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Modelling of photoinduced changes in chalcogenide glasses: a-Se and a-As_2Se_3

S. Kugler · J. Hegedüs · K. Kohary

Abstract The microscopic processes in chalcogenide glasses caused by illumination have been investigated using tight-binding molecular dynamics computer simulation. After the photon absorption we have treated the excited electron and hole independently. We found covalent bond breaking in amorphous networks with photo-induced excited electrons, whereas excited holes contribute to the formation of inter-chain bonds. We also observed a correlated macroscopic volume change of the amorphous sample. The interplay between photo-induced bond breaking and inter-chain bond formation leads to either volume expansion or shrinkage. Our results provide a new and universal description, which can explain simultaneously the photo-induced volume expansion and shrinkage. The model is supported by the results of recent measurements carried out by Y. Ikeda and K. Shimakawa.

1 Introduction

Photodarkening and photoexpansion in chalcogenide glasses have recently attracted large interest because of their scientific importance and of their potential applications. These phenomena are unique to chalcogenide glasses and they are not observed in the crystalline chalcogenides or in any other amorphous semiconductors. Materials showing photo-induced volume change can be classified into two different groups: films can either expand or shrink. Although amorphous selenium is considered as a model material for the chalcogenide glasses, very few experimental study of light induced volume changes can be found on the selenium based chalcogenide glasses in the literature. Recently Y. Ikeda and K. Shimakawa have published an in-situ measurement on a-Se and on As_2Se_3 [1].

For the photo-induced volume change simulations we used our recently developed tight-binding molecular dynamics (TB-MD) computer code (ATOMDEP program package for C [2], for Si [3], and for Se [4, 5]). The tight-binding model we used is analyzed in Ref. [6]. We applied the velocity Verlet algorithm to follow the motion of atoms with a time step equals to 2 fs. The temperature was controlled via the velocity-rescaling method.

We prepared 30 glassy selenium networks in a rectangular box with periodic boundary conditions. The size of our initial simulation cell was 12.78 A × 12.96 A × 29.69 A. Samples contained 162 atoms and the initial density was 4.33 g/cm^3. Our 'cook and quench' sample preparation procedure was the following. First, we choose the temperature of the system to be 5000 K for the first 300 MD steps to randomize the atomic positions. During the following 2200 MD steps we decreased linearly the temperature from 700 to 250 K, driving the sample through the glass transition and reaching the condensed phase. Then

S. Kugler (✉)
Department of Theoretical Physics, Budapest University of Technology and Economics, Budapest 1521, Hungary
e-mail: kugler@eik.bme.hu

S. Kugler
Department of Electronics and Computer Engineering, Tokyo Polytechnic University, Tokyo, Japan

J. Hegedüs
Department of Theoretical Physics and Material Sciences Center, Philipps University Marburg, Renthof 5, 35032 Marburg, Germany

K. Kohary
Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK

we set the final temperature to 20 K and we relaxed the sample for 500 MD steps (1 ps). In order to model the photo-induced volume changes, periodic boundary conditions were lifted along the z-direction at this point. Thus, this procedure provided us a slab geometry with periodic boundary conditions in two dimensions. The system was relaxed for another 40000 MD steps (80 ps) at T = 20 K.

2 Light induced phenomena

Photo excitations generate electron-hole pairs. We model this process in the following way: an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) was transferred when a photon is absorbed. This technique was first applied to describe the photo-induced effects in eight-member sulfur rings within the framework of density functional theory by Shimojo and his coworkers [7]. We used a similar method to test the photo-induced changes in different selenium clusters, like an eight-member ring and an 18-member linear chain. We observed photo-induced bond breaking inside these selenium clusters similarly to the case of sulfur.

In the amorphous selenium immediately after the absorption of a photon, a pair of electron and hole became separated in space. Therefore, they can be treated independently i.e. we can investigate the roles of excited electrons and holes separately. We ran two sets of computer simulations: first, to model the excited electron creation we put an extra electron into the LUMO and second, we annihilated an electron in HOMO (hole creation).

2.1 Electron excitation

A covalent bond between two-fold (C2) and three-fold (C3) coordinated atoms was broken (C2 + C3 ⇒ C1 + C2) in the majority of cases when an additional electron was put in the LUMO as illustrated in Fig. 1.

