

PHOTOINDUCED FLUIDITY ENHANCED BY ELECTRIC FIELD IN AMORPHOUS CHALCOGENIDES

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Current topics of photodarkening and photoinduced volume change are briefly reviewed. To get more insight into these phenomena which can be regarded as structural fluidity, the effects of d.c. electric fields on photodarkening in amorphous As_2Se_3 films are examined. It is observed that application of an electric field accelerates photodarkening, depending on the magnitude and polarity of the field. The results suggest that charge separation between photoexcited electrons and holes is an important factor for photoinduced fluidity to occur, supporting an electronic charging model of photodarkening and photoinduced volume change, as recently formulated.

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1. Introduction

Although a variety of models of photodarkening (PD) have been proposed (see for example [1,2]), none has been proved definite for all the materials in which it has been observed. These phenomena can be regarded as one of photoinduced fluidities of the structural network. The existing models can be classified into the following major categories: 1) change in the atomic (chalcogen) positions [3], 2) bond breaking and/or alternations between the atoms [4,5], and 3) macroscopic electronic charging of the illuminated region [6]. Structural fluidity, in principle, can be a macroscopic phenomenon and thus the models should explain the macroscopic natures of these photoinduced effects. The last model assumes movement of layer- or chain-like clusters of atoms by electronic repulsion. This model predicts no one-to-one correlation between photodarkening (PD) and photoinduced volume change (PVC) and requires charge separation between the photoexcited electrons and holes. It was considered that application of an external electric field might enhance the PD and PVC.

In the present study, we briefly review the current topics of photoinduced fluidity observed in amorphous chalcogenides. The effects of an electric field on PD in amorphous As_2Se_3 (a- As_2Se_3) films, as recently observed, are of interest in reaching a proper model of photoinduced fluidity. It is observed that the reaction time for PD to occur is shortened under a moderate electric field, depending on the biasing conditions (polarity), while the magnitude of the PD (saturation) is almost unchanged. Application of stronger electric fields, where the current-voltage characteristics become non-linear, enhances both the reaction rate and the magnitude of the PD. The results are discussed in terms of a model of macroscopic electronic charging of layer-like clusters in amorphous chalcogenides.

Structural changes induced by γ -, electron-, and ion-irradiation [7-9] can also be interpreted in terms of a macroscopic electronic charging model. Note, however, that the electronic charging model has been criticized by a quantitative argument [10]. This point will be addressed in the discussion section.

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2. Experimental details

a-As₂Se₃ films ($\sim 2 \mu\text{m}$ thick) were deposited onto indium tin oxide (ITO)-coated glass substrates by conventional thermal evaporation, and Au was evaporated as the top electrode to form a sandwich cell. The films were annealed at 473 K for 2 h before illumination. In the present study, in situ measurements of PD induced at 300 K were made. Two laser beams were used: an Ar ion laser ($h\nu = 2.41 \text{ eV}$) as the illuminating light and a He-Ne laser ($h\nu = 1.95 \text{ eV}$) as the probe light. The beams were directed such that they crossed each other at the sample. Illumination was made from the ITO side and the transmitted signal of the He-Ne probe beam was detected with a photodiode. The changes in the transmitted light were measured as a function of time. Further experimental details are described elsewhere [11,12].

The changes in the absorption coefficient, $\Delta\alpha$, were calculated from $\Delta\alpha = (-1/d) \ln (T/T_0)$, where T/T_0 is the transmitted signal relative to that measured before illumination and d is the sample thickness. A d.c. electric field of up to 10^5 V/cm was applied between the ITO and the Au electrode.

3. Experimental results

First, we review the recent experimental results obtained for the PD and PVS in amorphous chalcogenides. Fig. 1 shows an example of a surface height map for an a-As₂Se₃ film (Si substrate), obtained by a real-time *in-situ* surface height measuring system using a Twyman-Green interferometer [13]. The surface height map of the sample was obtained every 1/4 seconds with $\pm 10 \text{ \AA}$ in accuracy.

