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TRANSIENT AND METASTABLE PHOTODARKENING IN AMORPHOUS CHALCOGENIDES

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Transient photodarkening (PD), which is only observed during illumination, has been discovered in some amorphous chalcogenides. During illumination, total changes in absorption coefficient are a combination of transient and metastable part of PD. The transient PD decays as the illumination is switched off to give the usually observed metastable PD. The decay of the transient part, is similar to the decay of photocurrent in a-As_2Se_3 suggesting the importance of photocarriers in inducing PD. Although no metastable PD is observed for a-Se at 300 K, there exists transient PD.

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1. Introduction

Amorphous chalcogenides exhibit remarkable photo-induced changes in their physical properties upon optical excitations [1-3]. Two types of metastabilities, the defect-related and structure-related, are introduced and are evident from many studies. Presently amorphous chalcogenides are attracting added attentions, basically due to these metastabilities. Amorphous chalcogenides are finding uses in fabrication of imaging devices [2] and more recently as fascinating opto-mechanical devices for nano-technologies [3]. The study of photodarkening (PD), one of the main structure-related metastability, in amorphous chalcogenides has received renewed interest recently and efforts have been made to have a better understanding of these changes (see, for example, Refs. [1, 3] and [4]). Recently some theoretical calculations, based on ab-inito calculations and molecular dynamics, have been performed to understand these light-induced structural changes in a microscopic way [5, 6].

Experimentally, however, most of the changes in optical transmission have been studied *after* the illumination is switched off. The behavior and nature of the changes taking place *during* illumination have been less well investigated. Recently, we have studied the PD kinetics during illumination of a-As_2S_3 films, where a laser beam was used to illuminate the sample and the changes in its transmission simultaneously recorded [7]. These measurements gave us new insights into the time evolution of changes in the absorption coefficient, namely the percolative growth of the photo-darkened sites explains the time evolution of PD.

In the present paper, we report direct measurements of *transient* changes in the absorption coefficient at 50 and 300 K for a-As_2Se_3, 100, 200 and 300 K for a-As_2S_3 and at 300 K for a-Se films. We have found a significant transient change in the PD observed during illumination for a-As_2Se_3 and a-As_2S_3. The transient part decays after the illumination is turned off leaving only the usually observed metastable change. This decay behavior is similar to the decay of photocurrent in a-As_2Se_3. For a-Se a significant transient PD is observed at room temperature that vanishes as soon as the illumination is switched off and no metastable PD is observed.

2. Experimental

Thin films of amorphous As_2Se_3 (a-As_2Se_3), amorphous As_2S_3 (a-As_2S_3) and amorphous Se (a-Se) thickness, d~500 nm, were deposited onto glass (Corning 7059) substrates by thermal

evaporation in a vacuum of ~1x10^{-6} Torr. The films were annealed below the respective glass transition temperature (T_g) for 2 h for the case of a-As_2Se_3 and a-As_2S_3 and kept in vacuum for 24 h at room temperature for a-Se before being placed in an evacuated cryostat for the measurement of optical transmission. Two laser beams were used: an Ar ion laser ($h\nu$ = 2.41 eV, power = 80 mW/cm^2 and linear spot size ≈ 5mm) was used as the illuminating light and a He-Ne laser ($h\nu$ = 1.95 eV, power < 0.1 mW/cm^2 and linear spot size ≈ 0.5 mm) was used as the probe light. The beams were directed such that they crossed each other at the sample. The transmitted signal of the He-Ne probe laser beam was detected with a photo-diode and the changes in the transmitted light were measured as a function of time. Suitable filters were used so as not to allow the photo-diode to be subjected to any interference from the illumination provided by the Ar ion laser. The schematic diagram of this two-beam experimental set up is shown in Fig. 1.

