Journal of Optoelectronics and Advanced Materials Vol. 4, No. 3, September 2002, p. 595 - 604

DYNAMICS OF PHOTODARKENING IN AMORPHOUS CHALCOGENIDES

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We review the recent advances made in understanding the dynamics of photoinduced structural changes (PSC) and photodarkening (PD) in amorphous chalcogenides. The new results of the occurrence of transient and metastable changes in PSC and PD have shed new light in understanding the mechanism of these changes. We present measurements of these metastable and transient effects in evaporated films of a-chalcogenides. The results are discussed in terms of a macroscopic model in which, on photoexcitation, layer- or chain-like clusters of atoms are expected to expand and slip relative to each other.

(Received July 5, 2002; accepted July 22, 2002)

Keywords: Amorphous chalcogenide, Photodarkening, Transient and metastable changes

1. Introduction

Two types of reversible photoinduced effects are reported in amorphous semiconductors namely the structural changes and defect creation [1,2]. These photoinduced changes are returned to their original states by thermal annealing. Although these reversible changes, both for amorphous chalcogenides (a-Ch) have been studied for over two decades, its microscopic origin is still poorly understood [1-5].

The photoinduced defect creation affects device applications, e.g. the decrease of conversion efficiency (degradation) in solar cells, because such defects act as recombination centers, and hence these should be removed or minimized. In spite of great effort to overcome this degradation, it is still a difficult problem. Flexible or deformable structural network in amorphous materials may facilitate such a degradation.

The structural changes, on the other hand, accompany the change in refractive index (*n*), which may result in the change of bandgap and hence these effects can be useful for devices, such as optical memory applications, proposed by Ovshinsky nearly 30 years ago but an important part of the information technology even now and continuing to be so in the near future as well. *Giant* photoinduced volume changes (reversible) approaching $\Delta V/V \approx +0.04$ (expansion) for obliquely deposited amorphous $As_2Se(S)_3$ and $\Delta V/V \approx -0.08$ (contraction) for amorphous $GeSe(S)_2$ have been observed [6, 7], yielding also *giant* changes of bandgap. It is of interest whether the bandgap change is a direct consequence of volume change. Recent detailed study of photoinduced volume expansion (PVE) of a-As_2S_3 indicates that there seems to be no direct relation between PVE and the decrease of bandgap (photodarkening, PD) [8].

Photostructural change (PSC) and the related photodarkening (PD) are phenomena unique to glassy or amorphous chalcogenides and are not observed in amorphous group IV and V semiconductors (a-Si, a-As etc.), or in crystalline chalcogenides [9]. It is noted also that the PD disappears in some metal-doped chalcogenide glasses (e.g. by doping with Cu, Mn etc.) [10, 11].

It is believed that a change in the interaction of chalcogen lone-pair (LP) electrons is responsible for PD. The increase in LP-LP interactions yields a broadening of the valence band, causing a reduction in the bandgap (PD). The models, which have been put forward in support of the above mechanism, can be placed into the following categories: 1) a change in the atomic (chalcogen) positions [4], 2) bond breaking and/or alternations between the atoms [8, 12, 13], and 3) repulsion and slip motion of structural layers (RS model) [14]. Any model should be able to explain the observed behaviors of PD and PVE for As-based chalcogenides. Recent *in-situ* measurements of PD or PVE etc., have given a better understanding of these changes [13, 15, 16]. In the present article, we try to review the recently obtained interesting results on the reversible PD and PVE for As-based chalcogenides. We pay attention in particular to the time evolution of these changes (*in situ* measurements etc.), which is useful in understanding the dynamics of PD and PVE in more detail.

2. Principal experimental data

Assuming all the readers working in amorphous semiconductors are familiar with the basic definition of PD and PVE, we start from the metastable changes in PD and PVE. It is seen that bandgap decreases and thickness increases by illumination and that giant changes are induced in obliquely deposited films [7].

It was believed for a long time that PD and PVE were two different sides of the same phenomenon and hence one-to-one correlation should exist between PD and PVE. However, Ke.Tanaka [8] has experimentally shown that the time constants of the PD and the VE in As_2S_3 are different. It is observed that the PVE saturates earlier than the PD. These experimental observations, on the other hand, suggest that these two phenomena (PD and PVE) are not directly related to each other. However, as these measurements were done after switching off the illumination (metastable state), the correlation during illumination remains unclear.

