Universal feature of photo-induced volume changes in chalcogenide glasses

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Abstract

We have investigated in chalcogenide glasses the microscopic processes caused by illumination using tight-binding molecular dynamics computer simulation. After photon absorption we 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. Our results provide a new and universal description, which can explain simultaneously the photo-induced volume expansion and shrinkage. This model is supported by the results of recent measurements.
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1. Introduction

Chalcogenide glasses exhibit various changes in structural and electronic properties during illumination such as photo-induced volume change, photo-darkening, defect creation, and photo-induced change in the phase state. Some of the chalcogenide glasses show photo-induced volume expansion the rest shrinks during illumination [1,2]. Several investigations have been carried out in order to provide an explanation of the photo-induced phenomena [3–8], but an acceptable general theory is still missing. In this paper, we propose an universal description of the photo-induced volume changes in chalcogenides based on our tight-binding (TB) molecular dynamics (MD) simulations on amorphous selenium. Our proposed mechanism for photo-induced kinetics is supported by the first in situ surface height measurement by Ikeda and Shimakawa [9].

2. Sample preparation

For the photo-induced volume change simulations we used our recently developed TB-MD computer code (ATOMDEP program package for C [10], for Si [11], and for Se [12,13]). Self-consistency was taken into account via the on-site Hubbard term within the TB model [14,15]. We used the velocity Verlet algorithm to follow the motion of atoms with a time step equals to $\Delta t = 2$ 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 $12.78\,\text{Å} \times 12.96\,\text{Å} \times 29.69\,\text{Å}$ (*xyz*). Samples contained 162 atoms and the initial density was 4.33 g/cm³. Our 'cook and quench' sample preparation procedure was the following [12]. 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 K to 250 K, driving the sample through the glass

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transition and reaching the condensed phase. Then 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 40 000 MD steps (80 ps) at $T = 20$ K.

3. Excited electron creation

Immediately after a photon absorption the electron and the hole become separated in space on a femtosecond time scale. Therefore, they can be treated independently. We ran two sets of simulations: first, to model the excited electron creation we put an extra electron into the LUMO (lowest unoccupied molecular orbital), and second, we annihilated an electron in highest occupied molecular orbital, HOMO (hole creation). When an additional electron was put on the LUMO in the majority of cases, a covalent bond between a two-fold and a three-fold coordinated atoms was broken ($C_2 + C_3 \Rightarrow C_1 + C_2$). Our localization analysis revealed that the LUMO was localised at this site before bond breaking. Release of excitation restores all bond lengths to their original value.

The time development of photo-induced bond breaking due to excited electron and the corresponding volume expansion in one of our amorphous selenium sample is shown in Fig. 1. We selected from our simulations one which seems to be a typical run. Similar changes were observed in each amorphous selenium network. Before the excitation at 5 ps the bond length is about 2.55 Å. In this particular case bond breaking occurs at a weaker bond due to the C_3 site, which has a larger interatomic separations than the majority of the nearest-neighbor bonds with ~2.4 Å. During illumination this weak bond (2.55 Å) increases by 10–20% (in this example to ~3 Å) and it decreases to its original value after the excitation. We mea-

sured the corresponding volume change by calculating the variation in thickness of our amorphous selenium slab. The volume change follows the bond breaking and it shows damped oscillations on the picosecond time scale.

4. Hole creation

More interesting results were obtained during hole creation. We observed that inter-chain bonds were formed after creating a hole and they cause contraction of the sample (Fig. 2). This always happens near to atoms where HOMO is localised. Since HOMO is usually localised in the vicinity of a one-fold coordinated atom, the inter-chain bond formation often takes place between a one-fold coordinated atom and a two-fold coordinated atom ($C_{1,0} + C_{2,0} \Rightarrow C_{1,1} + C_{2,1}$, where the second subscript means the number of inter-chain bonds). However, sometimes we also observed the formation of inter-chain bonds between two two-fold C_2 coordinated atoms ($C_{2,0} + C_{2,0} \Rightarrow C_{2,1} + C_{2,1}$).

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 breakings and inter-chain bond formations have similar characteristics, as seen in Figs. 1 and 2. Nevertheless, in the five excited electron creation case, further bond breaking occurred not only at the C_3 sites, but as well at some C_2 sites. In the case of five hole creation, we observed that inter-chain bonds were formed between C_1 and C_2 sites and also between C_2 and C_2 sites.