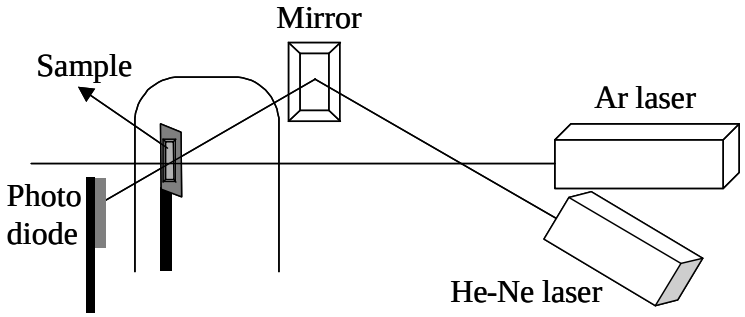

Fig. 1. Schematic illustration of the two beam experimental set up to study transient and metastable PD.

The changes in the absorption coefficient, $\Delta\alpha$, are calculated from $\Delta\alpha = \left(-1/d\right)\ln\left(T/T_0\right)$, where d is the film thickness and T/T_0 is the ratio of the measured transmission signals of the He-Ne laser during and on putting on the illumination.

3. Results

Figs. 2 and 3 show the time evolution of the changes in the absorption coefficient, $\Delta\alpha$, at 1.95 eV during various cycles of Ar laser illumination at 50 and 300 K for a-As_2Se_3 and at 300 K for a-Se, respectively. A similar type of behavior, as for a-As_2Se_3, is also observed for a-As_2S_3 but we will discuss the results of a-As_2Se_3 considering it to be a representative material. First we give the results of changes in $\Delta\alpha$ in a-As_2Se_3 films. For a-As_2Se_3 films, $\Delta\alpha$ increases rapidly at first at both temperatures before reaching close to saturation after some time. The magnitude of changes is larger at 50 K as compared to 300 K, which is consistent with the earlier results on amorphous chalcogenides (a-As_2S_3) [9]. When the Ar-laser illumination is switched off, a decrease in $\Delta\alpha$ is observed which reaches a constant value quite quickly. This portion of the total change is the *transient* part induced by illumination and the portion remaining after the illumination is switched off is the usually observed metastable PD. Thus the total increase in $\Delta\alpha$ for a-As_2Se_3 films, during illumination, is the sum of the transient and the metastable PD. The transient parts of the changes are found to be nearly 60% and 30 % of the total changes induced during illumination at 300 and 50 K, respectively. It should be noted that illumination is known to cause an increase in the thickness d of the films [8], but here d is assumed to be constant. The changes in d are around 5% at 300 K which is very small compared to the changes in $\Delta\alpha$ observed. It is also clear that an increase in d will result in a decrease in $\Delta\alpha$, which is opposite to that observed in PD.

Successive cycles of illumination with the Ar laser (laser on and off), after the metastable PD is reached (see Fig. 2), result in increase and decrease in $\Delta\alpha$ equal to the transient part observed after the first cessation of illumination. The cycling was repeated many times after the metastable state was reached, and every illumination confirmed the occurrence of only the transient PD.

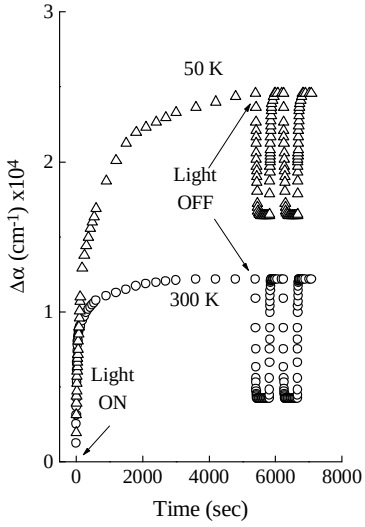

Fig. 2. Time evolution of changes in absorption coefficient, Δα, for a-As_2Se_3 films at 50 (D) and 300 K (O). ON and OFF stages of the Ar laser are indicated by the arrows.

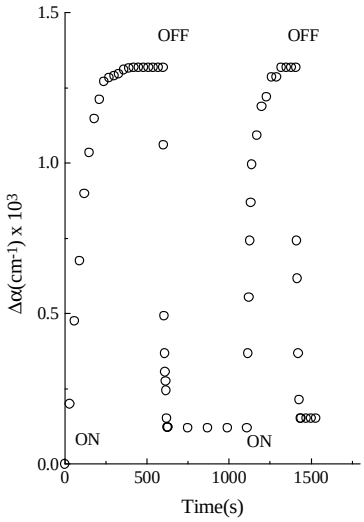

Fig. 3. Time evolution of changes in absorption coefficient, Δα, for a-Se films at 300 K. ON and OFF stages of the Ar laser are indicated by the arrows.