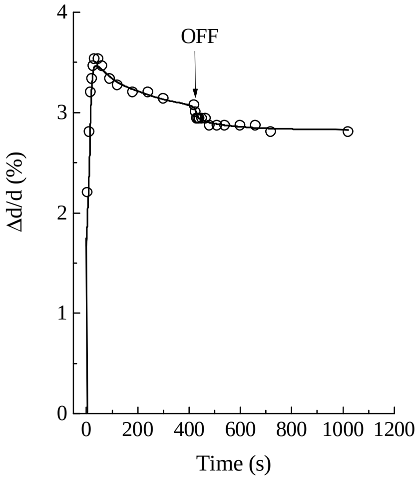


Fig. 1. Relative changes in thickness $\Delta d/d$ with time on switching the illumination on and off for obliquely deposited film of a-As_2S_3 (after [15]). The solid line is a guide to the eye.

To understand the dynamics of PD and PVE during illumination, *in-situ* measurements have been performed by us [15, 16] and are discussed here briefly. Fig. 1 shows the relative results of changes of thickness, $\Delta d/d$, with time during and after illumination obtained by *in situ* measurements of photoexpansion for a-As_2S_3 films [15]. As soon as the light (mercury lamp) is switched on, the thickness increases rather rapidly, reaches a maximum after approximately 30 s, and then decreases slowly with time. This decrease continues during the rest of the illumination. This behavior of decrease in thickness change *during* illumination is similar to that of the degradation of photocurrent [1, 2, 17] in amorphous chalcogenides. By turning off the illumination, the thickness decreases slightly. With the passage of time it decays slowly, due to relaxation of the structure, and reaches a metastable state which can be observed as usual PVE, i.e. PVE observed *after* illumination. This decay behavior of PVE after the illumination is switched off is found to be very similar to that of the decay of photocurrent [15].

The time evolution of changes (*in-situ* measurements) of the optical absorption coefficient with illumination has been studied for As_2S_3 in detail [16]. 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. 2. Note that $\Delta\alpha$ is calculated as $\Delta\alpha = (-1/d)\ ln(\Delta T)$, where d is the film thickness and ΔT the change in optical transmission which is defined here as $\Delta T = T/T_0$ (T_0 is the transmission when the illumination is put on and T is the transmission at any time t). The details of experimental conditions are described in the reference. 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 or n_p) 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 ($\alpha_0 = 150\ cm^{-1}$ 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. Taking into account the initial absorption coefficient α_0, Fig. 2 is replotted as Fig. 3, where the variation of the total absorption coefficient ($\alpha = \alpha_0 + \Delta\alpha$) with total absorbed photons (n_p). The solid lines are the fitting to a model, which will be discussed later**.** Note, however, that the *in situ* measurements of PVE have been done using white light and thus the change in PVE is not given as a function of n_p but as a function of time (see Fig. 1). Thus, the correlation between the rate of PVE and PD during illumination is difficult to comment upon.

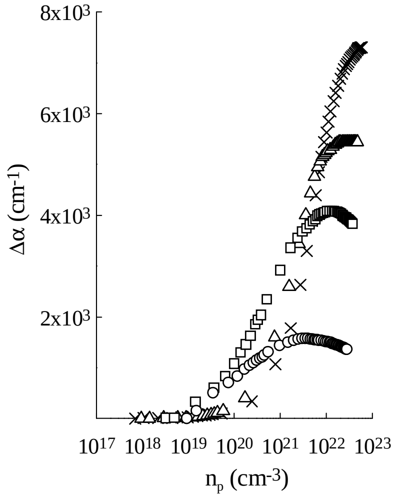


Fig. 2. *In situ* variation of changes in absorption coefficient $\Delta\alpha$ as a function of absorbed photons n_p at various temperatures. ×, Δ, □, and O show the changes at 50, 100, 200, and 300 K, respectively. Illumination is by Ar^+ laser ($20 mW/cm^2$) (after [16]).