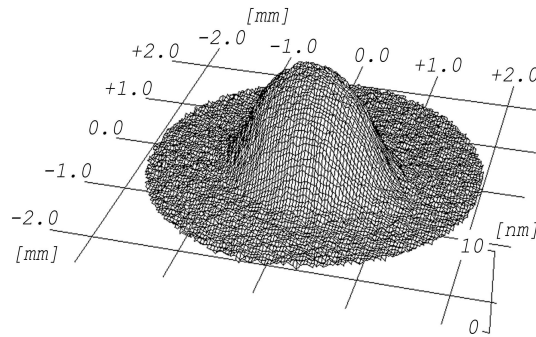


Fig. 1. An example of a surface height map for an a-As₂Se₃ film ($\lambda = 532 \text{ nm}$, 91 mW/cm^2). Note that the height scale is enlarged to about 10^5 times the horizontal scale.

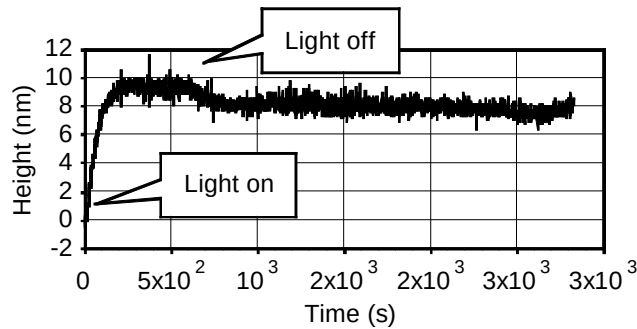


Fig. 2. Time evolution of the surface height for an a-As₂Se₃ film ($\lambda = 532 \text{ nm}$, 91 mW/cm^2).

Fig. 2 shows the time evolution of the surface height in an a-As₂Se₃ film deposited on a Si substrate. The height increased by 10 nm ($\Delta d/d \approx 2\%$) in 200 s of laser illumination ($\lambda = 532 \text{ nm}$, 91 mW/cm^2). After 600 s, the illumination was turned off. The surface height started decreasing and settled in 200 s at 2 nm less than the height before illumination ceased.

In Fig. 3, we show the results of transient and steady-state (metastable) PD in an a-As₂Se₃ film. The time evolution of the changes in the absorption coefficient, $\Delta\alpha$, at 1.95 eV is shown during various cycles of Ar-laser illumination at 50 (solid line) and 300 K (dashed line). This portion of the total change is the *transient* part induced by illumination and the portion remaining after stopping the illumination is the usually observed metastable PD. $\Delta\alpha$ increases and decreases very rapidly when the illumination is switched on and off, but in neither case does it return the original value, i.e. the metastable photodarkening is accumulated with each successive illumination cycle. The total increase in $\Delta\alpha$, 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.

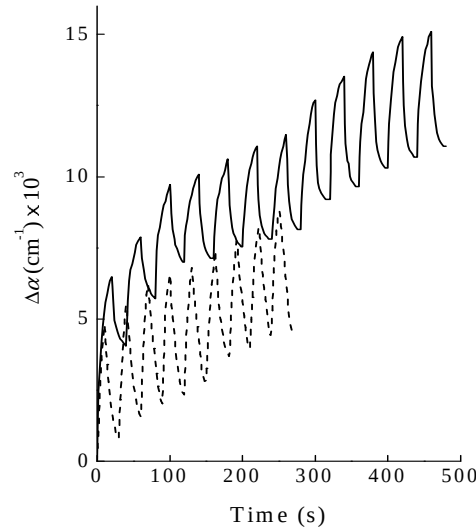


Fig. 3. Changes in the absorption coefficient $\Delta\alpha$ with short-duration illumination for an a-As₂Se₃ film at 50 K (solid line) and 300 K (dashed line). The Ar laser ON and OFF states are 20 s each at 50 K, and 10 s and 20 s at 300 K, respectively.