To understand the transient and metastable changes during the initial rapid increase of $\Delta\alpha$ in more detail, we have studied the changes in Δα for short-time illumination at 50 and 300 K, i.e., before reaching the saturated state shown in Fig. 2. The light was switched on and off for 20 s each at 50 K and 10 and 20 s, respectively at 300 K. The light was switched on for 20 s at 50 K instead of the 10 s used at 300 K, because $\Delta\alpha$ is still increasing rapidly even after 10 s at 50 K. The resulting changes in the absorption coefficient, Δα, at 50 and 300 K are shown in Fig. 4. At both temperatures, $\Delta\alpha$ increases and decreases very rapidly when the illumination is switched on and off, but in neither case does it return to the original values. The total increase in Δα is larger at 50 K as compared to 300 K. The cycle of increase and decrease is repeated with each illumination cycle. This shows that the transient as well as the metastable changes occur for short illumination times and that the metastable part accumulates with each successive illumination. The accumulation of the metastable changes is slightly faster at 50 K as compared to 300 K.

In a-Se (Fig. 3), Δα increases as the Ar laser is made incident on the films and after some time reaches saturation. As soon as the illumination is switched off, the changes in absorption coefficient quickly revert back to the level before illumination. On switching on the illumination again, a similar behavior as the initial illumination is observed and any changes induced reverts back to the original state when the Ar laser is switched off. This indicates that only transient part is induced by illumination that vanishes as the illumination is switched off. Even on repeating the on/off cycle several times, a similar behavior is observed and no metastable PD is observed.

4. Discussion

First we discuss the changes in Δα for a-As_2Se_3 as shown in Fig. 2. The results clearly show that during illumination there exists a transient part and the metastable part of PD. The transient part decays when the illumination is switched off and the changes in Δα reach the usually observed metastable PD. Thus, during illumination, the total changes are a combination of the transient and metastable part. Even for short time illuminations (Fig. 4) transient and metastable parts of PD are observed. The observation of transient and metastable PD, during illumination, both for short and long times of illumination, parallels the changes observed in thickness on illumination [10]. This seems to confirm the correlation which is suggested to exist between the metastable changes in thickness and band gap observed in amorphous chalcogenides, experimentally [9] as well as phenomenologically [10]. Observations of the transient part of PD and the thickness changes in amorphous semiconductors suggest that there may exist a correlation between these changes during illumination as well. However, as the changes in thickness were observed with white light [10], no further comments about the rate can be made at this stage.

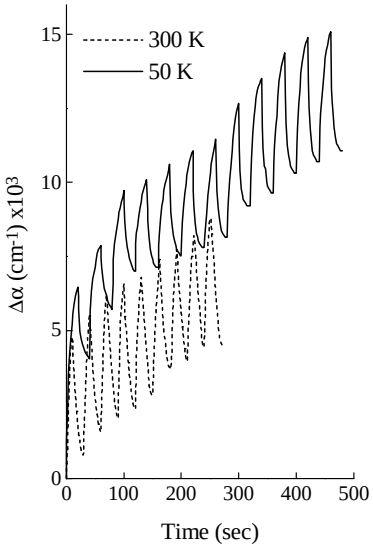

Fig. 4. Variation of changes in absorption coefficient, Δα, with time for short duration of illumination for a - As_2Se_3 films at 50 (solid line) and 300 K (dashed line). Ar laser ON and OFF stages is 20 s each at 50 K and 10 and 20 s respectively at 300 K.