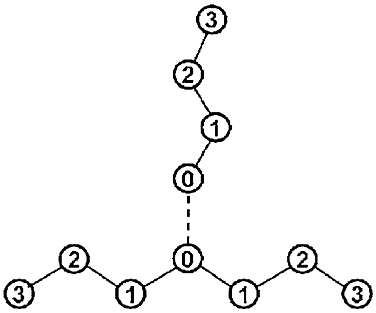

Fig. 1 Bond breaking due to electron addition in the LUMO of amorphous selenium network

Our localization analysis revealed that the LUMO was localized at this site before the bond breaking as it can be seen in Fig. 2. A release of excitation restores all bond lengths to their original value.

The time development of photo-induced volume expansion in one of our amorphous selenium sample due to an added electron is shown in Fig. 3. We have selected one sample from our simulations, which seems to be a typical run. Similar changes were observed in each amorphous selenium network. During the illumination, the weaker bond lengths increased by 10–20% and decreased to original values after the de-excitation. (Arrows show the excitation and de-excitations in the Fig. 3.) The volume change follows the bond breaking and it shows damped oscillations on the picoseconds time scale.

2.2 Hole creation

We observed that inter-chain bonds were formed after creating a hole and they cause contraction of the sample (see Fig. 4.). This contraction always appears near to atoms where HOMO is localized. Since HOMO is usually localized in the vicinity of a one-fold coordinated atom, the

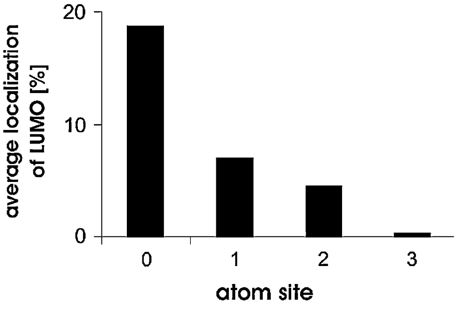

Fig. 2 Average localizations of LUMO at the atoms 0, 1, 2, 3 (see Fig. 1 for notations)

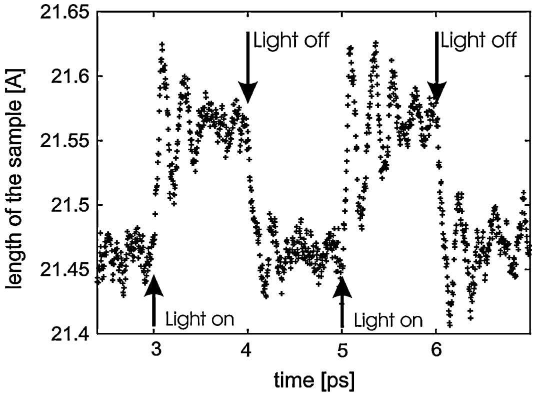

Fig. 3 Reversible thickness change of a-Se sample during photo-excitation

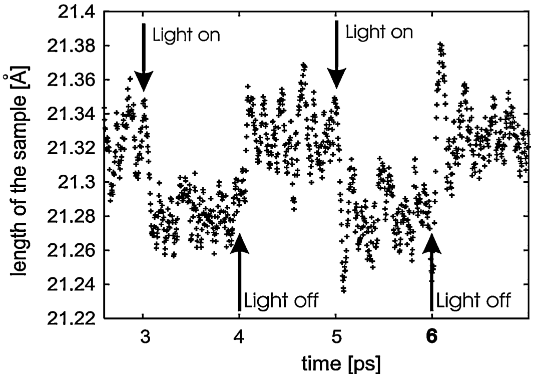

Fig. 4 Reversible photo-induced contraction due to the addition of a hole in a-Se as a function of time

inter-chain bond formation often takes place between a one-fold coordinated atom and a two fold-coordinated atom (C{1,0} + C{2,0} ⇒ C{1,1} + C{2,1}, where the second number means the number of inter-chain bonds). However, sometimes we also observed the formation of inter-chain bonds between two two-fold C2 coordinated atoms (C{2,0} + C{2,0} ⇒ C{2,1} + C{2,1}).

In order to model the collective effect of photo-induced changes in amorphous selenium, we also performed simulations with five excited electron creations and five hole creations. We put five excited electrons from the five highest occupied energy levels (one electron from one level) to the five lowest unoccupied energy levels (again, one electron to each level). We found similar effects as described above for single electron/hole creation: bond breaking's and inter-chain bond formations have similar characteristics. Nevertheless, in the five excited electron creation case, further bond breaking occurred not only at the C3 sites, but as well at some C2 sites. In the case of the five hole creation, we observed that inter-chain bonds were formed between C1 and C2 sites and also between C2 and C2 sites.

