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Invited Lecture

Study of photoinduced changes due to illumination in amorphous chalcogenides

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The theoretical developments for the creation of light-induced metastable defects (LIMD), photodarkening and photoinduced volume expansion in amorphous chalcogenides are reviewed. Recent results for some chalcogenide glasses are presented. The magnitude and effect of PD and PVE is determined quantitatively and compared with the experimental results.

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1. Introduction

It is established that three phenomena that are observed when samples of chalcogenide glasses (a-Chs) are illuminated by band gap light [1-3]; the creation of light-induced defects, photodarkening and photo volume expansion. Some glasses show volume contraction as well, for example, Ge-As-Se [4]. The creation of light-induced defects observed in a-Si:H is usually known as the Staebler-Wronski Effect (SWE) [5]. The covalent bonds in the amorphous structure get broken due to the band gap illumination or light soaking and hence the number of dangling (broken) bonds increases after the illumination. This is also called the generation of light-induced metastable-defects (LIMD) [3, 6-7]. SWE causes a reduction in the initial efficiency of a photovoltaic device fabricated from a-Si:H, e.g. a-Si:H solar cells, after a prolonged exposure to radiation, because the amorphous sample degrades due to enhanced broken bonds.

In chalcogenide glasses, along with the creation of LIMD, one also observes photodarkening (PD) – a reduction in the optical band gap occurs due to band gap illumination [7-9]. In a-As_2S_3, PD has also been observed by the below band gap illumination [10]. Also, a volume expansion (VE) in the samples of these glasses occurs by band gap illumination [7-9]. The photodarkening was first observed to be metastable, i.e., it disappeared by thermal annealing but remained even if the illumination was stopped. Now the transient photodarkening [11] has also been observed in a-As_2S_3, a-As_2Se_3 and a-Se. It disappears as soon as the illumination is stopped, which means that the material reverts back to its original state once the illumination has stopped. It is not established what causes the two types of PD, one that is metastable and gets reversed only by thermal annealing and the other that reverses back after stopping the illumination. Several models have been proposed for the occurrence of PD in a-Chs in the last two decades [7,9,11], however none has been successful in resolving all aspects observed in materials exhibiting photodarkening. One of the recent models is the repulsive electronic interaction [12]. As chalcogenides like $As_2Se(S)_3$ have layered structures, the charge carriers excited by illumination in these materials move in these layers. The hole mobility is larger than the electron mobility in these materials and hence photo-generated electrons reside mostly in the conduction band tail states while holes diffuse away faster in the unilluminated region through valence band extended and tail states. Therefore, the layers that absorb photons during the illumination become negatively charged, giving rise to a repulsive inter-layer Coulomb interaction, which increases the inter-layer separation and causes PVE. The same force is assumed to induce an in-plane slip motion that increases the LP-LP interaction and causes PD. However, a more recent calculation [13] indicates that the repulsive force is too weak to cause PVE. A molecular dynamics simulation for the mechanism of volume expansion has also been carried out recently [14].

It is now well established that two types of change may be induced when a sample of chalcogenide glass is illuminated at room temperature: one type disappears after the illumination is stopped and the other stays in quasi-stable form even after the illumination is stopped. However both types of change are photo-induced and occur due to illumination. Recent theoretical developments made in this field are reviewed in this paper, to study the changes that can occur under illumination and possible mechanisms for the two types of change. Extending Holstein's approach [15] and our previous work [16-17], a theory is developed to study the possible changes that can be induced due to illumination of chalcogenide glasses. As the absorption of light in these materials causes excitation of electron and hole pairs, the energy eigenvalues of such excited charge carriers are calculated by considering their strong interaction with the lattice. It is shown that the energies of the excited electron (negative charge) and hole

(positive charge) polarons get lowered due to the carrier-phonon interaction [17]. If the carrier-lattice interaction is very strong, the like excited charge carriers can get paired because of the negative-U effect [18] and the energy of such paired states also gets lowered. Thus, the hole polaronic state and paired hole states overlap with the lone pair and tail states in a-Chs, which expands the valence band and reduces the band gap energy and hence causes PD. Formation of polarons as well as pairing of holes increases the bond length over which such localizations occur, which causes VE.