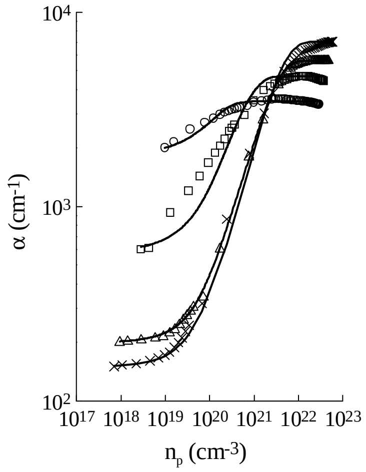


Fig. 3. Variation of absorption coefficient ($\alpha=\alpha_0+\Delta\alpha$) as a function of number of absorbed photons n_p at various temperatures. Description of symbols is the same as in Fig. 2. Solid line is the fitting obtained using Eq.(3) in the text (after [16]).

Next we show the results of transient PD in a-As_2Se_3 films (normally deposited). Fig. 4 shows 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. The details of the measurements are presented elsewhere [16]. For a-As_2Se_3 films, $\Delta\alpha$ increases rapidly at first at both temperatures before reaching close to saturation after some time. 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 stopping the illumination is the usually observed metastable photodarkening.

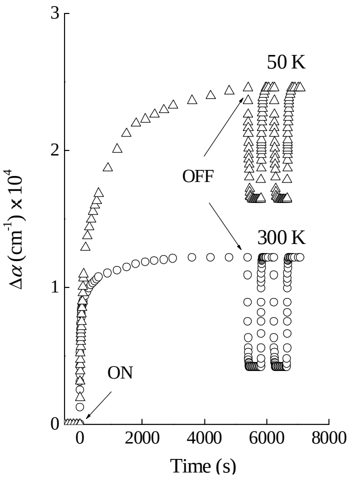


Fig. 4. Time evolution of changes in absorption coefficient, $\Delta\alpha$, for a-As_2Se_3 films at 50 (Δ) and 300 K (O). ON and OFF stages of the Ar laser are indicated by the arrows.

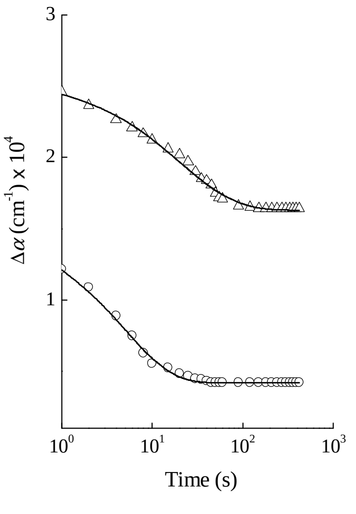


Fig. 5. The decay of the transient photodarkening after switching off the Ar laser for a-As_2Se_3 films at 50 (Δ) and 300 K (O). The solid lines are fittings using Eq. 4.

Fig. 5 shows the time dependence of the decay of the transient part at 50 and 300 K. The solid lines are a stretched exponential fit and will be discussed in the next section. The total increase in $\Delta\alpha$ for a-As_2Se_3 films, during illumination, is the sum of the transient and the metastable photodarkening. 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. Successive cycles of illumination with the Ar laser (laser on and off), after the metastable photodarkening is reached (see Fig. 4), result in increases and decreases 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 photodarkening.

To observe the transient and metastable changes during the initial rapid increase of $\Delta\alpha$ in more detail, we have studied the changes in $\Delta\alpha$ in a-As_2Se_3 for short-time illumination at 50 and 300 K, i.e., before reaching the saturated state shown in Fig. 3. The data are shown in Fig. 6. 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. 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 $\Delta\alpha$ 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.

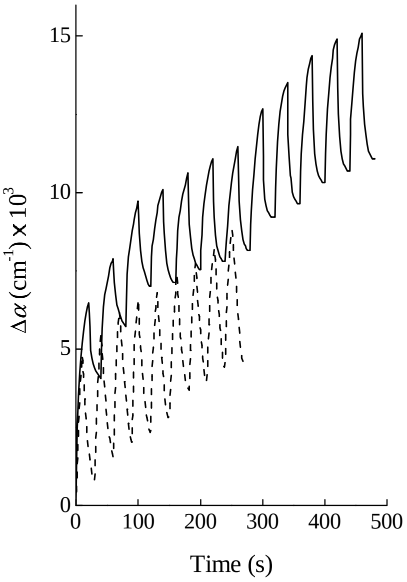
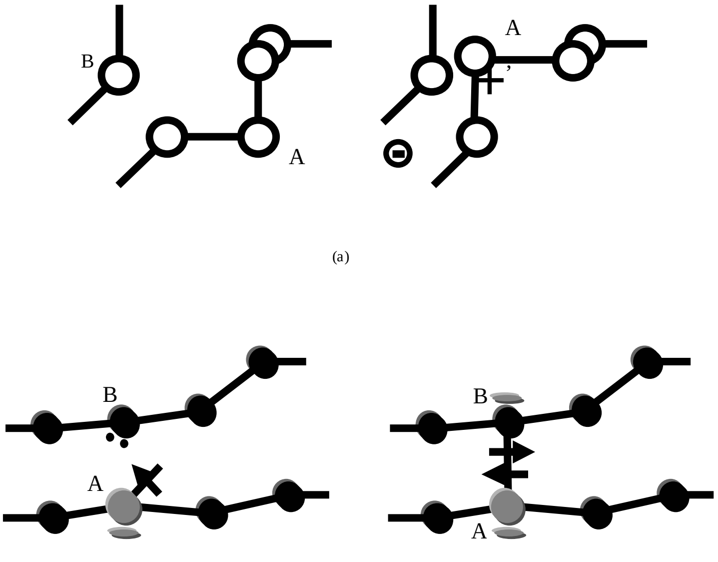