Next we discuss the decay of the transient changes in absorption coefficient, Δα, for a-As_2Se_3 after turning off the illumination. As discussed earlier, the transient change in Δα decays as the illumination is switched off and the changes finally reach the metastable state. The decays of the transient part at 50 and 300 K are shown in Fig. 5. Here, the decrease of the transient part is plotted as a function of time on a logarithmic scale. The scale is adjusted to show the starting time as the time when the Ar-laser illumination is switched off. The decay is faster at 300 K as compared to 50 K. The decay can be best explained by a stretched exponential function:

$$\Delta\alpha = C\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] + \Delta\alpha_s, \tag{1}$$

where t is time after the illumination is switched off, τ is the effective decay time, β is a dispersion parameter ($0 \le \beta \le 1$) and $\Delta\alpha_s$ is the saturated value of Δα (i.e. the metastable part of the changes). C is a temperature-dependent quantity (the absolute amount of transient PD) and its value is obtained by fitting to experimental data. The solid line in Fig. 5 shows the fitting of Eq. (1) to the experimental results. The fitting seems to be reasonable and it gives values of β and τ as 0.7 and 20 s at 50 K and 0.85 and 5 s at 300 K, respectively. The effective decay time τ decreases and the dispersion parameter β increases with increasing temperature.

Next, the role of photocarriers on PD will be discussed. In Fig.6, both the decays of transient PD and photocurrent for a-As_2Se_3 induced by Ar-laser illumination at 300 K, which are nomalized to the intial value, are plotted as a function of time. Note that the transient PD is subtracted from the metastable PD. It is evident from the figure that the photocurrent decays mostly within 3 seconds and is followed by residual photocurrent [11]. The transient PD (TPD), on the other hand, the decay looks slower than that of photocurrent. However, as stated before, the effective decay time for TPD is 5 seconds that is comparable to the decay of the photocurrent (~3 sec), suggesting that there may be a correlation between photocurrent and TPD. A slightly slower decay of TPD as compared to the decay of photocurrent is expected and can be considered as follows: The decay of transient PD is the motion of the layers to a new equilibrium position (structural relaxation) in slip and repulsion model and some delay time is necessary for the movement of clustered layers in mesoscopic scale to occur. Similarity between the photocurrent and TPD suggests that photocarriers play an important role in inducing PD as well.

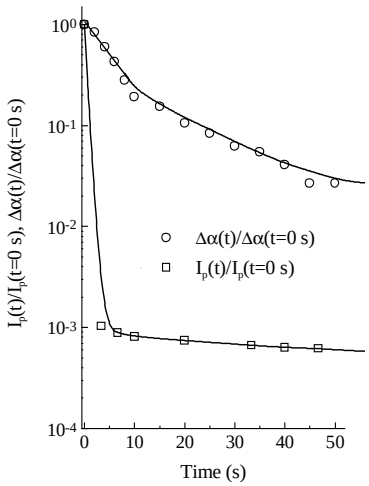

Fig. 5. The dacay of the transient part of PD after switching off the Ar laser for a-As_2Se_3 films at 50 and 300 K. The symbols have the same meaning as in Fig. 2. The solid line is the fitting using Eq. 1.

Next we take a look at the results of a-Se. It is reported (see for example [1]) that no PD is observed in a-Se at 300 K but it is observed at low temperatures. However, on measuring changes in absorption coefficient, $\Delta\alpha$, during illumination (see fig. 3), transient changes can be easily seen in a-Se at 300 K, which revert back to the original state as soon as the illumination is switched off. This shows that although there is no metastable PD in a-Se at 300 K, transient PD exists. The results presented till now dealt with the changes in $\Delta\alpha$ after the illumination was switched off, i.e., the metastable changes in PD. The reason for the observation of TPD and no metastable PD can be summarized as follows: It is well understood that PD is a reversible process, i.e., annealing near T_g in amorphous chalcogenides can reverse the changes. As the glass transition temperature of a-Se is just near room temperature [12] any changes induced in absorption coefficient at 300 K, during illumination are annealed out automatically as soon as the illumination is switched off leaving no metastable PD. This means that there exists only the transient part of PD at 300 K for a-Se.