2. Comparative mobility of charge carriers

Considering here only the extended states, the effective mass of an electron in the conduction and a hole in the valence band can respectively be written as [7]:

$$m_{ex}^{*} = \frac{E_L}{2(E_2 - E_c)a^{1/3}} m_e \,, \tag{1}$$

and

$$m_{hx}^{*} = \frac{E_L}{2(E_v - E_{v2})a^{1/3}} m_e \,, \tag{2}$$

where

$$E_L = \frac{\hbar^2}{m_e L^2} \,, \tag{3}$$

where a is the fraction of atoms contributing to the extended states, L is the average bond length in a sample, E_2 is energy of the centre of the conduction band where the imaginary part of the dielectric constant becomes maximum and E_{v2} is the corresponding energy in the valence band. E_c and E_v are the energies of the electron and hole mobility edges, respectively, and m_e is the free electron mass. Thus, $2(E_2 - E_c)$ and $2(E_v - E_{v2})$ become the width of the conduction and valence bands, respectively, and thus the effective mass of an electron in the conduction band and that of a hole in the valence band become inversely proportional to the corresponding band width [7]. In a-Chs, as the lone pair orbitals overlap with the valence band, the combination makes the valence band much wider than the conduction band and thus the hole effective mass becomes smaller than the electron effective mass in a-Chs. As a result, holes move faster than electrons in these materials. This is the basis for the repulsive electron model. However, in the tail states the charge carriers are localized.

3. Photo-excitation and phonon interaction

We consider here a model amorphous solid in the form of a linear chain of atoms. The electronic Hamiltonian in such a chain can be written as a sum of charge carrier ($\hat{H}_{el}$), phonon ($\hat{H}_{ph}$), and charge carrier-phonon interaction ($\hat{H}_I$) energy operators in the real coordinate space as [7,17]:

$$\hat{H} = \hat{H}_{el} + \hat{H}_{ph} + \hat{H}_I \,. \tag{4}$$

We assume that an absorbed photon excites an electron (e) in the conduction and a hole (h) in the valence band. We also assume that the carrier-phonon interaction is very strong.

3.1 Formation of an excited positive charged polaron

Let us first consider the case of an excited hole in the valence band with its eigenvector as:

$$| h,0 >= \sum_l C_l d_{0l}^{+} | 0 > \,, \tag{5}$$

where h denotes the hole and 0 denotes the valence band; the conduction band is denoted by 1. C_l represents the probability amplitude coefficient, $d_{0l}^{+} (= a_{0l})$ is the creation operator of a hole and a_{0l} is the annihilation operator of an electron in the valence states on site l and |0> represents the vacuum state with all valence states completely filled and all conduction states completely empty. Using Eqs. (4) and (5), one can solve the Schrödinger equation, $\hat{H} | h,0 >= W_h | h,0 >$, to get a secular equation as:

$$W_h C_l = (-\sum_n \frac{\hbar^2 \nabla^2}{2M} + \frac{1}{2} \sum_{m,n} M\omega_m^2 x_m x_n - A_l^h x_l - E_h^0) C_l + T_h (C_{l-1} + C_{l+1}) \,, \tag{6}$$

where W_h is the energy eigenvalue of the hole state, the first two terms within the parentheses correspond to the kinetic and potential energies of nuclear vibrations, x_n is the nth bond length of a diatomic molecule in the chain vibrating with a frequency ω_n, M is the atomic mass, A_l^h is the hole-phonon coupling coefficient, $E_h^0 = E_h^l$ is a constant of energy for a hole localized at site l and hence it is site independent and T_h is the hole transfer energy between nearest neighbours from l to $l \pm 1$ in the chain. Although the vibrating frequency ω_m has a subscript m, being the intra-molecular vibrational frequency of identical diatomic molecules, it is site independent [15-17]. Considering only the diagonal terms in the vibrating potential, multiplying Eq. (6) by C_l^{*} and then summing over all l, we get:

$$W_h = -\sum_n \frac{\hbar^2 \nabla^2}{2M} + \frac{1}{2} \sum_m \omega^2 x_m^2 - \sum_l A_l^h x_l \,|\, C_l \,|^2 - E_h^0 + T_h (C_{l-1} + C_{l+1}) C_l^{*} \,, \tag{7}$$

where $\sum_l C_l^* C_l = \sum_l |C_l|^2 = 1$ is used. Setting $\frac{\partial W_h}{\partial x_q} = 0$, W_h can be minimized with respect to the bond length, x_q. This gives the bond length at the minimum energy as:

$$x_q^{(0)} = \frac{A_q^h |C_q^{(0)}|^2}{M\omega^2}, \tag{8}$$

where the superscript (0) denotes the value of quantities at the minimum energy and subscript q denotes the q^{th} bond at which the hole is localized. The subscript q has been dropped from the frequency ω as it is independent of bond sites. The bond length increases by $x_q^{(0)}$ due to the localization of the hole on the bond. Substituting Eq. (8) in Eq. (7), we get the minimum energy of the hole, denoted by W_h^0, as:

$$W_h^0 = -E_h^0 - 2T_h - E_{hq}, \tag{9}$$

where E_{hq} represents the hole polaron binding energy obtained as:

$$E_{hq} = \frac{\left(A_q^{h\,2}/M\omega^2\right)^2}{48T_h}. \tag{10}$$

This is the energy by which the energy of an excited hole is lowered due to its interaction with the lattice from the free hole state energy, which is at $-E_h^0 - 2T_h$. This means that the hole energy state moves upward in the energy gap by releasing an energy E_{hq} to phonons. It is to be noted that both the bond length and hole polaron binding energy increase with the increase in the hole-phonon coupling coefficient, A_q^h.

3.2 Formation of an excited pair of polarons

The generation of excited electrons and holes occurs in pairs through photo-excitations in intrinsic materials. The excited electrons may form polarons in the conduction band and their energy will also be lowered. For a single pair of excited charge carriers on our linear chain, minimizing the energy with respect to x_q, we obtain [7]:

$$W_{eh} = E_e^0 - E_h^0 - U_{eh} - 2(T_e - T_h) - E_{eq} - E_{hq} \tag{11}$$

where W_{eh} is the energy eigenvalue of the excited pair, and E_e^0 and E_h^0 are the site independent energies of the excited electron and hole, respectively, without the lattice and Coulomb interactions between the excited charge carriers, U_{eh} is the Coulomb interaction energy between the excited pair, T_e is the energy of transfer of electron between nearest neighbours and E_{eq} is the electronic polaron binding energy, which can be obtained from Eq. (10) replacing the subscript h by e. It may be noted that if U_{eh} is negligibly small, such an excited pair cannot form an exciton. The energy of such an excited pair of charge carriers without the lattice interaction is obtained as:

$$W_{eh}^0 = E_e^0 - E_h^0 - U_{eh} - 2(T_e - T_h). \tag{12}$$

For the case of a free pair of charge carriers, one usually neglects U_{eh} and then the energy W_{eh}^0 is close to the optical energy gap in most materials. Subtracting Eq. (12) from Eq. (11), we get the reduction in the optical gap due to formation of excited pair of polarons as:

$$\Delta W = W_{eh} - W_{eh}^0 = -E_{eq} - E_{hq}. \tag{13}$$

A bond breaking due to such single excitation has been recently demonstrated by numerical simulation [14,19] as well. This can also be seen from Eq. (8), in that if the carrier-lattice interaction strong, i.e., A_q^h is large, the bond gets stretched and hence the bonding may become very weak and break. The excitation of an electron to the conduction and hole to the valence band also means that a hole will be localized on a weak bond and the bond will be stretched by x_q^0 and may break.

3.3 Pairing of like excited charge carriers due to phonon interaction

It is well established that Se-based chalcogenides have linear chain-like structures and hence are flexible. In such structures, the carrier-phonon interaction is considered to be very strong, which can induce pairing of like excited charge carriers on a bond, due to Anderson's –U effect [18], already known for valence band electrons. In most solids, usually one of the two interactions, electron-phonon or hole-phonon, is stronger than the other. Therefore, here we first consider that the hole-phonon interaction is stronger and therefore two holes can be paired on a bond and the two excited electrons will form two polarons elsewhere on the chain. The pairing of electrons in an antibonding orbital can also be studied in an analogous way. Accordingly, we consider that two pairs of electrons and holes are excited in the chain. Assuming that the separation between the electron and hole within an excited pair is large and the two holes are localized on the same bond, the secular equation in this case is obtained as:

$$\begin{aligned} W_{2h}C_l = [&2W_e^0 - 2E_h^l + 2A_l^h x_l \\ &+ \frac{1}{2}\sum_m M\omega^2 x_m^2 + U_{12}']C_l + 2T_h(C_{l-1} + C_{l+1}) \end{aligned} \tag{14}$$