Fig. 6. Variation of changes in absorption coefficient, $\Delta\alpha$, with time for short-duration illumination for a-As_2Se_3 films at 50 K (solid line) and 300 K (dashed line). Ar laser ON and OFF stages are 20 s each at 50 K and 10 s and 20 s respectively at 300 K.

3. Discussion

As already stated, a change in the interaction of chalcogen lone-pair (LP) electrons should be responsible for PD to occur. We briefly review the models presented by various authors to explain these photoinduced structural changes in amorphous chalcogenides. First we discuss the bond-twisting model [4,18]. An important step in the understanding of the mechanism of the photostructural changes was the suggestion that changes in positions of atoms (bond-twisting of Se or S) without bond breaking can be possible, as illustrated in Fig. 7 (a) [4]. In this figure, A and A’ are alternative sites for a-Se atom within the chain. B depicts a Se atom belonging to a neighboring chain. A photon should be absorbed by a particular LP orbital (atom A), which thus becomes *positively* charged. This particular positively charged atom moves closer to another nearest-neighbor chalcogen atom by bond twisting. A stronger LP-LP interaction can yield a broadening of the VB, and thus results in PD. Recently, this original bond-twisting model has been slightly modified as follows [18]: As electrons are more localized than holes in nature, *negatively* ionized chalcogen atoms by trapping photoexcited electrons are responsible for PVE (and PD) through some unspecified processes. The similar spectral dependence between the photoconductivity and PVE may indicate the importance of free-carrier generation (not excitonic or not geminate pair generation). This may suggest that optical excitation of electron and hole itself is not responsible for structural changes. This point will be discussed latter again in the model of repulsive and slip motion.

Based on the *in situ* measurements of EXAFS for a-Se [9, 13] the bond alteration model was presented by Kolobov et al. [9, 13] to explain PSC induced by illumination. This idea was presented based on an observed increase in the coordination number by about 5 % in the excited state for a-Se. Associated with the change in coordination, the disorder (mean-square relative displacement) also increases under illumination. After illumination, the local change of coordination disappears whereas the light-induced structural disorder remains [10]. The observed increase in the coordination number suggests the formation of 3-fold coordination of Se. If an excited Se atom finds itself close to another Se atom belonging to a nearest-neighbor chain, its unpaired electron in the former LP orbital may interact with LP electrons of the neighboring chain, creating an inter-chain bond. A pair of 3-fold neutral sites Se_3^0-Se_3^0 will be formed as shown in Fig. 7 (b) [13]. The formation of inter-chain bonds may induce a local distortion, resulting in an increase in the mean-square relative displacement of the EXAFS spectrum. This bond alternation model is somewhat similar to the model proposed by Elliott [12] who suggested that the excitation of an electron into the conduction band (anti-bonding state) changes the balance between the attractive and repulsive interactions in the system resulting in a change of intermolecular bonds (covalent bonds) and weaker intramolecular bonds, inducing PD and PVE for compounds materials (i.e. As_2S_3 etc.).



(a)

(b)

Fig. 7. (a) Bond-twisting model (after [4]) and (b) bond-breaking model (after [13]).

The microscopic models proposed for elemental Se [4, 9, 13, 18], however cannot account the occurrence of PVE. For example, a distortion around 3-fold coordination pair itself suggests "contraction" around the network. Probably, overall network changes, which are initiated by bond-twisting or bond alternation, should be taken into consideration in PVE.