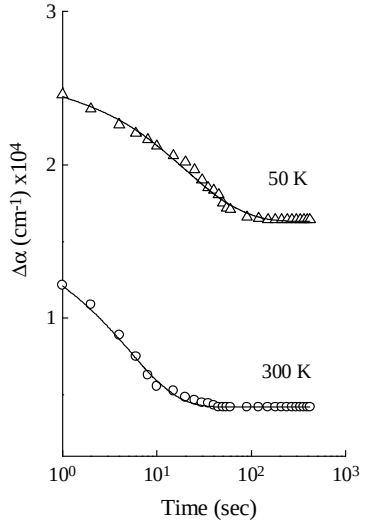

Fig. 6. Decay of transient part of PD and the decay of photocurrent in a-As_2Se_3 films at 300 K.

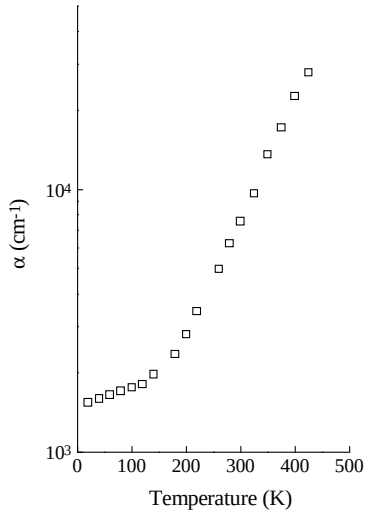

Fig. 7. Temperature dependence of absorption coefficient, α, for a-As_2Se_3 films.

In order to clarify whether the transient changes in absorption coefficient are caused by photoelectronic or thermal mechanisms, we determined the temperature dependence of the absorption coefficient, α, for a-As_2Se_3 (as a representative of amorphous chalcogenides) that is shown in Fig. 7. $\Delta\alpha$

was estimated at different temperatures from the transmission intensity of the He-Ne laser light, as explained earlier. The room-temperature value of α at 1.95 eV for the films used in the present work is estimated from direct measurements and was found to be 7.8 x 10^3 cm^{-1}. This was then used to convert $\Delta\alpha$ to α. The transient part of $\Delta\alpha$ is approximately 8000 cm^{-1} at 50 and 300 K for a-As_2Se_3, as is evident from Fig. 1. To obtain such a large change in $\Delta\alpha$ purely by a thermal mechanism, a temperature increase of nearly 275 K at 50 K and nearly 100 K at 300 K would be required. This is unreasonably higher than expected from the Ar laser illumination in the present experimental conditions. It can thus be concluded that the transient changes are not thermally induced.

Note the present decrease in the transmission (increase in absorption coefficient) at 1.95eV (He-Ne laser) can not be considered as similar to the "optical stopping" effect as observed in As-S films, where the He-Ne laser light is stopped by switching on a He-Cd laser in the path of the He-Ne laser light [13]. The optical stopping effect may be considered as an opto-electronic property while the present PD appears to be pure photo-structural property. It is considered that the He-Ne laser light (the guided light) uses its energy to excite the trapped electrons that are introduced by the light of the He-Cd laser. This leads to the stopping of He-Ne laser light. Note the He-Ne laser (1.95 eV) is sub-gap illumination for the case of As-S samples (band gap ~ 2.5 eV) studied in the optical stopping experiments. In the present experiment, the probe and the action lasers are He-Ne laser and Ar-laser, respectively, which are the band gap illumination and above band gap illuminations, respectively. Thus, the situation is very different from the above mechanism. Thus, we rule out optical stopping in the present experimental conditions.

5. Conclusions

We have made a direct observation of the transient changes of absorption coefficient, $\Delta\alpha$, in a-As_2Se_3 films at 50 and 300 K. During illumination, the total changes constitute transient and metastable PD, with the transient changes decaying when the illumination is switched off to give the usually observed metastable PD. The transient changes are nearly 60 % and 30 % of the total changes, observed during illumination, at 300 and 50 K, respectively. These transient changes are purely due to photoelectronic mechanisms. The decay of transient part after stopping the illumination is explained by a stretched exponential function. The decay of transient part is similar to the decay of photocurrent and thus suggesting the importance of number of photo-carriers. These photo-carriers assist site switching resulting in PD. Further illumination, after the metastable state is reached, induces only transient changes in $\Delta\alpha$. For a-Se, we have observed a significant transient PD at 300 K that vanishes and the changes revert back to the original state as soon as the illumination is switched off.

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