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Percolative growth of photodarkening in amorphous As_2S_3 films

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The time evolution of changes in the optical absorption coefficient with illumination has been studied for a-As_2S_3 films at 50, 100, 200, and 300 K in order to characterize the dynamics of photodarkening. The magnitude of the changes is larger at the lower temperatures. A model of photon-assisted site switching is proposed for the variation of photodarkening with time, in which the fractional growth in the concentration of photodarkened sites is expressed by a stretched exponential function.

The study of changes in the band gap and volume of amorphous chalcogenides induced by illumination has received renewed interest recently and attempts have been made to understand these changes (see, for example, Refs. 1 and 2). However, most measurements have been made after, rather than during, illumination. Tanaka[2] has suggested, in his detailed study of photo-induced volume and band gap changes in a-As_2S_3, after illumination, that the rate of photodarkening (PD) is slower than that of the volume changes. Kuzukawa *et al.*[3,4] in their studies of photo-induced volume changes (PVC) and PD in obliquely deposited As-based chalcogenide films, have suggested a correlation between the changes in volume and band gap by illumination and annealing (band gap decreases when the volume expands and vice versa). However, the above conclusions were based on measurements of PVC and PD *after illumination*. The behavior and dynamics of PD *during illumination* remain unclear.

Recently, we have reported *in situ* measurements of photo-induced volume changes (PVC) in obliquely deposited a-As_2S_3 films and found transient and metastable changes in thickness during illumination.[5] Ducharme *et al.*,[6] in their work on photodarkening of bulk a-As_2S_3, observed a continuous increase in the average photodarkening (PD) with illumination and no saturation was observed. Since the response time is long for thick samples, it is not easy to characterize the time dependence of the changes in bulk material. Other workers have also reported preliminary studies on *in situ* photo-induced changes in the optical transmission of amorphous chalcogenides.[7–9] The effect of metal additives on the time dependence of the optical transmission in a-As_2Se_3 films has also been reported.[10]

In the present work, we report *in situ* measurements of PD by measuring the changes in the optical absorption coefficient with time for obliquely deposited a-As_2S_3 films at 50, 100, 200, and 300 K. The results can be explained using the idea of a percolative growth of photodarkened sites with illumination by photon-assisted site switching (PASS). The fraction of photodarkened sites is expressed by a stretched exponential function.

Thin films of a-As_2S_3 (thickness, $d \sim 0.5\,\mu m$) were obliquely deposited by thermal evaporation onto glass (Corning 7059) substrates. The angle between the normal to the substrates and the direction of incident molecules was fixed at 80°. Note that the density of films deposited at this angle is nearly half to that of films deposited at normal incidence. The lower density is considered to be responsible for the

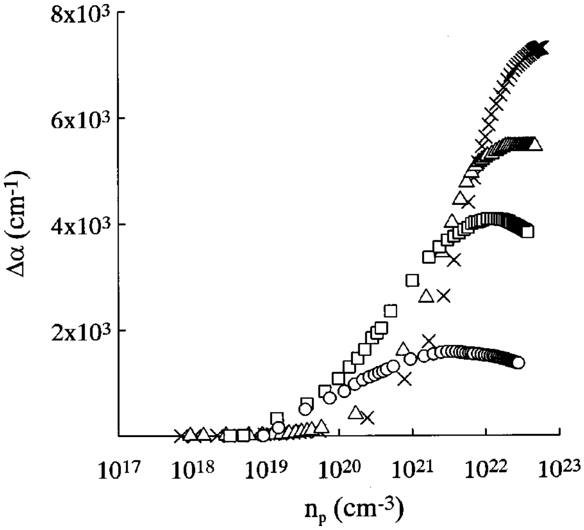

FIG. 1. *In situ* variation of changes in absorption coefficient ($\Delta\alpha$) as a function of number of absorbed photons (n_p) at various temperatures. ×, △, □, and ○ show the changes at 50, 100, 200, and 300 K, respectively. Illumination is by an Ar^+ laser (20 $\mathrm{mW/cm^2}$).

