump beam was turned on and transmission was recorded as a function of time during 2 hours. Figure 1 presents typical evolution of transmission with time at a wavelength close to the band gap for various compositions.

First experimental results clearly reveal the existence of fast PD phenomena. Regarding irradiation of as-deposited films, the fast PD step is followed by a slow PB process for x=5, 10, and 20. For x=20, at irradiation wavelength of 593 nm, absorption coefficient is higher (45 000 cm^{-1}, instead of ~20 000 cm^{-1} for the 2 first samples).

In that case, PB seems to be even slower. For x=30, when α~66 000 cm^{-1} no slow phenomenon is observed after 2 hours irradiation; when α~32 000 cm^{-1} PB is observed but is not saturated after 2 hours irradiation.

For x=20 irradiated at 635 nm and x=30 irradiated at 690 nm, one can observe a slow PD effect, occurring after the fast PD and before the beginning of the increase of transmission. The PB process seems to start only after saturation of the slow PD process (Khan et al., 2012). For x=40, slow PB is observed and seems to saturate after 2 hours irradiation.

Kinetics of PB depends on absorption coefficient of the layer at irradiation wavelength (Ganjoo et al., 2006, 2000) and the phenomenon is fastest for 15 000 $cm^{-1}<\alpha<25\ 000\ cm^{-1}$. It thus could be of interest to work with a tunable laser to precisely choose irradiation wavelength.

Long exposure during 8 hours at 690 nm of a film (x=30) was performed. Fig.2 presents the evolution of the transmission at 640 nm with time for this film.

A PB effect occurs after the fast PD observed during the first seconds, as observed in Figure 1. Nevertheless, it seems that kinetic of PB is particularly slow and that PB does not saturate, even after 8 hours irradiation.

The kinetic of PD and PB depends on fluence of pump beam (Khan et al., 2012), absorption coefficient at irradiation wavelength (Ganjoo et al., 2006), and temperature (Barik et al., 2011) but in case of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ system, it also depends on vitreous composition and when x increase, PB magnitude becomes lower.

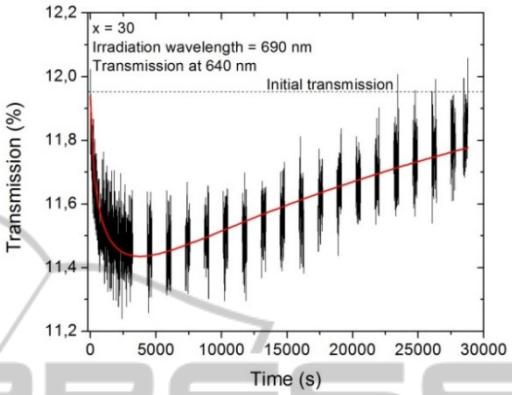

Figure 2: Evolution of transmission at 640 nm for an as-deposited film (x=30) under 690 nm irradiation light (8 hours exposure).

PB effect in $GeSe_2$ can be related to either photooxidation (Spence and Elliott, 1989; Tichý et al., 1995; Yan et al., 2011) or structural ordering. Irradiations here are performed under inert atmosphere and observed PB can thus be related to a decrease in the density of localized states at the edge of the conduction band, which enlarges the band gap, leading to its blue shift (Nang et al., 1979).

Photosensitivity of samples seems to decrease with x (by adding Sb_2Se_3). In a similar system (Ge-As-Se), several authors show that photosensitivity decrease with rigidity (mean coordination number) of the network (Calvez et al., 2010; Khan et al., 2014). This is not the case in Ge-Sb-Se system because photosensitivity increases with rigidity. Another mechanism should take place.

Disorder is mainly due to homopolar Ge-Ge and Se-Se bonds which are found in as-deposited films. PB process is thus proposed as the increase of heteropolar Ge-Se bonds density (Ganjoo et al., 2006; Kotsalas et al., 1998; Yan et al., 2011). Considering these assumptions, one can explain the decrease of PB magnitude when x increases with the lower number of homopolar Ge-Ge and Se-Se bonds in films.

3.2 Modeling

To model the kinetics of photoinduced response, a combination of stretched exponential functions that describe PB and PD can be used (Ganjoo et al.,

Table 1: Fitting parameters obtained from equation (3) for as-deposited films from $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ at various irradiation wavelengths. Absorption coefficient is given for each film at irradiation wavelength.

x	Irradiation wavelength (nm)	Thickness (nm) ± 1nm	Absorption coefficient (cm^{-1})	C_d	τ_d (sec)	β_d	ΔT_{sd}	τ_b (sec)	β_b	ΔT_{sb}
5	593	595	18434	11.9	72.5	0.68	41.9	1372.8	0.50	11.9
10	593	690	22582	4.9	77.3	0.67	7.01	1441.9	0.49	9.3
20	593	778	45385	0.9	207.3	0.68	10.1	786000	0.5	5.1
	635	778	25800	5.1	531.5	0.68	19.9	7181.2	0.48	7.9
30	593	827	66073	1.4	16.5	0.68	11.4	$1.3.10^7$	0.50	3.07
	690	827	32589	1.2	912.3	0.68	14.4	74000	0.50	4.0
40	690	1567	30981	1.0	16.5	0.72	8.3	1.10^7	0.50	3.6
	808	1567	7526	0.6	12.7	0.73	9.4	1.10^7	0.50	1.6