Both these basic models consider only *particular atoms* which are excited by photoirradiation. It is difficult to understand, however, that how and why particular atoms can be excited in a solid. The top of the VB is formed by LP *bands*, and hence there is no reason why particular atoms should be excited selectively. In fact, the bandgap illumination is known to be more effective in inducing PD (localized states are not selectively excited). It is therefore suggested that the "mesoscopic or macroscopic" interaction is dominant for both PD and PVE to occur, because LP electrons have equal probabilities of being excited. Therefore, electrons or holes in the extended states (or band-tail states) can be regarded as being responsible for PD or PVE, but not individual atoms [14].

Now, let us briefly review the model of repulsion and slip motion of structural layers (RS model) shown in Fig. 8 [14]. As a typical example, PD and PVE for a-$As_2Se(S)_3$ which is known to have basically layered structures, should be discussed. During illumination, the photocreated electrons should reside mostly in the CB tails, while the photocreated holes diffuse away to the unilluminated region through VB and VB tails, since the mobility of electrons is much lower than that of holes in amorphous chalcogenides. Thus the layers which absorb photons become negatively charged, giving rise to a repulsive Coulomb interaction between layers which produces a weakening of the van der Waals forces, and hence the interlayer distance increases (PVE).

This process is indicated by the arrow E (process E) in Fig. 8. The experimentally observed widening of the valence angle subtended at sulphur atoms within a layer and hence subsequent increase in the distance between two arsenic atoms bridged by a chalcogen atom on illumination [19] can be explained by the repulsive force involved in the process E (dashed arrow); the reaction of repulsive force between layers acts as a compressive force for each layer. Note, however, that the third coordination sphere (As-S-As-S) remains unchanged, which suggests that the dihedral angle between the two adjacent AsS_3 pyramids changes simultaneously with the increase in the valence angle at the bridging chalcogen atom. It is expected, however, that no change in the LP-LP interaction occurs in this process and hence the PD is not induced at this stage.

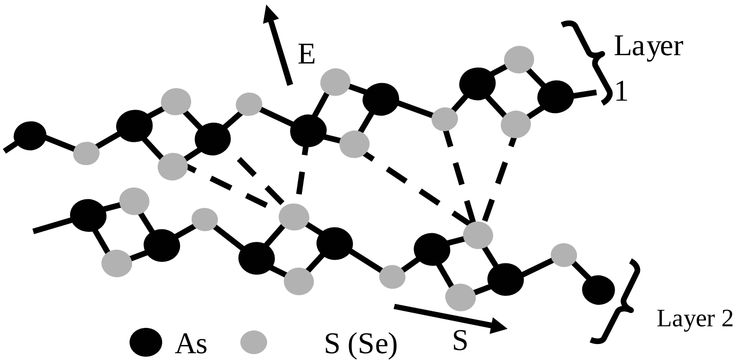


Fig. 8. The repulsion and slip motion of layered cluster model (after [14]). The arrows E and S indicate the expansion (due to repulsion) and the slip motions, respectively. The difference in local enviroments (and hence LP interactions) between chalcogen atoms is indicated by the broken lines.

A slip motion along the layers should also take place with the occurrence of the E process between neighboring clusters. This slip motion is shown by the arrow S (process S). As the energy required for a slip motion along layers is expected to be greater than that for expansion normal to layers, the rate of S may be lower than process E. This can be supported by the fact that cleaving is very easy for layered materials, for example graphite.

Both the processes E and S occur owing to the same repulsion force between the layers, but only process S is expected to be directly related to PD. If the neighboring layer slips away from the equilibrium position, an increase in the energy of the highest occupied states (VB) is expected owing to an increase in the total LP-LP interactions. This leads to a widening of the VB, but the CB remains almost unchanged [20], resulting in PD.

All the above models deal mainly with the metastable PD and let us now consider the mechanism to understand the dynamics of changes *during* illumination. The dynamics of PD and PVE can be described well in terms of configurational-coordinate (CC) diagram for all three models mentioned above, since a quasi-thermal equilibrium between the ground and photoinduced states can be established. A double-well potential with a barrier separating these states (i.e. two-level systems) can be simply assumed. A CC configuration as shown in Fig. 9 is used to study the time evolution of changes in PD for the repulsion and slip motion model. To explain the behavior of the variation of the total absorption coefficient ($\alpha=\alpha_0 + \Delta\alpha$) with total absorbed photons (n_p), we consider the films to contain clusters that act as potential sites for PD. On illumination, these clusters undergo *photon-assisted site switching* (PASS) forming photodarkened sites (PDS), which are associated with higher energy (Y) than the original state (X).

