

Modelling of photo-induced changes in chalcogenide glasses: a-Se and a-AsSe

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Abstract

The microscopic processes in amorphous selenium caused by light-illumination have been investigated using molecular dynamics 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. 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. In the non-ideal case, a part of the microscopic processes is metastable and the total expansion includes the transient and metastable changes. We can describe this macroscopic effect, too. Our rate-equation models for a-Se and a-AsSe are supported by the results of recent measurements carried out by Y. Ikeda and K. Shimakawa.

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1. Introduction

In recent years chalcogenide glasses received particular attention because of their application in data storage devices such as optical discs and because of the possible future devices based on chalcogenide materials like non-volatile phase-change memories. Chalcogenide glasses exhibit various changes in physical properties during illumination such as photo-induced volume change, photo-darkening, defect creation, and photo-melting. The microscopic structural changes are facilitated by two factors common to chalcogenide glasses: the low average coordination number and the structural freedom of the non-crystalline state. During the illumination some of the films can expand (a-As₂S₃, a-As₂Se₃, etc.), and some shrink (a-GeS₂, a-GeSe₂, etc.) [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 his co-workers [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]). Self-consistency was taken into account via the on-site Hubbard term within the TB model [13,14]. We used the velocity Verlet algorithm to follow the motion of atoms with a time step equal 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 in the x , y and z -directions

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12.78, 12.96 and 29.69 Å, respectively. 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 to 250 K, driving the sample through the glass 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 lowest unoccupied molecular orbital (LUMO), 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 localized at this site before bond breaking. Release of excitation restores all bond lengths to their original value.

Photo-induced bond breaking is depicted in Fig. 1. The time development of photo-induced volume expansion in one of our amorphous selenium sample is shown in Fig. 2. Similar changes were observed in other amorphous selenium networks, too. Before the excitation the bond length of the to-be-broken bond 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 inter-atomic 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. The volume change follows the bond breaking and it shows damped oscillations on the picosecond time scale.

4. Hole creation

Very interesting results were obtained during hole creation. We observed that inter-chain bonds were formed after creating a hole (Fig. 3) and they cause contraction of the sample (Fig. 4). This always happens near to atoms where HOMO is localized. Since HOMO is usually localized in the vicinity of a one-fold coordinated atom, the inter-chain bond formation often takes place between a

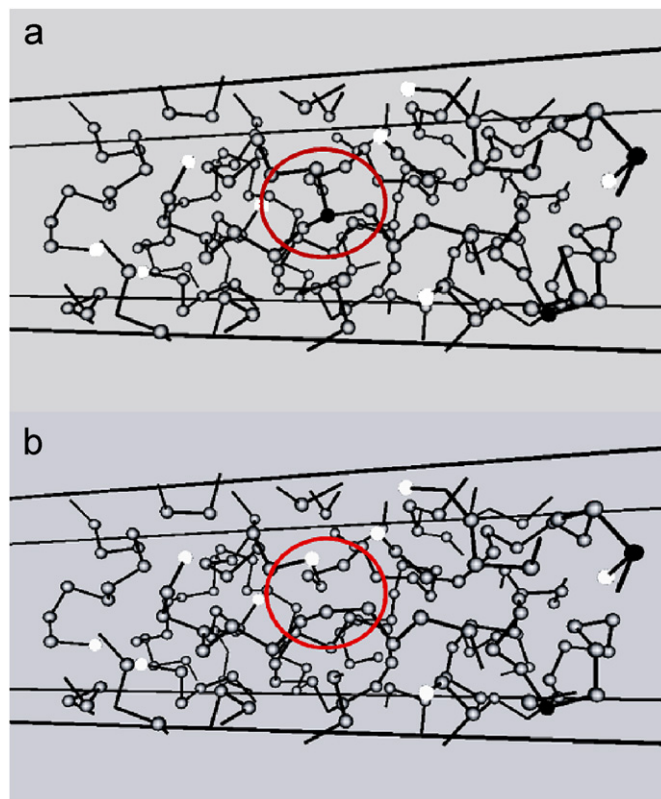


Fig. 1. Upper figure (a) shows the atomic structure before photo-excitation while the bottom figure (b) depicts the selenium network during illumination. Bond-breaking is caused by excited electron and is marked by circle. Different colors denote different coordination numbers: white (1), gray (2) and black (3). We have applied free boundary condition in one direction along the black lines which depict the boundaries of the simulation box.