3 Macroscopic models

3.1 Ideal glassy structure

The light induced volume expansion and volume shrinkage in amorphous selenium occur simultaneously and these are additive quantities as our molecular dynamics simulations have confirmed it. The expansion of the thickness d_e is proportional to the number of excited electrons n_e ($d_e = \beta_e n_e$), while the shrinkage d_h is proportional to the number of created holes n_h ($d_h = \beta_h n_h$), where the parameters β_e and β_h are the average thickness changes caused by an excited electron and a hole, respectively. The time dependent equation of thickness change can then be written as:

$$\Delta(t) = d_e(t) - d_h(t) = \beta_e n_e(t) - \beta_h n_h(t) \quad (1)$$

Assuming $n_e(t) = n_h(t) = n(t)$ we get

$$\Delta(t) = (\beta_e - \beta_h)\, n(t) = \beta n(t), \quad (2)$$

where β is a characteristic constant of different chalcogenide glasses related to photo-induced volume (thickness) change. The sign of this parameter governs whether the material shrinks or expands. The number of electrons excited and holes created is proportional to the duration time of illumination. Their generation rate G depends on the number of incoming photons and on the photon absorption coefficient. After the photon absorption, the separated excited electrons and holes migrate within the amorphous sample and then eventually recombine. A phenomenological equation for this dominant process can be written as:

$$dn_e(t)/dt = G - C\, n_e(t)\, n_h(t), \quad (3)$$

where C is a constant. Using $n_e(t) = n_h(t) = n(t)$ and $\Delta(t) = \beta\, n(t)$, we obtain a fundamental equation for the time dependent volume change, namely,

$$d\Delta(t)/dt = G\beta - (C/\beta)\, \Delta^2(t). \quad (4)$$

Solution of this nonlinear differential equation is obtained as:

$$\Delta(t) = \beta(G/C)^{1/2} \tanh((GC)^{1/2} t). \quad (5)$$

Figure 5 shows the measured time evolution of the surface height [1] in the interval of 0–300 s together with its best fit.

After the light is turned off (G = 0), Eq. (4) can be written as

$$d\Delta(t)/dt = -(C/\beta)\Delta^2(t), \quad (6)$$

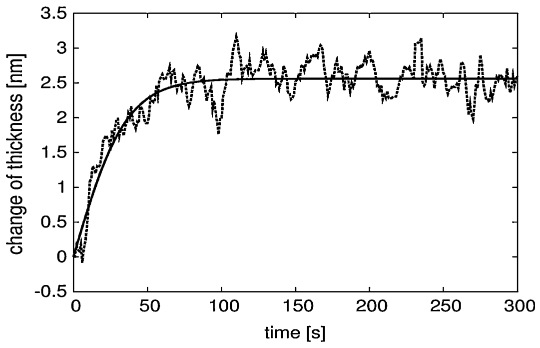

Fig. 5 Time development of volume expansion in amorphous selenium (dashed line) and its theoretical fit (solid line)

with the solution

$$\Delta(t) = a/(a(C/\beta)\,t + 1). \tag{7}$$

Figure 6 displays the measured volume change and the fitted theoretical curve to the measured data. Light was switched off at t = 800 s.

3.2 Non-ideal glassy network

In the ideal case we assumed that each local structure variations were reversible and the original local structures were reconstructed after the electron-hole recombination. However, the result of a measured volume change on flatly deposited a-As_2Se_3 film is quite different from the ideal selenium case (See: Fig. 2b in Ref. [1]). To explain the difference we must take into account a large number of irreversible changes in the local atomic arrangement i.e. after turning off the light the local configuration remains the same and there is no electron-hole recombination. (The structure modelling of two component chalcogenide glasses is a difficult problem [8]). The total volume change includes both the reversible and irreversible changes and it can be written as:

$$\Delta_{total}(t) = \Delta_{rev}(t) + \Delta_{irr}(t). \tag{8}$$

The reversible part follows Eqs. (4), (6) during and after the illumination, respectively, with the corresponding solutions given in Eqs. (5), (7).