Now, we turn to electric biasing effects on the PD. Fig. 4 shows the time evolution of the changes in the absorption coefficient, $\Delta\alpha$, at 1.95 eV (He-Ne laser) [14]. The illuminating light intensity was 100 mW/cm² (Ar ion laser). The biasing conditions for an external electric field of 5×10^4 V/cm (applied voltage 10 V) are as follows: Triangles represent a positive voltage on the ITO (illuminated side), circles a minus voltage on the ITO, and squares correspond to zero bias. The samples were annealed at 473 K in each cycle of the measurements. It was found that the initial transmittance T_0 takes almost the same value, indicating that the PD is reversible. The solid lines are the fittings obtained using the following stretched exponential function:

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

where t is the time after the illumination is switched on, τ the effective reaction time, $\Delta\alpha_s$ the saturated value of $\Delta\alpha$, and β a dispersion parameter ($0 < \beta < 1.0$). The fitting seems to be reasonable and gives values of $\Delta\alpha_s$, τ , and β , all of which will be discussed in the next section.

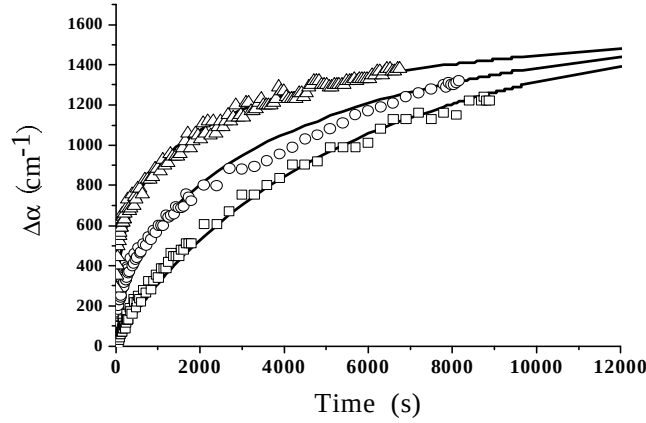


Fig. 4. Time evolution of the changes in the optical absorption coefficient $\Delta\alpha$. Triangles, circles and squares represent positive, negative, and zero biasing conditions on the ITO (illuminated side), respectively. The solid curves are fits obtained using Eq. (1).

Fig. 5 shows the time evolution of the changes in the absorption coefficient, $\Delta\alpha$, as a function of the magnitude of the electric field (positive biasing condition) [14]. The illuminating light intensity was 100 mW/cm^2 (Ar ion laser). All notations are described in the figure caption. The reaction rate increases with biasing electric field. The solid curves are the fits obtained using Eq. (1). Under strong biasing conditions, $\Delta\alpha$ increases with bias voltage.

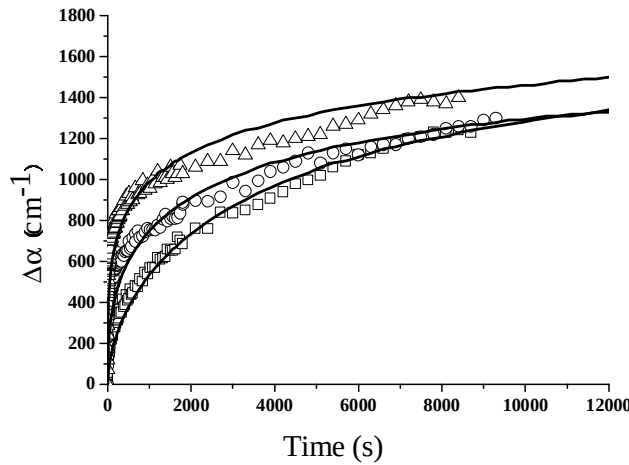


Fig. 5. Time evolution of the changes in the absorption coefficient $\Delta\alpha$. Triangles, circles and squares represent external electric fields (positive bias on the ITO) of 10^5 V/cm , $5 \times 10^4 \text{ V/cm}$, and zero, respectively. The solid curves are fits obtained using Eq. (1).

It is of interest to discuss the photoconductivity which can be affected by the biasing conditions. Below 10 V ($= 5 \times 10^4 \text{ V/cm}$) for the both polarities, almost linear current-voltage characteristics were observed under dark and illuminated conditions. Above 10 V , a non-linearity appears for both the dark and illuminated conditions. Note that this non-linearity cannot be due to a thermal effect, because it occurs at nearly the same voltage for dark and illuminated conditions. Note also that any interfacial effects, such as Schottky or blocking type effects, can be ignored in the present sample configuration because the I-V characteristics are independent of the biasing polarity (symmetric I-V characteristics). As discussed in the following section, it will be noticed that the

saturated value of $\Delta\alpha$ increases with strong biasing conditions, in which non-linear I - V characteristics appear, although $\Delta\alpha$ takes the almost same value under a moderate biasing condition.

