ADP011501

TITLE: Current Understanding of Photoinduced Volume and Bandgap Changes in Amorphous Chalcogenides

TITLE: International Workshop on Amorphous and Nanostructured Chalcogenides 1st, Fundamentals and Applications held in Bucharest, Romania, 25-28 Jun 2001. Part 1

Journal of Optoelectronics and Advanced Materials, Vol. 3, No. 2, June 2001, p. 167 - 176

CURRENT UNDERSTANDING OF PHOTOINDUCED VOLUME AND BANDGAP CHANGES IN AMORPHOUS CHALCOGENIDES

K. Shimakawa, A. Ganjoo

Department of Electrical and Electronic Engineering, Gifu University,
Gifu 501-1193, Japan

The terms "photodarkening (PD)" and "photostructural changes (PSC)" have been used equivalently in the study of photoinduced changes in amorphous chalcogenides. A recent observation, e.g. the rate of PVC is higher than that of PD under bandgap illumination, demonstrates that there is no one-to-one correlation between the two phenomena. Furthermore, recent results on the dynamics of PSC (in-situ measurements) have shed new light on our understanding of D and PVC and the current understanding should be modified. A review is given on these topics through the recently obtained interesting results on the reversible PD and PVC for As-based chalcogenides. We pay attention in particular to the time evolution of these changes (*in situ* measurements etc).

(Received May 29; 2001; accepted June 11, 2001)

Keywords: Amorphous chalcogenides, Photostructural change, Bandgap

1. Introduction

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 [1-5]. It is noted also that the PD disappears in some metal-doped chalcogenide glasses (e.g. by doping with Cu, Mn etc.) [6,7]. For a long time, PD was believed to be the result of PSC and hence one believed that there is one-to-one correlation between PD and PSC. An element of uncertainty has existed in the literature in establishing a relation between PD and volume expansion (VE). Recent experimental results by Ke.Tanaka [8] indicated that the rate of VE is greater than that of PD for bandgap illumination. Under subgap illumination, however, VE increases more gradually than PD. This seems to indicate that no direct correspondence exists between PD and VE. These results, however, were obtained for metastable PD and PVC, the mechanisms during illumination (dynamics) are still unclear.

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 [2], 2) bond breaking and/or alternations between the atoms [5, 9, 10], and 3) repulsion and slip motion of structural layers (RS model) [11]. Any model should be able to explain the observed behaviors of PD and PSC (VE for As-based chalcogenides). The study of PD and PSC has therefore received renewed interest, and new attempts, e.g. through an in-situ measument of PD or PSC etc., have been made to understand these changes [10, 12, 13]. In the present article, we try to review the recently obtained interesting results on the reversible PD and VE 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 deeply the dynamics of PD and VE.

2. Principal experimental data

As we expect that most of readers engaged in amorphous chalcogenides know what PD is, only the principal results for these reversible changes are summarized here (for the readers who are also interested in the historical background of PD, see the review papers [1-5]): 1) a decrease in the optical gap, e.g. $\Delta E_g/E_g \approx -2$ % in As_2S_3 (PD); 2) a volume expansion (VE), e.g. $\Delta V/V \approx 0.5$ % for As_2S_3; 3) a change in the first sharp diffraction peak (FSDP) in X-ray measurements for As_2S_3. All these changes can be reversed by annealing near the glass transition temperature.

First, we start from the metastable changes in PD and VE. Recent systematic experimental data of PD and VE for amorphous chalcogenides are informative and one of examples for the obliquely deposited a-As_2Se_3 is shown in Fig.1. It is found that giant reversible changes are induced in obliquely deposited films [14]. The relative change $\Delta d/d$ in thickness and relative change $\Delta E_g/E_g$ in optical bandgap are shown for various treatments: A, as deposited; B after pre-illumination annealing; C, after illumination; D, after post-illumination annealing. The full circle represents the thickness estimated by mechanical measurement [14]. The film thickness decreases (thermal contraction) and the bandgap increases (thermal bleaching) by annealing. On illumination, the thickness increases (VE) and the bandgap decreases (PD). Post-illumination annealing decreases the thickness and increases the bandgap. The above observations seem to indicate that there exist some correlation between PD and PVC.