where the subscript $2h$ on W_{2h} denotes the localization of the two holes and W_e^0 is the energy of an electronic

polaron derived in an analogous way to Eq. (9) for a hole polaron, and is obtained as:

$$W_e^0 = E_e^0 - 2T_e - E_{eq}. \quad (15)$$

Following the steps used in deriving Eqs. (6) and (7), here again we can minimize the energy with respect x_q to get:

$$\begin{aligned} W_{2h}^0 &= 2W_e^0 - 2E_h^0 + 4T_h + U_h - E_{hh} \\ &= 2(E_e^0 - E_h^0) - 4(T_e - T_h) + U_{12}' - 2E_{eq} - E_{hh} \end{aligned}, \quad (16)$$

where

$$E_{hh} = \frac{1}{6T_h}\left(\frac{(A_q^h)^2}{M\omega^2}\right)^2. \quad (17)$$

The bond length of a bond on which such a pairing occurs is obtained as:

$$x_q^{hh} = \frac{2A_q^h C_q^* C_q}{M\omega^2} = 2x_q^0, \quad (18)$$

which is twice as large as when only a single hole polaron [Eq. (8)] is formed.

The energy of two excitations without the charge carrier-phonon interaction, can be written as:

$$W_{2h}^{00} = 2(E_e^0 - E_h^0) - 4(T_e - T_h) + U_{12}'. \quad (19)$$

Thus, the energy of a pair of excitations with two holes localized on a bond is lowered by ΔE_{hh} given as:

$$\Delta E_{hh} = W_{2h}^{00} - W_{2h}^0 = 2E_{eq} + E_{hh}. \quad (20)$$

In an analogous way, one can derive the lowering of energy, ΔE_{ee} of a pair of excited electrons localized on an antibonding orbital of a bond and two hole polarons localised separately elsewhere as:

$$\Delta E_{ee} = 2E_{hq} + E_{ee}, \quad (21)$$

where E_{ee} can be obtained from Eq. (17) replacing the subscript *h* by *e*. It may be noted here that unlike the case of pairing of excited holes on a bond, pairing of excited electrons on a bond can not occur easily because these electrons are excited in an anti bonding orbital. In this case, the two hole polaron energy states move upward in the band gap and the paired electron energy states in the conduction band move downward, resulting in narrowing of the the band gap.

4. Results

This is clearly demonstrated here for the first time why the hole effective mass is smaller than the electron effective mass in chalcogenide glasses. We have also shown here that the localisation of an excited hole on a bond increases its bond length and the bond can break. Such a localisation occurs by the formation of a hole polaron due to strong interaction between the hole and lattice vibrations. The hole polaron state has an energy lower than the free hole state and moves upward, mixing with the lone pair orbitals in chalcogenides that widens the valence band and narrows the band gap. Such a strong charge carrier-phonon interaction is possible in a-Chs because of their linear flexible structure and weak coordination, which can also induce pairing of excited holes on a bond. In this case, the length of a bond increases twice as much as in the case of polaron formation and the binding energy is eight times larger than the polaron binding energy. Such paired hole states contribute significantly to both photo darkening and photo volume expansion. The photo darkening is caused by the lowering of the paired hole state energy and such a state widens the valence band even further and hence reduces the band gap. As the bond length expands twice as much as in the case of single hole polaron, this contributes significantly to volume expansion as well. Moreover, pairing of holes on a bond breaks the bond because of the removal of covalent electrons and causes photo-induced bond breaking in a-Chs, as has already been established.

Let us get some estimates of the possible reduction in the band gap due to formation of polarons and bipolarons (paired holes) on a bond. Depending on the material, ΔE_{hh} [Eq. (20)] can be in the range of a fraction of an eV. We have estimated ΔE_{hh} in As_2S_3 as follows. The energy of lattice vibration of a bond can be written as [7]:

$$E(q) = E_0 + \frac{1}{2}M\omega^2(q - q_0)^2, \quad (22)$$

where E_0 and q_0 are the energy and the interaction coordinate, respectively, at the minimum of the vibrational energy. The vibrational force along the interaction coordinate can be obtained as:

$$A = \left(\frac{\partial E}{\partial q}\right)_{q=0} = -M\omega^2 q_0. \quad (23)$$