2002; Khan et al., 2012). PD is usually described as follows:

$$\Delta T = C_d\left[\exp\left\{-\left(\frac{t}{\tau_d}\right)^{\beta_d}\right\}\right] + \Delta T_{sd} \quad (1)$$

Then, PB can be written as:

$$\Delta T = \Delta T_{sb}\left[1 - \exp\left\{-\left(\frac{t}{\tau_b}\right)^{\beta_b}\right\}\right] \quad (2)$$

In equations (1) and (2), subscripts d and b stand for darkening and bleaching, respectively. ΔT represents the change in transmission occurring during irradiation. C_d is a temperature dependent constant and corresponds to the total amount of transient PD. This value is obtained during the experimental data fitting. t is the illumination time in seconds. τ is the effective time constant, and β is the dispersion parameter ($0 \leq \beta \leq 1$). ΔT_s is the saturated value of ΔT (i.e. the metastable part of the changes).

The whole kinetics of photosensitivity in case of as-deposited film is a summation of equations (1) and (2):

$$\Delta T = C_d\left[\exp\left\{-\left(\frac{t}{\tau_d}\right)^{\beta_d}\right\}\right] + \Delta T_{sd} + \Delta T_{sb}\left[1 - \exp\left\{-\left(\frac{t}{\tau_b}\right)^{\beta_b}\right\}\right] \quad (3)$$

The experimental data fit well to the stretched exponential functions forms detailed in equation (3) as shown in Figure 1 (red curves). Fitting parameters calculated from theoretical equations are listed in Table 1 for as-deposited films.

Our results confirm previous studies (Khan et al., 2012; Yan et al., 2012) showing that PD is faster than PB. Behavior of thin films under irradiation is nevertheless different depending on their composition. For x=5 and 10, PD has a time constant of around 75 seconds and PB has a time constant of 1400 seconds.

For x=20 and 30, a slow PD is observed after the fast PD process, occurring during the first minute. That is the reason why the time constants obtained from the fits are larger (531 sec and 912 sec). We thus highlight existence of two different kinetics for the PD, which may be relevant for TPD and metastable part of PD. Regarding this results, it is nevertheless difficult to say if PB starts after saturation of the PD process or if there is a competition between the two phenomena from the beginning of irradiation.

When x=40, only the fast PD is observed, with a time constant of around 15 seconds, followed by a slight increase of the transmission which seems to saturate after 2 hours of irradiation.

In order to differentiate the transient and metastable part of PD, pump beam was turned on and off alternatively, every 5 minutes during 2 hours. On turning the pump beam off after a first irradiation, the transmission increases further and saturates quickly (Fig. 3), but does not reach the initial transmission value, revealing the metastable part of PD. When illumination is subsequently turned on, transmission decreases to reach the value before illumination was switched off. The on/off cycles of pump beam are relevant for the TPD. Indeed, TPD occurs only during illumination and disappears when pump beam is turned off. This phenomenon is probably of the same nature as the TPD observed in As-based chalcogenide films and is due to bond switching and atomic movement. Fig. 3 demonstrates that TPD as well as metastable part of PD occur at short illumination time, but metastable part accumulates with each successive illumination. This effect was already observed in As-based thin films (Flaxer et al., 2009).

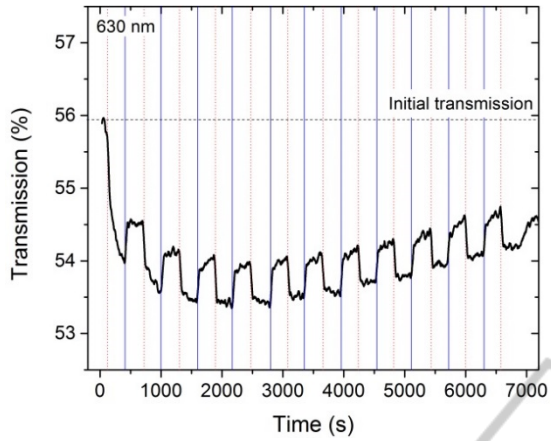

Figure 3: Observation of reversible transient PD in $(GeSe_2)_{90}(Sb_2Se_3)_{10}$ PLD thin films irradiated at 593 nm during 2 hrs. Dotted red line corresponds to pump beam turn on and blue line to pump beam turn off.

4 CONCLUSIONS

Our experiments clearly demonstrate that TPD is an instantaneous process, which systematically occurs during irradiation of $(GeSe_2)_{100-x}(Sb_2Se_3)_x$ PLD thin films, and is associated with a slower PD process, corresponding to the metastable part of the phenomenon. Irradiation of as-deposited films induces PB, with a higher effective time constant, which starts after saturation of both TPD and PD. This phenomenon does not systematically saturate after 2 hours exposure and its kinetic depends on fluence of irradiation beam, absorption coefficient of the film at the irradiation wavelength. Its magnitude depends also on composition, as for high Sb_2Se_3 content, PB appears to be very weak.

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