4. Discussion

Before proceeding with the discussion of the experimental data, we briefly summarize the model of macroscopic electronic charging on layer-like clusters in amorphous chalcogenides [6]. In this model, photoexcited electrons remain in the illuminated region and holes diffuse away into the un-illuminated region, owing to the higher diffusion coefficient of holes in amorphous chalcogenides. Then the illuminated region becomes charged negatively, leading to the expansion and slip of the layer-like clusters, causing photoexpansion and photodarkening. Use of an electric field may assist charge separation if the field is properly applied, and may enhance the occurrence of PD and PVC, since the relative numbers of photoexcited electrons or holes should increase with applied field. The experimental results seem to confirm the above prediction.

In the previous section, it was shown that fitting to the experimental data produces the physical parameters, $\Delta\alpha_s$, τ , and β . We tabulate these quantities in Tables 1 and 2, as obtained from Figs. 4 and 5, respectively. It is seen from Table 1 (for a moderate biasing condition) that the rate of PD, which can be defined as $1/\tau$, increases with electric field, while the saturated value of the PD, $\Delta\alpha_s$, takes almost the same value, irrespective of the presence or absence of the field. This means that under the present biasing condition (5×10^4 V/cm) the saturated number of photodarkened sites is independent of the magnitude of the field, although the presence of the field accelerates photodarkening.

Looking at the experimental data (Fig.4 and Table 1) in more detail. Positive biasing on the ITO increases the relative concentration of electrons in the illuminated area (near the ITO), because holes drift away to the un-illuminated Au counter-electrode, giving the highest reaction rate (shortest reaction time). Negative biasing on the ITO gives a reaction rate intermediate between those for positive and zero biasing. The number of holes increases with negative biasing as electrons diffuse away to the Au counter-electrode. However, as the diffusion coefficient (or drift mobility) of electrons is smaller than that of holes, electronic charging (positive in this case) is expected to be smaller than that for positive biasing. The zero biasing case therefore gives the lowest reaction rate among the three biasing conditions.

Let us look again at Fig. 5 and Table 2, describing the time evolution of the changes in the absorption coefficient, $\Delta\alpha$, as a function of the magnitude of the field under positive biasing. It is known that the magnitude of the PD (determined by the change of the bandgap) depends strongly on temperature and weakly on illumination intensity [1-3]. At the same temperature and intensity at which the illumination is made, application of a moderate electric field may accelerate only the occurrence of PD. However, as shown in Fig.5 and also in Table 2, application of a strong electric field, in which non-linear I - V characteristics appear, enhances both the reaction rate and the magnitude of the PD. This phenomenon is of interest and a detailed report will be presented in a future publication.

To confirm that holes are the more mobile carrier in a-As₂Se₃, the photovoltage (the Dember effect), V_p , has been measured at 300 K under the present conditions (Ar ion laser, 100 mW/cm²). We obtained $V_p = 160$ meV with the expected polarity, i.e. the illuminated ITO electrode is negative and the Au counter-electrode is positive, indicating that holes are more mobile than electrons. The photovoltage can be expressed by [15]

$$V_p \approx \frac{kT}{e} \ln \left(\frac{\sigma_i}{\sigma_d} \right), \quad (2)$$

where σ_i and σ_d are the photoconductivity and dark conductivity, respectively. Under the present conditions, $(\sigma_i/\sigma_d \approx 10^2)$ V_p is estimated to be ~ 150 meV [14], which is almost the same value as that obtained experimentally.

Table 1. Fitting parameters obtained using Eq. (1). $\Delta\alpha_s$ is the saturated value of the change in the optical absorption, τ the effective reaction time, and β the dispersion parameter. The biasing voltage is 5×10^4 V/cm.