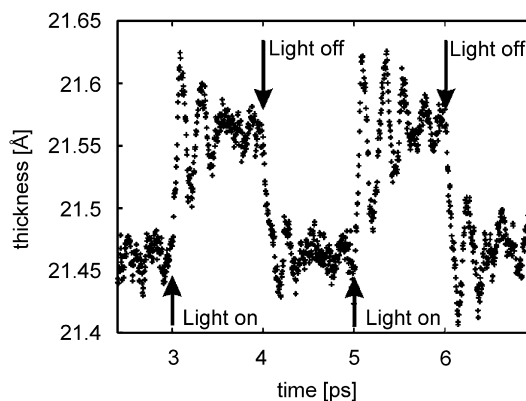


Fig. 2. Photo-induced local expansion due to photo-excited electrons: thickness of a representative sample is depicted as a function of time. Arrows indicate creation of one electron (light on) and its annihilation (light off).

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 ($C_{2,0} + C_{2,0} \Rightarrow C_{2,1} + C_{2,1}$).

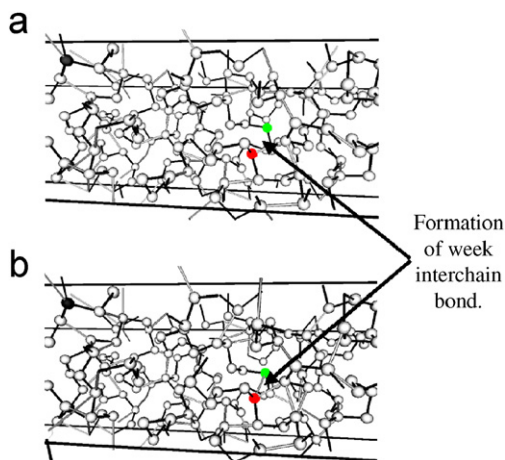


Fig. 3. Photo-excited hole leads to the formation of weak inter-chain bonds, they are colored as gray, while covalent bonds are colored as black. Weak inter-chain bonds correspond to inter-atomic distances between 3.0 and 3.4 Å, while covalent bonds are between 2.3 and 2.7 Å. Upper panel (a) shows the atomic structure before illumination and the lower panel (b) depicts the amorphous network during photo-excitation. Weak inter-chain bond formation takes place where HOMO is localized.

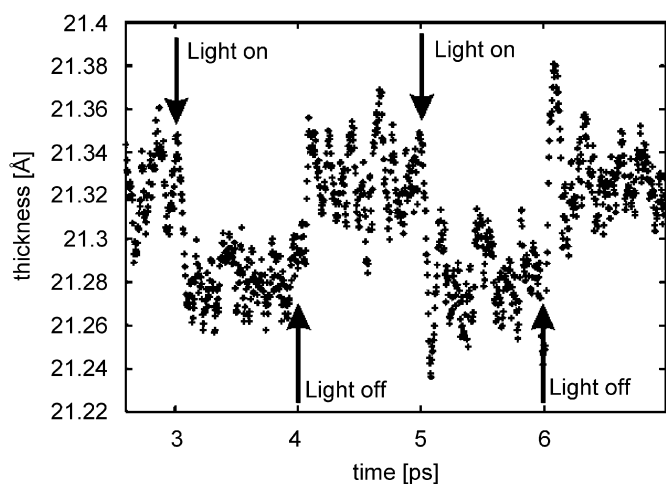


Fig. 4. Photo-induced local contraction is caused by photo-excited holes. Thickness of a representative sample is depicted as a function of time. Arrows indicate hole creation (light on) and annihilation (light off).