Let us consider that, before illumination, there exist N_T clusters in the ground state. "Clusters" may be considered as equivalent to the "layers" in the RS model. The rate of the growth of the number (N) of the PDS with the number of absorbed photons (n_p) can be expressed as:

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

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 $k_p=An_p^{\beta-1}$ and $k_r=Bn_p^{\beta-1}$, respectively, where A and B are constants that depend on temperature and illumination intensity, and β is a dispersion parameter ($0<\beta<1$). The dispersive nature in the reaction rates, k_p and k_r, should originate from cooperative motions of layerd clusters. 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. The fraction of PD occurrence $C(n_p)$ at any n_p is defined as $C(n_p)=N/N_s$. $C(n_p)$ lies between 0 and 1 (0 for the intial state, i.e., before illumination when no sites are converted, and 1 when all the potentially available sites are converted to photodarkened sites).

The effective medium approximation (EMA) can be used to calculate the optical absorption coefficient of a random medium [16, 21]. Note that originally the EMA was used to calculate the dc conductivity of a random mixture of particles under the assumption that the inhomogeneous surroundings of a particle can be replaced by an effective medium [22]. The total network conductivity σ_m in D dimension is given as

$$\left\langle \frac{\sigma-\sigma_m}{\sigma+(D-1)\sigma_m} \right\rangle_{\sigma} = 0\,, \tag{3}$$

where σ is a random value of conductivity. Springett [23] extended the idea of EMA for the evaluation of the ac behavior of a random system by replacing the conductivity by a complex form ($\sigma^*=\sigma_1+i\sigma_2$). As the optical constants are closely related to σ^*, i.e. the complex dielectric constants, $\varepsilon^*=\varepsilon_1-i\varepsilon_2=\sigma_2/\omega-i\sigma_1/\omega$, the optical absorption coefficient $\alpha(\omega)$ can be also calculated through the relation of $\alpha(\omega)=\sigma(\omega)/cn\varepsilon_0$, where c is the light velocity and n the refractive index.

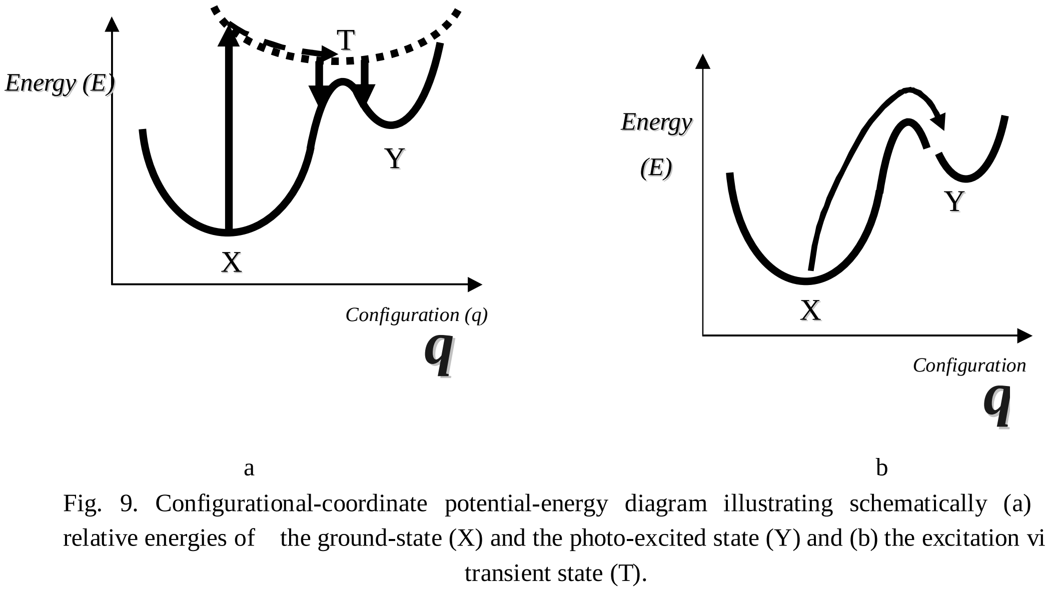
Using the derived $C(n_p)$ (from Eq.(2)) along with Eq.(3), we can evaluate α as a function of n_p. The fitting to α as derived from Eq.(3) is reasonably good at all temperatures and is shown by the solid lines in Fig. 3. The description of the symbols is given in the figure caption. Details of the fitting parameters, N_p and β, are given elsewhere [16]. It is expected that a percolative growth of photon-assisted site switching of “cluster” to PD sites takes place.