giant changes that occur in volume and band gap.[4] Obliquely deposited films were used in the present work as illumination induces giant changes in band gap.[5] These giant changes make it easier to measure the changes in absorption coefficient more precisely. The films were annealed at 443 K for 2 h before making the measurements. They were then placed in an evacuated cryostat for the measurement of optical transmission at various temperatures. The samples were illuminated with an argon ion laser ($h\upsilon = 2.42\,\mathrm{eV}$, power $= 20\,\mathrm{mW/cm^2}$) with a light spot diameter of 5 mm. The change in optical transmission, ΔT (here $\Delta T = T_0/T$, T_0 is the transmission when the illumination is put on and T is the transmission at any time, t) of the films was monitored by the voltage drop across a photodiode and the illumination continued until ΔT saturated (approximately 30 min under the present experimental conditions). The changes in the optical absorption coefficient of the film, $\Delta\alpha$, were calculated as $\Delta\alpha = (-1/d)\ln(\Delta T)$, where d is the film thickness and determined as a function of the number of absorbed photons. The number of absorbed photons was estimated as $n_p = N_{inc}\alpha(1-R)^2 t$, where α is the absorption coefficient, ($\alpha = \alpha_0 + \Delta\alpha$; α_0 is the initial absorption coefficient and $\Delta\alpha$ is the change in absorption coefficient), R is the reflection coefficient and t is the time of illumination. N_{inc} is the number of incident photons. Note that the conditions, $\alpha d \ll 1$ and $\alpha d < 1$, are satisfied at low and high temperatures, respectively. It should be noted that the illumination causes an increase in the thickness of the films, but d is assumed to be constant in the present work as d changes by around 5% at 300 K,[5] which is very small compared to the changes in the absorption coefficient, $\Delta\alpha$. Also, if d increases, it will result in a decrease in $\Delta\alpha$, which is opposite to that observed in PD ($\Delta\alpha$ increases in PD).

The variation of the changes in absorption coefficient ($\Delta\alpha$) with the number of absorbed photons (n_p), at different temperatures, is shown in Fig. 1. Initially, $\Delta\alpha$ increases slowly with n_p, followed by a large increase and then almost saturation. The magnitude of the changes decreases with increasing temperature with $\Delta\alpha$ being a maximum at 50 K (in spite of a slow initial variation with time) and smallest at 300 K. At 50 and 100 K, the changes are very slow to start with and increase rapidly as n_p increases, while at 200 and 300 K, there is a more continuous growth of $\Delta\alpha$. The slow initialization at low temperatures is attributed to a smaller number of absorbed photons, as the initial absorption coefficient is small at lower temperatures ($\alpha_0 = 150\,\mathrm{cm^{-1}}$ at 50 K). With increasing time of illumination, the number of absorbed photons rises owing to an increase in the absorption coefficient resulting in a large PD at low temperatures.

To explain the behavior of $\Delta\alpha$ during illumination, and to understand the dynamics of PD, we consider the films to contain clusters of atoms that act as potential sites for photodarkening. On illumination, these clusters undergo *photon-assisted site switching* (PASS) forming photodarkened sites (PDS), which are associated with higher energy than the original state. Let us consider that, before illumination, there exist N_T clusters in the ground state. The rate of the growth of the number (N) of PDS with the number of absorbed photons (n_p) can be expressed as

$$\frac{dN}{dn_p} = k_p(N_T - N) - k_r N, \tag{1}$$

where k_p is the promotion rate and k_r the recovery rate. Assuming a time-dispersive reaction for the PASS, the forward and backward reactions can be expressed as $k_p = A n_p^{\beta-1}$ and $k_r = B n_p^{\beta-1}$, respectively, where A and B are constants that depend on temperature and illumination intensity, and β is a dispersion parameter $(0 < \beta < 1)$. The dispersion parameter β is assumed for simplicity to be the same for both the forward and backward reactions. N is then given as

$$N = N_S\left\{1 - \exp\left[-\left(\frac{n_p}{N_p}\right)^{\beta}\right]\right\}, \tag{2}$$

where $N_S = AN_T/(A+B)$ and $N_p = [\beta/(A+B)]^{1/\beta}$ are the saturated number of photodarkened sites and the effective number of photons, respectively. Both N_S and N_p will have a temperature variation (due to the temperature-dependent β, A, and B). This type of stretched exponential growth has also been suggested for the light-induced creation of defects and for thermal crystallization.[11,12] The fraction of PD occurrence $C(n_p)$ at any n_p is defined as $C(n_p) = N/N_S$ [see Eq. (2)]. $C(n_p)$ lies between 0 and 1 (0 for the initial state, i.e., before illumination when no sites are converted, and 1 when all the potentially available sites are converted to PDS).