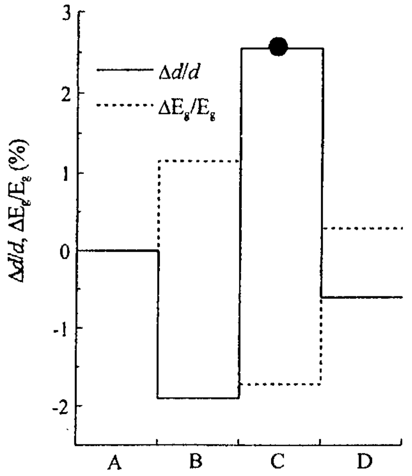
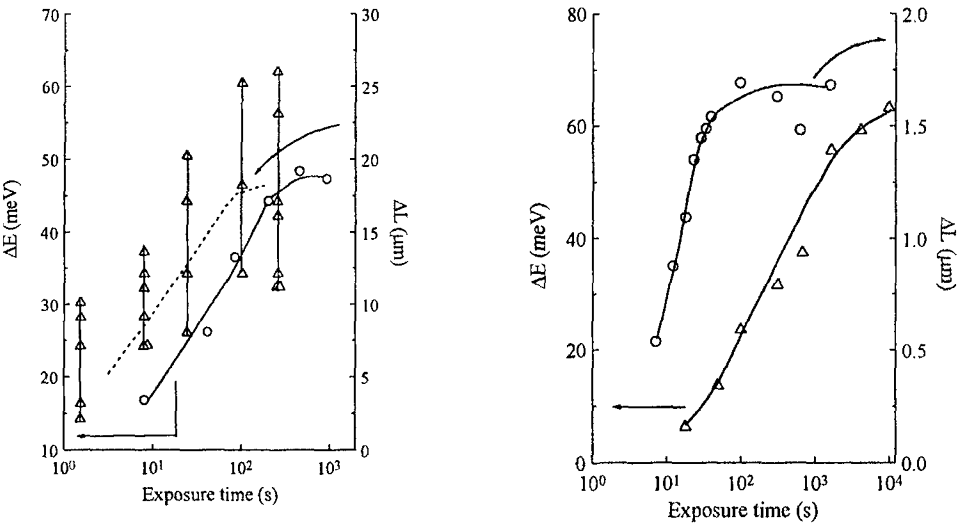


Fig. 1. Variation in relative changes in thickness d and optical bandgap E_g of a-As_2Se_3 (after [14]). Measurement conditions are described in the text.

It was believed for a long time that PD and VE were two different sides of the same phenomenon and hence one-to-one correlation should exist between PD and VE. Recently, however, Ke.Tanaka [8] has experimentally shown that the time constants of the PD and the VE in As_2S_3 are different. That is, the VE saturates earlier than the PD for bandgap illumination as shown in Fig.2 (a). In contrast, under subgap illumination PD saturates earlier than the VE as shown in Fig. 2(b). These experimental observations, on the other hand, suggest that these two phenomena (PD and VE) are not directly related to each other.

The composition dependence of PD in the As-Se system is of interest and this is shown in Fig. 3 which is plotted from the Table in ref. [15]. The magnitude of PD increases linearly with the As-content in this composition region. From this result, we expect that arsenic atoms may play an important role in inducing PD. Note, however, that PD is not found in pure amorphous arsenic (a-As) [16], whereas PD occurs in pure Se [2]. The fact that PD disappears in metal-doped chalcogenides is of interest, where it is reported that by the incorporation of Cu, Ag, Zn [6], and of Mn and rare earths [7], PD vanishes.



a

b

Fig. 2. Photoexpansion ΔL and photodarkening ΔE as a function of exposure time in a-As_2S_3 for (a) bandgap and (b) subgap illumination (after [8]).

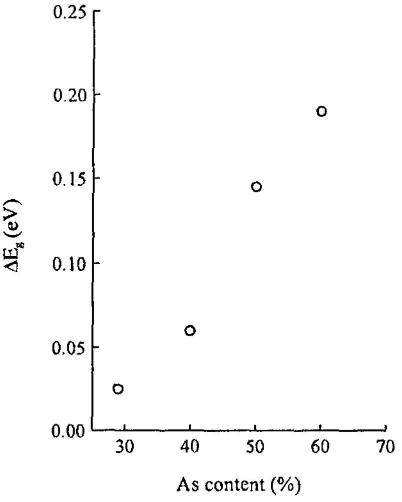


Fig. 3. The dependence of As-content on the magnitude of photodarkening ΔE_g in As-Se system.