5. Kinetics of volume change

The results confirm that the volume expansion/shrinkage are additive value, i.e. the expansion d_+ is proportional
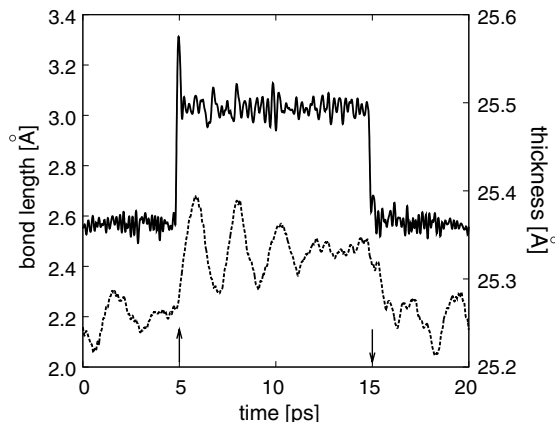

Fig. 1. Atomic distance separation of breaking bond (solid line) and thickness of sample (dotted line) as a function of time. Arrows indicate that at 5 ps an excited electron was created while at 15 ps it was annihilated.
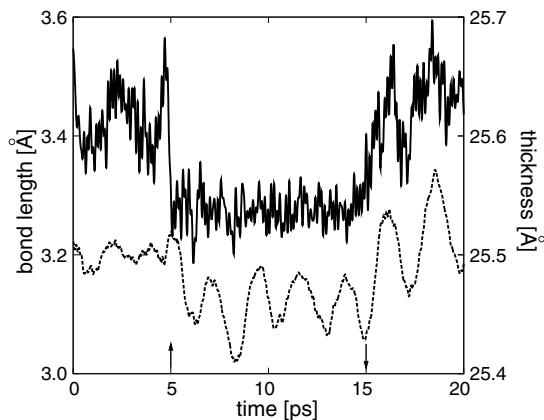

Fig. 2. Atomic distance separation of inter-chain bond (solid line) and thickness of sample (dotted line) as a function of time. Arrows indicate that at 5 ps a hole was created while at 15 ps it was annihilated.

to the number of excited electrons n_e $(d_+ = \overline{B}_+ n_e)$ while the measure of shrinkage d_- is proportional to number of created holes n_h $(d_- = \overline{B}_- n_h)$. The parameter $\overline{B}_+$ $(\overline{B}_-)$ is the average volume (thickness) change caused by an excited electron (hole). The time dependent volume change is equal to $\Delta(t) = d_+(t) - d_-(t) = \overline{B}_+ n_e(t) - \overline{B}_- n_h(t)$. Assuming $n_e(t) = n_h(t) = n(t)$ we get

$$\Delta(t) = (\overline{B}_+ - \overline{B}_-)n(t) = B_\Delta n(t), \tag{1}$$

where B_Δ is a characteristic constant of the chalcogenide glass related to photo-induced volume change and it is a unique parameter for each glass. The sign of this parameter governs whether the material shrinks or expands.

The number of excited electrons and created holes is proportional to time during illumination. Their generation rate G depends on the photon absorption coefficient and the number of incoming photons. After photon absorption, excited electrons and holes migrate within the amorphous sample and then eventually they recombine. A phenomenological equation for this dominant process can be written as

$$\frac{dn_e(t)}{dt} = G - Cn_e(t)n_h(t), \tag{2}$$

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

$$\frac{d\Delta(t)}{dt} = GB_\Delta - (C/B_\Delta)\Delta^2(t). \tag{3}$$

Solution of this nonlinear differential equation is equal to

$$\Delta(t) = B_\Delta \sqrt{\frac{G}{C}} \tanh\left(\sqrt{GC}t\right). \tag{4}$$

After the light is turned off Eq. (3) reduces to

$$d\Delta(t)/dt = -(C/B_\Delta)\Delta^2(t), \tag{5}$$

with a solution of $\Delta(t) = a/(a(C/B_\Delta)t + 1)$.

5.1. a-Se measurement

Photo-induced expansion in amorphous selenium was measured by the first in situ surface height measuring system based on optoelectronic and image processing technologies [9]. This new method provides a record of data due to volume change (changes in the surface height) as a function of time during and after illumination. It was found that the film height increased rapidly by 2.5 nm (with a film thickness change of 0.5%) with illumination ($\lambda = 532$ nm, 91 mW/cm^2) and decreased as soon as the light was turned off. Fig. 3(a) shows the measured time evolution of surface height in amorphous selenium films in the interval of 0–400 s and our theoretical curve using Eq. (4). Fig. 3(b) displays the measured decay and the fitted theoretical curve.