We now recall the effective medium theory.[13,14] The effective medium approximation (EMA) can be used to calculate the conductivity of a random mixture of particles under the assumption that the inhomogeneous surroundings of a particle can be replaced by an effective medium. Assuming a random mixture of particles of two different conductivities, i.e., a volume fraction C having a conductivity σ_1 and the remainder part σ_2, substantially smaller than σ_1, simple expressions for dc conductivity have been obtained.[13,14] Springett[15] extended the idea of EMA for the evaluation of the ac behavior of a random system by replacing the conductivity by a complex admittance. As the optical constants are closely related to the complex dielectric constants, the ab-

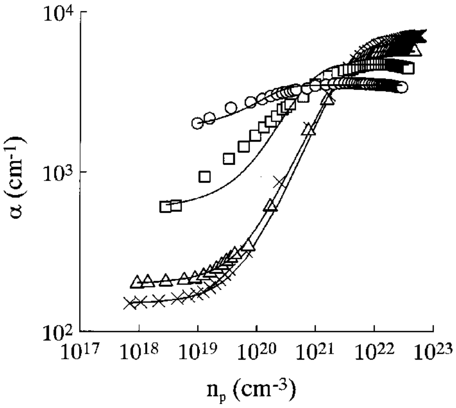

FIG. 2. Variation of absorption coefficient ($\alpha = \alpha_0 + \Delta\alpha$) as a function of number of absorbed photons (n_p) at various temperatures. Description of symbols is the same as in Fig. 1. Solid line is the fitting obtained using Eq. (4) in the text.

sorption coefficient in a two-phase system can be calculated using the idea of EMA.[16] Note that EMA has been used to interpret optical properties in μc-Si,[16] and composite media.[17] Sheng[17] has concluded that EMA can yield realistic results of optical properties if the microstructure is properly taken into account. In our work, we assume the clusters of atoms that undergo PASS are roughly spherical in shape and the number of these clusters increases with the number of absorbed photons. We now extend EMA to explain the photo-induced structural changes observed in the present work.

Following Springett,[15] the set of equations for the conductivity σ_m of a two-phase system are

$$\left(\frac{\sigma_m}{\sigma_1} - \frac{\sigma}{\sigma_1}\right)^2 = (X^2 + Y^2)^{1/2} + X,$$

where

$$2X = \left(\frac{\sigma}{\sigma_1}\right)^2 + \frac{1}{2}\frac{\sigma_2}{\sigma_1} - \left[\left(\frac{\varepsilon}{\varepsilon_1}\right)^2 + \frac{1}{2}\frac{\varepsilon_2}{\varepsilon_1}\right](\tan\delta_1)^{-2},$$

$$Y = \left(\frac{1}{4}\frac{\sigma_2}{\sigma_1} + \frac{\varepsilon\sigma}{\varepsilon_1\sigma_1} + \frac{1}{4}\frac{\varepsilon_2}{\varepsilon_1}\right)(\tan\delta_1)^{-1},$$

$$\sigma = \tfrac{1}{4}\{3C(n_p) - 1\}\sigma_1 + \tfrac{1}{4}\{2 - 3C(n_p)\}\sigma_2,$$

$$\varepsilon = \tfrac{1}{4}\{3C(n_p) - 1\}\varepsilon_1 + \tfrac{1}{4}\{2 - 3C(n_p)\}\varepsilon_2,$$

$$\text{and } \tan\delta_1 = \frac{\sigma_1}{\omega\varepsilon_0\varepsilon_1}. \tag{3}$$

Here, σ_1 and σ_2 are the real parts of the conductivity and ε_1 and ε_2 are the background dielectric constants of the two phases. In this paper, we take $\sigma_1\,(\varepsilon_1)$ and $\sigma_2\,(\varepsilon_2)$ to correspond to $C=1$ and 0, respectively. For simplicity, ε_1 and ε_2 are assumed to be equal. σ_m is the real part of the conductivity of the volume fraction $C(n_p)$. ω ($=3.68\times10^{15}\,\mathrm{s}^{-1}$) is the frequency of light (Ar$^+$ laser). The absorption coefficient, α, is connected to the real part of the conductivity by the relation

TABLE I. Initial absorption coefficient (α_0), (Ref. 18) dispersion parameter (β), and effective number of photons (N_p) at various temperatures.