Most of the above measurements on PD have been made after, rather than during, illumination and the various conclusions have been drawn for metastable PD. To clear the dynamics of PD during illumination, the time evolution of changes in the optical absorption coefficient with illumination has been studied for As_2S_3 in detail (*in situ* measurement) [13]. 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.4. 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 figure caption. 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 (α_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.4 is replotted as Fig.5, 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 in section 3.

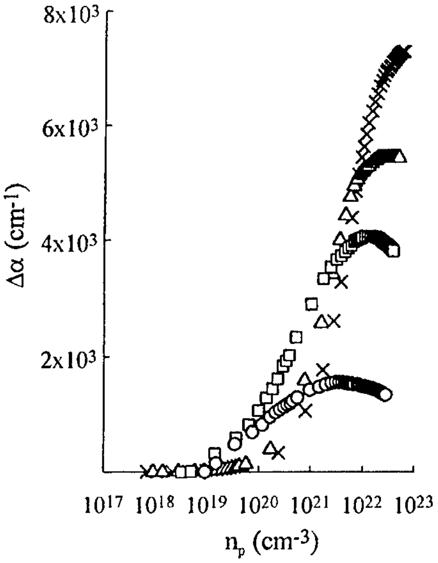


Fig. 4. *In situ* variation of changes in absorption coefficient $\Delta\alpha$ as a function of absorbed photons n_p at various temperatures. ×, Δ, □, and O show the changes at 50, 100, 200, and 300 K, respectively. Illumination is by Ar$^+$ laser (20mW/cm^2) (after [13]).

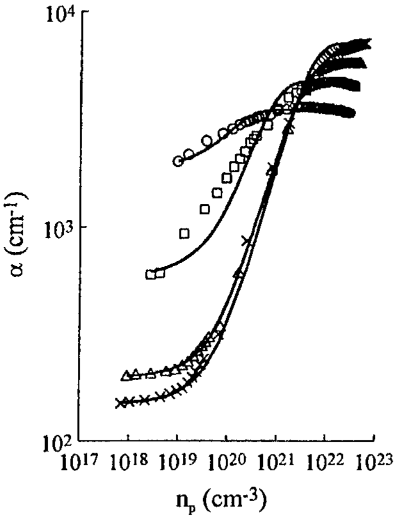


Fig. 5. Variation of absorption coefficient ($\alpha=\alpha_0+\Delta\alpha$) as a function of number of absorbed photons n_p at various temperatures. Description of symbols is the same as in Fig.4. Solid line is the fitting obtained using Eq.(3) in the text (after [13]).

In situ measurements of photoexpansion have also been made for As_2S_3 [12]. Fig. 6 shows the relative changes of thickness, *Δd/d*, with time during and after illumination. 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 [4, 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 VE [2], i.e. VE observed *after* illumination. This decay behavior of VE after the illumination is switched off is found to be very similar to that of the decay of photocurrent [12].

To understand the behavior of the initial rapid increase of thickness in more detail, the changes of thickness with time for short time illumination (before showing the maximum change in Fig. 6) have been studied. The light was put on and off for 5 and 10 s, respectively. The results for the relative changes in thickness are shown in Fig. 7. The thickness decreases rapidly as it is switched off, but does not return to the original value. This indicates that the total increase of VE is a combination of transient and metastable VE, the latter remaining as the observed VE *after* switching off the illumination. This behavior shows that the metastable VE occurs even for short time illumination, and accumulates with successive illuminations. It is suggested that the observed VE is purely due to photoelectronic effects and not due to thermal effects [12]. Note, however, that the in situ measurements of PVC have been done by white light and thus the change in PVC was not given as a function of n_p. The correlation between the rate of PVC and PD during illumination has not been established, and hence difficult to comment upon.