The RS model may further be supported by the following experimental results. As already stated, the PD effect disappears in metal-doped chalcogenides [10, 11]. This can be explained as follows: atoms of an introduced metals, 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 ability of both PVE as well as the slip motion. Furthermore, the introduction of such a strong constraint also induces dangling bonds which act as recombination centers [24] and which reduce the number of photoexcited free carriers considerably. We now know that constraint of structural network reduces PD.

As already suggested, one more important factor for structural changes to occur is the *charge separation* during illumination [14, 18]. The RS model predicts also that no PVE and PD can occur in very thin films, because then 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 As_2S_3 films thinner than 50 nm [25]. Application of an electric field may assist charge separation if the field is properly applied and may enhance PD. It is of interest to examine whether this kind of field effect is found or not.

From the similar spectral dependence between the PD and the photoconductivity in As_2S_3 [18], and the similar behaviors between PVE and photoconductivity during and after stopping the illumination [15], free-carrier generation but not geminate (excitonic) pairs is suggested to be responsible for the structural changes, which seems to be consistent with the RS model.

We now discuss the transient changes of photodarkening observed in a-As_2Se_3 as shown in Fig. 4. *During* illumination the total changes are composed of a transient part and a metastable part with the transient part decaying on stopping the illumination and the changes in $\Delta\alpha$ becoming the usually observed metastable photodarkening. Even for short-time illuminations (Fig. 6), transient and metastable parts of photodarkening are observed. The mechanism can be understood as follows from the CC diagram shown in Fig. 9(b). During illumination, the clusters in the ground state, on absorbing photons, undergo site switching and switch over to an excited state which may be the transient state (T), a state higher in energy than the metastable state. The clusters may switch from the ground state to metastable state via the transient state. On switching off the illumination, the clusters relax to the metastable state and some of the clusters relax back to the ground state. The part which relaxes back to the ground state is the transient part of PD and the remaining part which relaxes to the metastable state (a new equilibrium state) is the metastable part of the changes.



a b

Fig. 9. Configurational-coordinate potential-energy diagram illustrating schematically (a) the relative energies of the ground-state (X) and the photo-excited state (Y) and (b) the excitation via a transient state (T).

Next, we discuss the decay of the transient part at 50 and 300 K as shown in Fig. 5. The logarithmic 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 described by a stretched exponential function:

$$\Delta\alpha = C\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] + \Delta\alpha_s, \qquad (4)$$

where t is the time after the illumination is switched off, τ is the effective decay time, β is a dispersion parameter ($0 \leq \beta \leq 1$) and $\Delta\alpha_s$ is the saturated value of $\Delta\alpha$ (i.e. the metastable part of the changes). C is a temperature-dependent quantity (equal to the total amount of transient photodarkening) and its value is obtained by fitting to the experimental data. The solid line in Fig. 5 shows the fitting of Eq. (4) to the experimental results. The fitting seems to be reasonable and 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.

4. Conclusions

A review was given on the topics through the recently obtained interesting results on the reversible photinduced volume changes (PVC) and photodarkening (PD) for amorphous chalcogenides, in particular for As-based chalcogenides. We paid attention for the time evolution of these changes (*in situ* measurements etc) and discussed the origin of PVE and PD in terms of the model of repulsion and slip motion of clustered layers. Recently obtained results of in-situ measurements of photodarkening in a-As_2Se_3 were also presented. During illumination, the total changes constitute transient and metastable effects. The transient changes decay when the illumination is switched off to give the usually observed metastable photodarkening or expansion. Further illumination, after the metastable state is reached, induces only transient changes. The results can be interpreted in terms of photoinduced structural changes, which involve the charging and movement of layer- or chain-like clusters of atoms.

In the end, we wish Dr. Ovshinsky a happy 80th birthday and wish him good health in the years to come.

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