5.2. a-AsSe measurement

The result of an other measurement on a-AsSe is quite different (Fig. 2(a) in Ref. [9]). To explain the difference
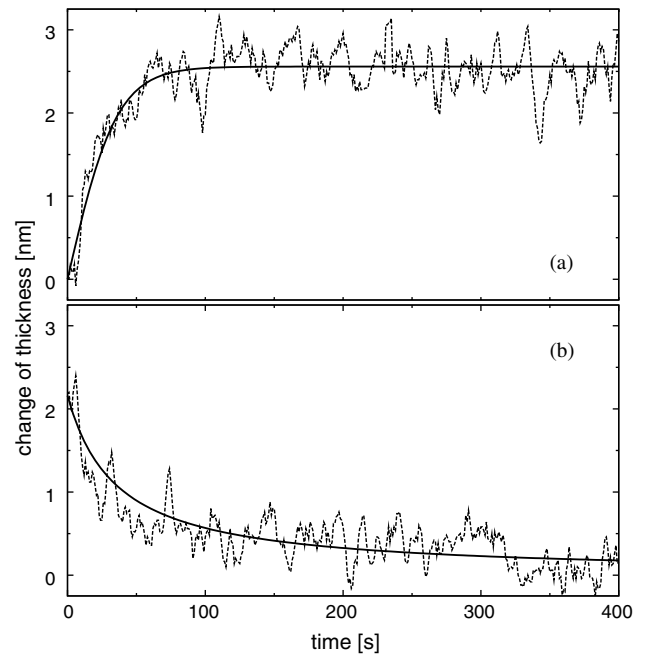

Fig. 3. Measured photo-induced changes in amorphous selenium. (a) Expansion due to illumination (dotted line) and fitted curve (solid line). (b) Shrinkage after switching off illumination (dotted line) and fitted theoretical curve (solid line).
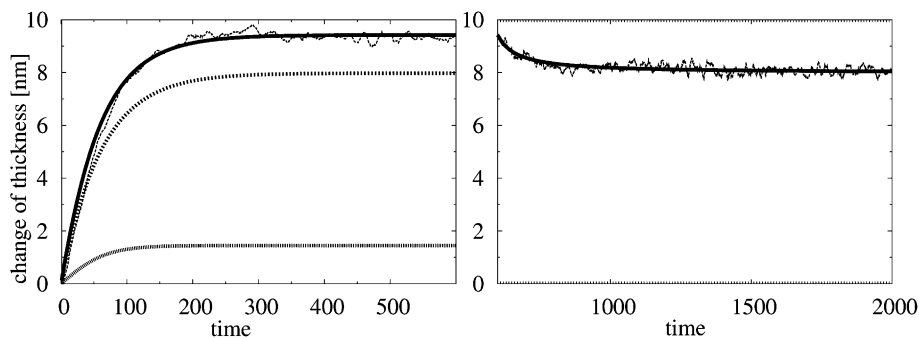

Fig. 4. Measured photo-induced changes in amorphous AsSe. Left panel: expansion due to illumination (thin solid line) and fitted curve (solid line). Two dotted lines represent the reversible and irreversible parts of the theoretical curve. Right panel: shrinkage after switching off illumination (dotted line) and fitted theoretical curve (solid line).

we must take into account a large number of irreversible changes in the local atomic arrangement. The total expansion includes the reversible and irreversible changes:

$$\Delta(t) = \Delta_{\mathrm{rev}}(t) + \Delta_{\mathrm{irr}}(t). \tag{6}$$

During and after the illumination the reversible part follows Eqs. (3) and (5) ($\Delta_{\mathrm{rev}}(t) = \Delta(t)$). The solutions are the same. After illumination there is no volume change caused by irreversible microscopic effects. During illumination the irreversible expansion is governed by

$$\frac{\mathrm{d}\Delta_{\mathrm{irr}}(t)}{\mathrm{d}t} = G_{\mathrm{irr}} - C_{\mathrm{irr}}\Delta_{\mathrm{irr}}(t), \tag{7}$$

differential equation. The solution in this case is given by

$$\Delta_{\mathrm{irr}}(t) = \frac{G_{\mathrm{irr}}}{C_{\mathrm{irr}}}(1 - \mathrm{e}^{-C_{\mathrm{irr}}t}). \tag{8}$$

The best fit is displayed in Fig. 4. Left panel displays the expansion due to illumination while the right panel shows the shrinkage after switching off the illumination.

6. Conclusion

We proposed a new explanation of photo-induced volume changes in chalcogenide glasses. We found covalent bond breaking in systems with excited electrons, whereas holes contribute to the formation of inter-chain bonds. The interplay between photo-induced bond breaking and inter-chain bond formation leads to either volume expansion or shrinkage. Our microscopic explanation of the macroscopic photo-induced volume change is consistent with the first in situ surface height measurements.

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