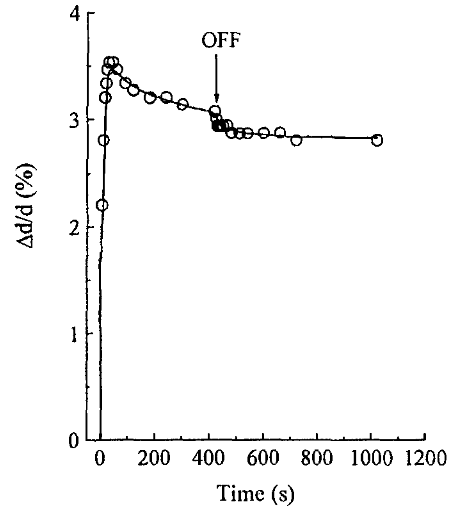


Fig. 6. Relative changes in thickness *Δd/d* with time for a-As_2S_3 (after [12]).

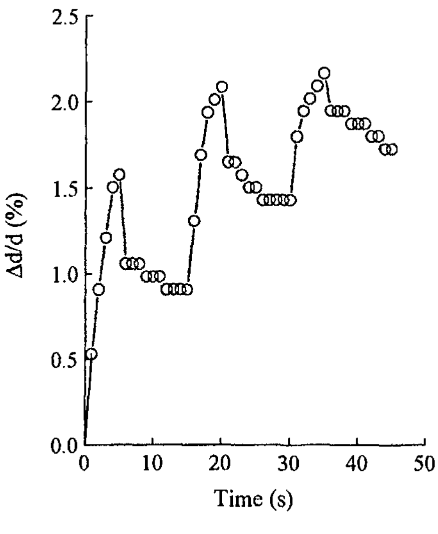


Fig. 7. Relative changes in thickness *Δd/d* with time for short duration of illumination for a-As_2S_3. Light ON and OFF states is 5 and 10 s, respectively (after [12]).

3. Discussion

As already stated, a change in the interaction of chalcogen lone-pair (LP) electrons should be responsible for PD to occur. Any model, classified into three categories (see Introduction), should basically explain the observed behaviors, microscopically and macroscopically.

To understand an elemental process of PD, pure a-Se (not compounds) should be taken into consideration. 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. 8 (a) [2]. 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, which can be induced by an attractive Coulomb interaction between the two atoms. A stronger LP-LP interaction can yield a broadening of the VB, and thus resulting 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 VE (and PD) through some unspecified processes. The similar spectral dependence between the photoconductivity and VE may indicate the importance of free-carrier generation (not excitonic or 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.

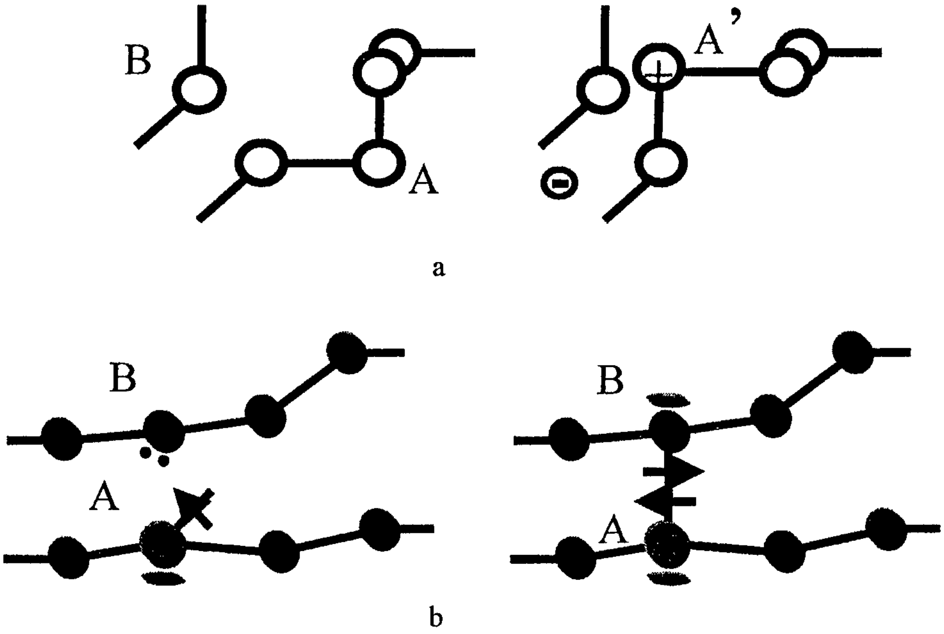


Fig. 8. (a) Bond-twisting model (after [2]) and (b) bond-breaking model (after [10]) which are applied to a-Se.