Using this in Eqs. (10) and (17) , we obtain:

$$\frac{E_{hh}}{T_h} = 8\frac{E_{hq}}{T_h} = \frac{1}{6}\left(\frac{M\omega^2 q_0^2}{T_h}\right)^2. \quad (24)$$

For As_2S_3, the phonon energy of a symmetric mode is 344 cm^{-1} [6]. Using this and applying Toyozawa's criterion [7,20] of strong carrier-phonon interaction as $E_{hp} \geq T_h$, we get T_h = 12.33 meV from Eq. (24), which gives

E_{hq} = 12.33 meV , E_{hh} = 98.40 meV and ΔE_{hh} = 0.123 eV. This agrees very well with the observed reduction in band gap in As_2S_3 of about 0.16 eV [7, 21]. A similar narrowing in the band gap is expected when two excited electrons can get paired on an anti-bonding orbital and two hole polarons are formed elsewhere. In this case, however, as no bond breaking occurs, the substance will go back to the original state after the exciting energy source (illumination is stopped). In materials where the excited pairs of charge carriers form only a pair of polarons, without any pairing of like charge carriers, the reduction in band gap will be equal to $E_{ep} + E_{hp} \sim 2E_{hp}$ = 25 meV. Reductions in band gap in various materials, estimated from the experimental data [21] are listed in Table 1. Accordingly, most observed reductions are found to be in the range 0.02 – 0.17 eV.

Table 1. Band gap reduction, ΔE estimated from the observed data [21] in various amorphous materials.

Amorphous Materials	ΔE (eV)
As_2S_3	0.16
GeS_2	0.17
S	0.12
As_2Se_3	0.07
Se	0.06
$GeSe_2$	0.03
As_2Te_3	0.06
Sb_2S_3	0.02

5. Discussion

It is shown that in materials with a strong carrier-lattice interaction, the excited charge carriers can form excited polarons. In addition, like excited-charge carriers can get paired as self-trapped bi-polarons on a bond, because energetically a paired like charge carrier excited state is more stable. The planar structure of chalcogenides with weak coordination enables these materials to be more flexible and hence possess stronger carrier-phonon interactions than a-Si:H. The energy states of both polarons and bi-polarons are found to be lower than those of excited free charge carriers. Thus the energy states of the hole polaron and bi-polaron (paired holes) move up further in the lone-pair orbitals and tail states, which expands the valence band. Likewise, the energy states of electron polarons and bi-polarons (paired electrons) in the anti-bonding orbitals lower the conduction mobility edge. These effects together are responsible for the reduction in the band gap and hence photodarkening. It should be noted however that all the above possibilities might not occur together in the same material. In materials where the electron-lattice interaction is larger than the hole-lattice interaction, the formation of the electron polaron and bi-polaron will be more efficient and materials with stronger hole-lattice interaction will have more efficient hole polaron and bi-polaron formation. Accordingly, a varying degree of photodarkening is expected to occur in different materials, and this is quite in agreement with the results listed in Table 1.

It has been established [7,9] that pairing of holes on a bond breaks the bond as soon as two excited holes get localized on it. It is also possible to get a bond broken due to the localization of a single hole on a bond. The bond breaks due to the removal of either one of the covalent electrons or both, as it happens in the paired hole situation, and a pair of dangling bonds is created. Such light-induced defects are reversible by annealing. However, pairing of excited electrons does not break a bond - it only reduces the band gap and such an excited state will be reversed back to the original one after switching off the illumination. This concept can be applied to explain the observation of metastable and transient PD. The former occurs due to either formation of hole polarons or pairing of holes or both, such that bonds get broken, which cannot be recovered by stopping the illumination, because of the required activation energy. It remains metastable and the material reverses back to its original form by thermal annealing. The latter occurs due to pairing of electrons and/or formation of polarons without any bond breaking, and then the material reverses back to its original form after the illumination is stopped. Usually the transient PD is observed in more cases than the metastable PD. This is because there are three processes contributing to the transient PD; pairing of electrons, formation of positive charge polarons (without bond breaking) and negative charge polarons, in comparison with only two possible channels of formation of positive charge polarons (with bond breaking) and pairing holes contributing to metastable PD.

It may be noted that in this paper only a single linear chain is considered, and therefore inter chain interactions are omitted. Inclusion of such interactions will be considered in our future work.

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