Observation of photobleaching and intensity dependent kinetics in $Ge_{22}As_{22}Se_{56}$ thin films under sub-bandgap light illumination

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Abstract. We experimentally demonstrate photobleaching (PB) in $Ge_{22}As_{22}Se_{56}$ thin films, when illuminated with a diode pumped solid state laser (DPSSL) of wavelength 671 nm, which is far below the optical bandgap of the sample. Interestingly, we found that PB is a slow process and occurs even at moderate pump beam intensity of 0.2 W/cm^2, however the kinetics remain rather different.

1. Introduction

Recently, the demand for chalcogenide glasses (CG) in light wave technology has increased substantially, because of their prominent photoinduced effects. Among the numerous photoinduced effects shown by CG, the most notable effects are photodarkening (PD) in As-based chalcogenides [1] and PB in Ge-based chalcogenide [2]. Besides the fundamental interest of PD/PB in CG, these effects find immense technological applications in high bit rate waveguide writing [3] and also in dense holographic recording [4]. Hence a comprehensive understanding of PD/PB comprising of transient and metastable part is therefore of crucial importance for many of these applications. In contrast, light illumination in Ge-based CG mostly results in PB and is assumed to be of irreversible in nature. However, recent studies on $GeSe_2$ thin films have shown that irreversible PB is accompanied by transient PD. Many models have been proposed to explain the observed PB in Ge-based chalcogenides, but none of them proved to be definite for all compositions. In this paper, we present the interesting results of PB in $Ge_{22}As_{22}Se_{56}$ thin films when illuminated with sub-bandgap light of 671nm. Further, we move on to show that intensity of the illuminating light has a predominant role in determining the kinetics of PB. In our experiments, we observed a 10-fold increase in reaction time when intensity is reduced from 2 to 0.2 W/cm^2. Notably, the kinetic curve of PB follows a stretched exponential function.

2. Experimental

Bulk $Ge_{22}As_{22}Se_{56}$ glass was prepared by melt quenching method from 99.999% pure As, Ge and Se materials. The cast sample was used as the source material for deposition and thin film of average thickness ~1.0 μm was prepared by thermal evaporation in a vacuum of about 1×10^{-6} Torr. PB in these films is studied by a pump probe optical absorption method by using the experimental set up

described previously [5]. We have chosen the wavelength of the pump beam as 671nm (from a DPSSL) and kept the intensity of pump beam at 2W/cm^2. The probe beam was a low intensity white light in the wavelength regime of 450-1000 nm. During illumination, the transmission of the sample was recorded using a spectrometer with photodiode array as detector and had the capability to collect the entire optical spectrum in 2ms. In our experiments, the entire optical spectrum was collected in real time of 100 ms/spectrum.

3. Results and Discussions

First we recorded the transmission spectra of as prepared $Ge_{22}As_{22}Se_{56}$ at an intensity of 2W/cm^2. Thereafter we turned on the pump beam and continuously measured the spectrum within an interval of 100ms until the whole effect saturates. After initial PD, PB begins to start nearly at 300 seconds, continuously grow and saturates within an hour. Figure 1 shows the surface plot of transmission as a function of time on selected wavelengths close to the optical bandgap of the sample. To compare the effect of intensity on the kinetics of PB we have done the same experiment at a different intensity of 0.2mW/cm^2 for the same sample. Interestingly, the whole effect is reproducible even at low intensities.