To get information about the excited states of photostructural changes under illumination, *in situ* measurements of EXAFS have been performed for a-Se [5, 10]. A reversible increase in the coordination number by about 5 % in the excited state is observed. 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]. Thus the change in coordination number is *transient* phenomenon (not metastable change), which has been observed in VE (see Fig. 7). 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. 8 (b) [10]. 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. The formation of triply coordinated pairs in the photoexcited state (during illumination) is also supported by the Raman scattering data [5, 19]. This bond alternation model is somewhat similar to the model proposed by Elliott [9]: Excitation of an electron into the conduction band (anti-bonding state) changes the balance between the attractive and repulsive interactions in the system. This results in a change of intermolecular bonds (covalent bonds) and weaker intramolecular bonds, inducing PD and VE for compounds materials (i.e. As_2S_3 etc.).

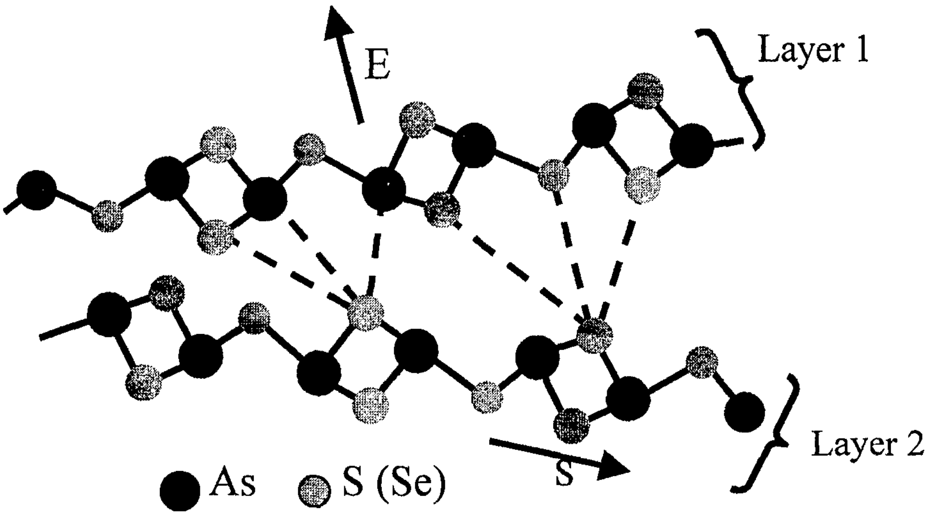


Fig. 9. The repulsion and slip motion of layered cluster model (after [11]). The arrows E and S indicate the expansion (due to repulsion) and the slip motions, respectively. The difference in local enviroments (and hence LP interactions) between chalcogen atoms is indicated by the broken lines.

The microscopic models proposed for elemental Se [2, 5, 10, 18], however cannot account the occurrence of VE (see Fig. 8). 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 VE [20]. Some other shortcoming for these models can be difficulty of unification, i.e. how to explain the PD in compound materials? Answer to the above questions should be required in particular for the case of compound chalcogenides.

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 VE 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 VE, but not individual atoms [11].

Now, let us briefly review the model of repulsion and slip motion of structural layers (RS model) [11]. As a typical example, PD and VE 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 (VE).

This process is indicated by the arrow E (process E) in Fig. 9. 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 [21] 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. 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.

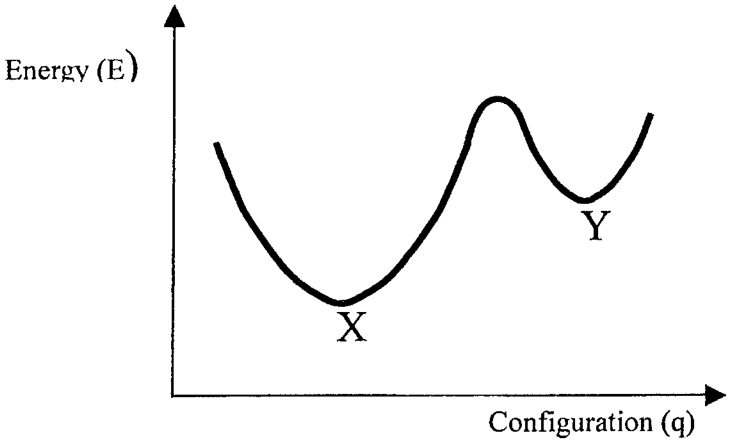


Fig. 10. Configurational-coordinate potential-energy diagram illustrating schematically the relative energies of the ground-state (X) and the photo-excited state (Y).