Temperature (K)	α_0 (cm^{-1})	β	N_p (cm^{-3})
50	150	0.85	2.8×10^{21}
100	200	0.80	1.8×10^{21}
200	700	0.70	3.5×10^{20}
300	2000	0.60	8.0×10^{19}

$$\alpha = \frac{\sigma_i}{nc\varepsilon_0}, \tag{4}$$

where the subscript i is 0, 1, or m to represent σ_0, σ_1, or σ_m, respectively. σ_1 and σ_0 are estimated from the saturated and initial absorption coefficient, respectively. n is the long-wavelength refractive index ($n = \sqrt{\varepsilon_1} = \sqrt{\varepsilon_2}$), c is the velocity of light, and ϵ_0 is the permittivity of the vacuum. Our main assumption is that the optical absorption of a two-phase system can be treated by the effective medium approach used for the ac conductivity. It has already been suggested that this approach yields realistic results.[16,17]

Using the derived $C(n_p)$ [from Eq. (2)] along with Eqs. (3) and (4), we can evaluate α as a function of n_p. Taking into account the initial absorption coefficient α_0,[18] we replot Fig. 1 as Fig. 2, where we show the variation of the total absorption coefficient ($\alpha = \alpha_0 + \Delta\alpha$) with total absorbed photons (n_p) and fit Eq. (4) to the experimental data, which is shown by the solid lines. The fitting to α, as derived from Eq. (4), is reasonably good at all temperatures. The description of the symbols is given in the figure caption. The fitting gives us the dispersion parameter β and the effective photon number for site switching N_p, and these are listed in Table I along with the initial absorption coefficient α_0. The variation of fitting parameters β and N_p with temperature is shown in Fig. 3. Both N_p and β decrease with temperature. As N_p is inversely proportional to the sum of A and B, it is expected from the observed temperature variation that the reactions will be faster at higher temperatures as compared to

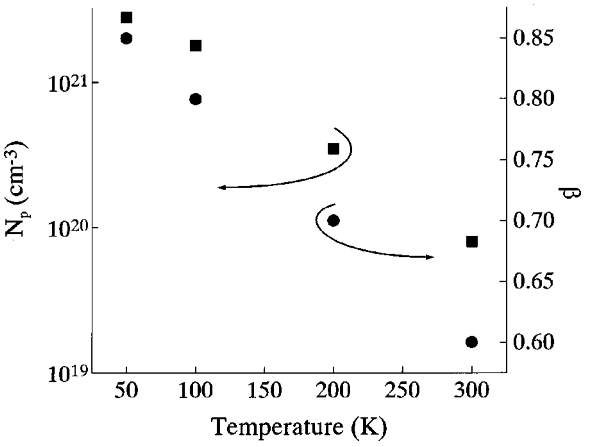

FIG. 3. Variation of dispersion parameter (β) and effective number of photons for site switching (N_p) as a function of temperature.

lower temperatures. The variation of dispersion parameter, β, with temperature, is opposite to that observed in transport-related studies,[19] where it is found to increase with increasing temperature. As the physical meaning of the dispersion parameter is not fully understood at present[11] the reason for this discrepancy is not clear.

Based on the above results and the discussion, the dynamics of PD during illumination can be understood in detail. Before illumination, all the potential sites are in the ground state, which by PASS switches over to the photodarkened state by illumination in a random way. A proposed mechanism for PASS has been proposed earlier.[20] It involves charging and slip motion of clusterlike sites. Here it is proposed that the site switching may lead to a percolative growth of PD with time during illumination.

In order to clarify whether the observed change in the absorption coefficient is an outcome of photoelectronic or thermal mechanisms, we have estimated the temperature rise during illumination for the present experimental conditions. The temperature rise ($\Delta Temp$) of a sample can be estimated as[21,22] $\Delta Temp = I_{abs}/\kappa r$, where κ is the thermal conductivity of the substrate (12.6 mW/cm K for glass[23]), r is the radius of the light spot (0.25 cm) and I_{abs} is the absorbed light intensity, i.e., $I\alpha d$. Here d, α, and I are the film thickness, absorption coefficient, and incident power, respectively. Taking the maximum absorption coefficient measured in the present work, I_{abs} is estimated to be $\sim$1.6 mW which gives a temperature rise of $\sim$0.6 K. This is negligibly small for such a large PD to occur. Thus, it can be concluded that the observed PD is purely due to photoelectronic effects.

In summary, we have studied the time (absorbed photon number) variation of changes in the optical absorptioncoefficient for obliquely deposited a-As_2S_3 films at various temperatures. The magnitude of changes in the absorption coefficient is largest at the lowest temperature (50 K) and becomes smaller as the temperature goes up to 300 K. A percolative growth of photon-assisted site switching of atomic sites in clusters to photodarkened sites is proposed in which the fraction of PD occurrence is expressed by a stretched exponential function.

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