	Bias condition		
	Positive on ITO	Negative on ITO	Zero
$\Delta\alpha_s$ (cm ⁻¹)	1700	1700	1600
τ (s)	2000	4200	5500
β	0.40	0.60	0.90

Table 2. Fitting parameters obtained using Eq (1). $\Delta\alpha_s$ is the saturated value of the change in the optical absorption, τ the effective reaction time, and β the dispersion parameter.

	Electric field (V/cm)		
	Zero	5×10^4	1×10^5
$\Delta\alpha_s$ (cm ⁻¹)	1600	1600	1900
τ (s)	4500	3000	2800
β	0.60	0.42	0.30

We should now discuss the validity of the electronic charging model [6]. It was observed that the application of an electric field accelerates the PD, depending on the magnitude and polarity of the field. These experimental observations support the macroscopic charging model. This model may further be supported by the following experimental results. The PD effect disappears in metal-doped chalcogenides [16,17]. This can be explained as follows: atoms of an introduced metal, such as copper, may act as bridging atoms between the layers and hence reduce the flexibility of the layer network. Such bridging will then reduce the capability for fluidity. Furthermore, the introduction of such a strong constraint also induces dangling bonds which act as recombination centers and reduce the number of photoexcited free carriers considerably. We now know that constraint of the structural network reduces the photoinduced fluidity.

The electronic charging model also predicts that no PVC and PD can occur in very thin films, because the photoexcited holes cannot diffuse away from the illuminated region and hence the layer surface area will remain electrically neutral. It was reported, in fact, that no PD can be induced in As₂S₃ films thinner than 50 nm [18]. From the similar spectral dependence between the PD and the photoconductivity in As₂S₃, and the similar behaviors between PVC and photoconductivity during and after termination of the illumination [19], free-carrier generation but not geminate (excitonic) pairs is suggested to be responsible for the structural changes, which seems to be consistent with the electronic charging model.

We should also discuss the transient changes observed for the PD and PVE during illumination. The total changes consist of transient and metastable components. The transient component decays when the illumination is switched off and only the metastable PD is observed after cessation of the light. The mechanism can be understood in the following way. Upon absorbing a photon, a “cluster” in the ground state is transferred to the excited state *via* the transient state. The relaxation of the transient state may proceed along two different pathways, either back to the ground state (the transient component) or into the metastable or a new equilibrium state (the metastable component). It may also be easy to explain the transient phenomena observed in PVC and PD by the electronic charging model.

It should be mentioned that the electronic charging model has been criticized by Emelianova et al. [10]. They discuss and examine the model in a quantitative manner [10]. Using Poisson’s equation and taking a value for Young’s modulus, the total deformation of the sample due to electronic charging has been estimated. They suggest that photoinduced structural changes caused by the Coulomb interaction due to electronic charging is not capable of explaining the experimentally observed values of the changes (volume expansion). As they stated [10], however, the calculation is based on the assumptions of homogeneous material properties and microscopically homogeneous

photoinduced charge distributions. The electronic charging model, however, is not based on a microscopically homogeneous charge distribution, since the excitation of “layer-like nano-scale clusters”, which are not uniformly distributed through the sample in a microscopic sense, has been taken into consideration [6]. In the usual excitation conditions, Shimakawa et al. [6] estimated that the charging energy stored in such clusters reached 10 % of the van Der Waals energy between the layers. This energy may be enough to expand structural networks in amorphous chalcogenides.

5. Conclusions

We briefly reviewed the current topics of photoinduced fluidity observed in amorphous chalcogenides. In particular, we concentrated on the dynamics of the photoinduced fluidity. To reach a proper model of the photoinduced fluidity, the electric biasing effects on photodarkening have been examined in a-As₂Se₃ films. Application of a moderate electric field shortens the reaction time of the PD, depending on the biasing conditions (polarity) of the electric field, while the magnitude of the PD is the same as that without an electric field. Application of a strong electric field, for which nonlinear I-V characteristics are observed, enhances both the reaction rate and the magnitude of the PD. The results suggest that charge separation between photoexcited electrons and holes is a dominant factor in the occurrence of PD and PVC. This may support a recently formulated electronic charging model of photodarkening and photoexpansion [6].

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