Both the process 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. Refer to corresponding crystalline form, as shown in Fig. 9, Sulphur atom B is more closely surrounded by sulphur atoms from the neighboring layer, while sulphur atom A has a different configuration. 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 [22], resulting in PD. The total free energy of the system in well annealed samples should be minimized and hence the atomic or molecular configurations can be taken to be at the minimum LP-LP interactions. Thus quasistable states (higher energy states) can be induced by illumination, owing to both E and S processes. The potential energy stored in a layer (the disc-shaped layers of radius of 1 nm placed at a separation of 0.5 nm for a simple assumption) during illumination conditions is estimated to be 6-60 meV [11]. This repulsive energy can induce VE by reducing the attractive van der Waals energy which is estimated to be about 750 meV for each layer [23]. The energy introduced into the layers is about 1-10 % of the van der Waals energy, which seems to be reasonable for inducing VE about 0.5 %.

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 VE can be described well in terms of configurational-coordinate (CC) diagram for all three models mentioned above, since a quasi-thermal equiliblium 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. 10 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

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

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 $k_p=An_p^{\beta-1}$ 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 [13, 24]. 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 [25]. The total network conductivity σ_m in D dimension is given as

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

where σ is a random value of conductivity. Springett [26] extended the idea of EMA for the evaluation of the ac behavior of a random system by replacing the conductivity by a complex admittance ($\sigma^*=\sigma_1+i\sigma_2$). 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. The description of the symbols is given in the figure caption. Details of the fitting parameters, N_p and β, are given elsewhere [13]. 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 [6.7]. 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 VE as well as the slip motion. Furthermore, the introduction of such a strong constraint also induces dangling bonds which act as recombination centers [27] and which reduce the number of photoexcited free carriers considerably. We now know that constraint of structural network reduces PD. A pressure dependence of PD confirms the importance of constraint. The magnitude of PD in As_2S_3 reaches maximum at ~5 kbar and decreases gradually, vanishing at ~57 kbar [28]. Under high pressure, the motion of the layers is suppressed and VE cannot occur and hence no slip motion leads to no PD. On the other hand, the fact that the magnitude of PD increases with the As-content in As-Se system (see Fig. 3) can be explained as follows: It is known that a-Se is formed mostly by linear chains. Introduction of As atoms bridge these Se chains and partially layered structure can be produced. This in turn increases the magnitude of PD, since the number of layered clusters can be increased in higher As-content in As-Se system. The reason why PD occurs in pure Se can be due primary the repulsion force between linear chains. Repulsive force due to electronic charges between layers is expected to be more stronger than that between chains. It is noted, however, that As-rich system (more than 40 % of As-content) may have different structural unit, e.g. As_4Se_4 molecule. A linear increase of PD with As-content cannot simply be explained in terms of the present model. This point is unclear [4]. As already suggested, one more important factor for structural changes to occur is the *charge separation* during illumination [11, 18]. The RS model predicts also that no VE 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 [29]. Application of 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 VE and photoconductivity during and after stopping the illumination [12], 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. However, this model has been criticized in a view of hole diffusion length: The major difficulty in the RS model suggested by Ke. Tanaka [18] may be the temperature dependence of VE. The VE becomes greater at lower temperatures, while the hole diffusion length will be shorter at low temperatures. To our view, however, the ability of *charging negatively* in illuminated region should not only be dominated by "diffusion length (or mobility) of holes". The number of free- and or tail-electrons in layers increases at low temperatures, since recombination time increases with decreasing temperature ($G\tau$ product), while the number of holes also increases with decreasing temperature. Complete diffuse-away of holes in illuminated region, e.g. longer than micrometers [18], however, is not required for VE and PD to occur in the RS model. Large difference of diffusion coefficient between electron and hole may still produce excess electrons in layers, yielding large VE and PD at lower temperatures. Thus we prefer the RS model to account the VE and PD in amorphous chalcogenides.

Finally, we should argue the transient effect of PD. As the transient VE has been found experimentally [12], similar transient PD should be observed and these should be related to photocurrent. The detail of these will be presented elsewhere [30].