We now consider the irreversible component. During the illumination, the generation rate of irreversible microscopic change is time dependent. Let's consider that an upper limit exists for the maximum number of electrons and holes causing irreversible changes and denoted by $n_{e,irr,max}$ and $n_{h,irr,max}$, respectively. To simplify the derivation let us assume that $n_{e,irr,max} = n_{h,irr,max}$. In this case, one can write the electron generation rate as :

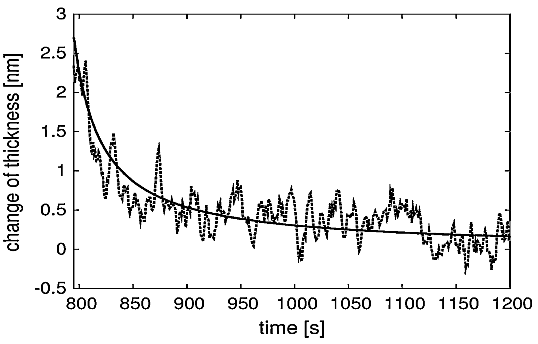

Fig. 6 The measured shrinkage of a-Se (dashed line) and the fitted curve (solid line) after stopping the illumination

$$G_e(t) = C_e\,(n_{e,irr,max} - n_e(t)). \tag{9}$$

Note that there is no recombination term in Eq. (9). Following Eq. (4), we obtain that the irreversible expansion is governed by:

$$d\Delta_{irr}(t)/dt = G_{irr} - C_{irr}\Delta(t). \tag{10}$$

Equation (10) then leads to the solution:

$$\Delta_{irr}(t) = (G_{irr}/C_{irr})\,(1 - \exp\{-C_{irr}t\}). \tag{11}$$

Using Eq. (11) in Eq. (8), the best fit of the volume expansion ($\Delta_{total}(t)$), and that of the reversible and irreversible parts (Δ_{rev} (t), and Δ_{irr} (t)) are displayed in Fig. 7.

After illumination there is no volume change caused by the irreversible microscopic effects. Figure 8 shows the shrinkage after switching off the illumination, which is the fit as obtained in the reversible case.

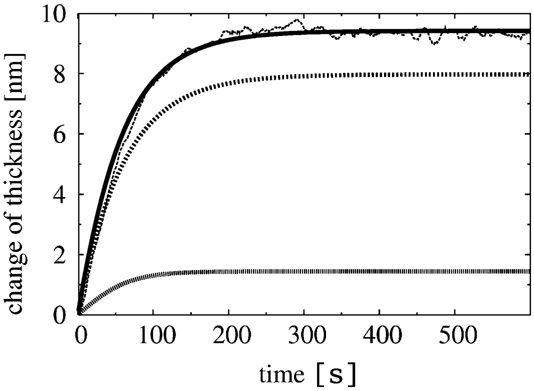

Fig. 7 Time development of volume expansion of a-As_2Se_3. Thin solid line is the measured curve, thick solid line is the fitted line ($\Delta_{total}(t) = \Delta_{rev}(t) + \Delta_{irr}(t)$). Lower dashed curve is the best fit of $\Delta_{rev}(t)$ while upper one is that of the irreversible part $\Delta_{irr}(t)$

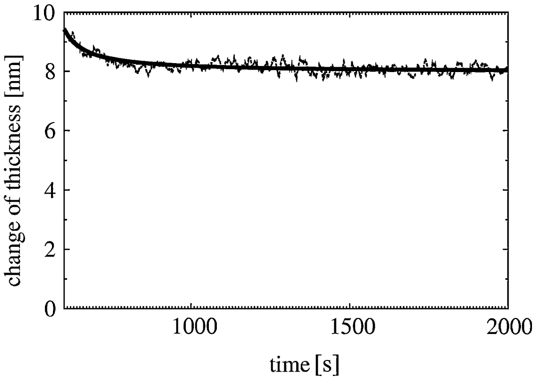

Fig. 8 The measured decay (thin solid line) and the fitted theoretical curves (thick solid line) for the shrinkage as a function of time after stopping the illumination

4 Conclusion

We have found that the covalent bond breaking occurs in chalcogenide glasses with excited electrons, whereas holes contribute to the formation of inter-chain bonds. In the ideal situation both processes are reversible. The interplay between photo-induced bond breaking and inter-chain bond formation leads to either volume expansion or shrinkage. In the non-ideal case, only a part of the processes is irreversible and the total expansion includes the reversible and irreversible changes. Our microscopic explanation of the macroscopic photo-induced volume change is consistent with the first in-situ surface height measurements.

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