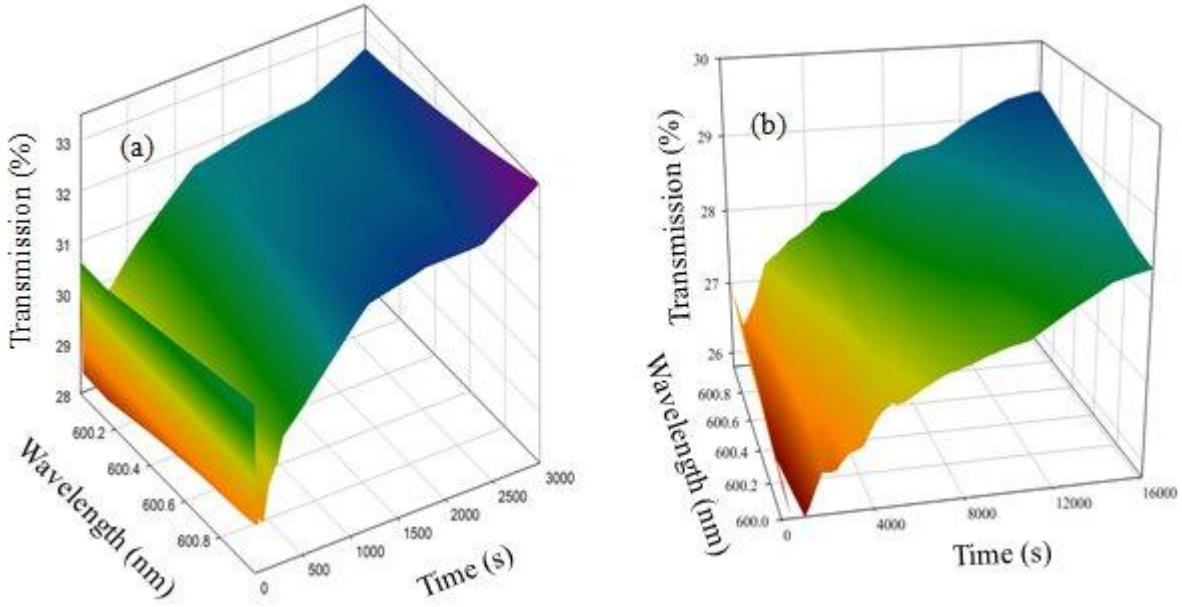

Figure 1. Transmission spectra of $Ge_{22}As_{22}Se_{56}$ thin film at different times when illuminated with a 671 nm DPSSL of intensity (a) 2W/cm^2 and (b) 0.2W/cm^2.

After demonstrating PB in of $Ge_{22}As_{22}Se_{56}$ thin film, it is of great importance to explain the observed effects. At this point, we conjecture that the there exist compositional heterogeneities (As-As, Ge-Ge etc) in the film, which were created from the vapour that contains various atomic fragments. When such a film is illuminated with 671nm, compositional heterogeneities associated with As-Se and Ge-Se responds rather independently and a considerable fraction of metastable homopolar bonds present in the atomic fragments are broken and subsequently converted into energetically favoured heteropolar bonds. The reduction in As homopolar bonds results in PD, however that of Ge atoms leads to photobleaching. Thus we observe an unusual coexistence of PB and PD and the reaction happens in the following way [6]:

$$As_{x-y}Se_z + yAs + h\nu \longleftrightarrow As_xSe_z \quad (1)$$

$$GeSe_a + Se_b + h\nu \longleftrightarrow GeSe_{a+b} \text{ where } a < 2 \leq a+b \quad (2)$$

It is worth mentioning here that PB happens due to internal structural rearrangements due to photo-illumination along with photo-oxidation of the sample forming a new species GeO_2 [7].

Among the reactions described above, rate equation determining PD can be written as

$$\Delta T = C[\exp\{-(\frac{t}{\tau_d})^{\beta_d}\}] + \Delta T_{Sd} \quad (3)$$

and that for PB:

$$\Delta T = \Delta T_{Sb}[1-\exp\{-(\frac{t}{\tau_b})^{\beta_b}\}] \quad (4)$$

where the subscript 'd' and 'b' corresponds to PD and PB respectively. ΔT_s, τ, β and t are metastable part, effective time constant, dispersion parameter and illumination time respectively. The net rate equation for the whole process is a summation of respective PD and PB as following:

$$\Delta T = C[\exp\{-(\frac{t}{\tau_d})^{\beta_d}\}] + \Delta T_{Sd} + \Delta T_{Sb}[1-\exp\{-(\frac{t}{\tau_b})^{\beta_b}\} \quad (5)$$

The experimental data at both the intensities fit very well to the stretched exponential function described by equation (5). Further, the fitting parameters calculated from the theoretical fit are listed in table 1. From the table 1, it can be very well understand that PD is a very fast process and the reaction time is of the order of a few 100's of seconds. However on the contrary, PB is a slow process and takes an induction time to start. Interestingly, as we move from higher to lower intensity, magnitude of photoinduced effects remain the same, but the kinetics show a sharp contrast. In our experiments, we observed 10 times decrease in kinetics, when the intensity of the pump beam was decreased from 2 to 0.2 W/cm^2.

Table 1. Fitting parameters obtained from equation 5 corresponding to PD/PB at different intensities for the wavelength 600 nm. The subscript d and b refer to darkening and bleaching respectively.

Intensity (W/cm^2)	τ_d (s)	β_d	ΔT_{Sd}	τ_b (s)	β_b	ΔT_{Sb}
2	12	0.97	0.905	920	0.65	0.185
0.2	260	0.45	0.918	5500	0.72	0.174

4. Conclusions

In conclusion, we observed PB in $Ge_{22}As_{22}Se_{56}$ thin film, when illuminated with a DPSSL of wavelength 671 nm, which is far below the optical bandgap of the sample. Our experimental results clearly demonstrate that intensity of the illuminating beam has a predominant role in determining the kinetics of PD/PB. PB in these samples is explained by considering the compositional heterogeneities associated with the film while evaporation.

5. Acknowledgement

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