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 PVC and PD in terms of the model of repulsion and slip motion of clustered layers.

Acknowledgements

We would like to thank Keiji Tanaka, Alex Kolobov, and Ted Davis for stimulating discussions. We also acknowledge a Grant-in-Aid for Scientific Research from the Ministry of Education and Science in Japan.

References

[1] K. Tanaka, J. Non-Cryst. Solids, **35&36**, 1023 (1980).
[2] Ke. Tanaka, Rev. Solid St. Sci., **4**, 641 (1990).
[3] G. Pfeiffer, M. A. Paesler, S. C. Agarwal, J. Non-Cryst. Solids, **130**, 111 (1991).
[4] K. Shimakawa, A. V. Kolobov, S. R. Elliott, Adv. Phys., **44**, 475 (1995).
[5] A. V. Kolobov, K. Tanaka, Handbook of Advanced Electronic and Photonic Materials and Devices Vol. **5**, edited by H. S. Nalwa (Academic Press, San Diego) p.47, 2001.
[6] J. Z. Liu, P. C. Taylor, Phys. Rev. Lett., **59**, 1938 (1987); Phys. Rev., **B41**, 3163 (1990).
[7] M. Iovu, S. Shutov, S. Rebeja, E. Colomeyco, M. Popescu, J. Optoelectronics and Advanced Materials, **2**, 53 (2000).
[8] Ke. Tanaka, Phys. Rev., **B57**, 5163 (1998).
[9] S. R. Elliott, J. Non-Cryst. Solids, **81**, 71 (1986).
[10] A. V. Kolobov, H. Oyanagi, K. Tanaka, Ke. Tanaka, Phys. Rev., **B 55**, 726 (1997).
[11] K. Shimakawa, N. Yoshida, A. Ganjoo, A. Kuzukawa, J. Singh, Philos. Mag. Lett., **77**, 153 (1998).
[12] Ashtosh Ganjoo, Y. Ikeda, K. Shimakawa, Appl. Phys. Lett., **74**, 2119 (1999).
[13] Ashtosh Ganjoo, K. Shimakawa, H. Kamiya, E.A. Davis, Jai Singh, Phys. Rev., **B62**, R14601 (2000).
[14] Y. Kuzukawa, Ashtosh Ganjoo, K. Shimakawa, Y. Ikeda, Philos. Mag., **B79**, 249 (1999).
[15] S. B. Gurevich, N. N. Ilyashenko, B. T. Kolomiets, V.M. Lyuvin, Proc. 6th Int. Conf. on Amorphous and Liquid Semiconductors, ed. By B. T. Kolomiets (Nauka, Moscow) p.451, 1975.
[16] E. Mytilineou, P. C. Taylor, E.A. Davis, Solid State Commun., **35**, 497 (1980).
[17] K. Shimakawa, S. Inami, S. R. Elliott, Phys. Rev., **B42**, 11857 (1990).
[18] Ke. Tanaka, Philos. Mag. Lett., **79**, 25 (1999).
[19] A. V. Kolobov, H. Oyanagi, A. Roy, K. Tanaka, J. Non-Cryst. Solids, **232-234**, 80 (1998).
[20] A. V. Kolobov, private commun.
[21] C. Y. Yang, M. A. Paesler, D. E. Sayers, Phys. Rev., **B36**, 9160 (1987).
[22] T. Watanabe, H. Kawazoe, M. Yamane, Phys. Rev., **B38**, 5677 (1988).
[23] Ke. Tanaka, Solid St. Commun., **54**, 867 (1985).
[24] K. Shimakawa, J. Non-Cryst. Solids, **266-269**, 233 (2000).
[25] S. Kirkpatrik, Rev. Mod. Phys., **45**, 574 (1973).
[26] B.E. Springett, Phys. Rev. Lett., **31**, 1463 (1973).
[27] J. Hautala, S. Yamasaki, P. C. Taylor, J. Non-Cryst. Solids, **114**, 85 (1989).
[28] G. Pfeiffer, M. A. Paesler, J. Non-Cryst. Solids, **114**, 130 (1989).
[29] Ke. Tanaka, S. Kyoya, A. Odajima, Thin Solid Films, **111**, 195 (1984).
[30] Astosh Ganjoo, K. Shimakawa, this conference.