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, as seen in Figs. 1–4. 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 five hole creation, we observed that inter-chain bonds were formed between C₁ and C₂ sites and also between C₂ and C₂ sites.

5. Kinetics of volume change

The results confirm that the volume expansion/shrinkage are additive value, i.e. the expansion d_+ is proportional to the number of excited electrons n_e ($d_+ = \bar{B}_+ n_e$) while the measure of shrinkage d_- is proportional to number of created holes n_h ($d_- = \bar{B}_- n_h$). The parameter \bar{B}_+ (\bar{B}_-) is the average volume change caused by an excited electron (hole). The time dependent volume change is equal to $\Delta(t) = d_+(t) - d_-(t) = \bar{B}_+ n_e(t) - \bar{B}_- n_h(t)$. Assuming $n_e(t) = n_h(t) = n(t)$ we get

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

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

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

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,

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

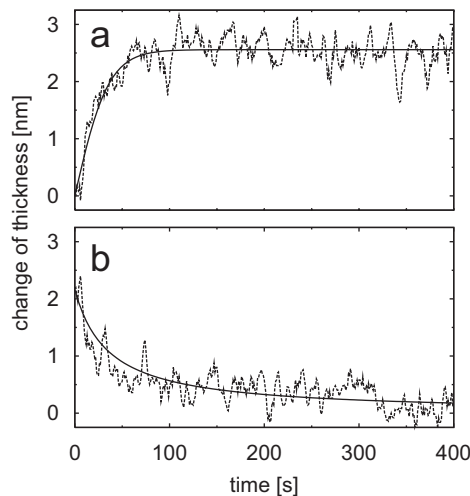


Fig. 5. Measured photo-induced changes in amorphous selenium. Upper panel: expansion due to illumination (dotted line) and fitted curve (solid line). Lower panel: shrinkage after switching off illumination (dotted line) and fitted theoretical curve (solid line). During the fitting procedure only one independent parameter had to be determined.

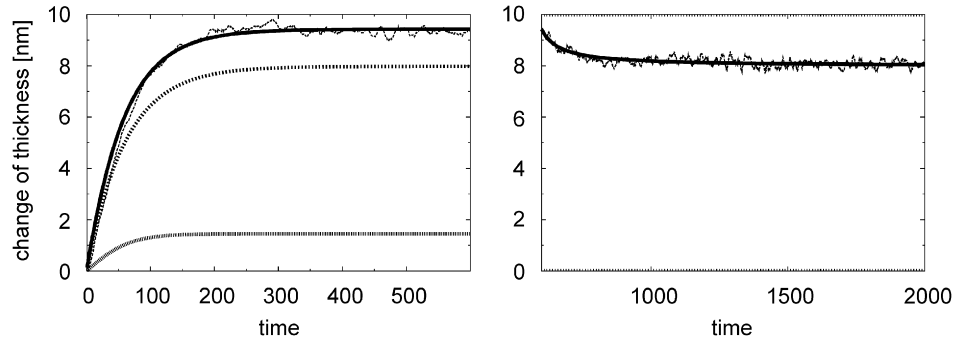


Fig. 6. Measured photo-induced changes in amorphous AsSe. Left panel: expansion due to illumination (thin solid line) and fitted curve (solid line). Two dotted lines represent the transient and metastable parts of the theoretical curve. Right panel: shrinkage after switching off illumination (dotted line) and fitted theoretical curve (solid line). In order to describe the metastable volume change two independent fitting parameters were needed.

Solution of this nonlinear differential equation is equal to

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

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

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

with a solution of $\Delta(t) = a/(a(C/B_{\Delta})t + 1)$. Since we can measure the steady-state volume expansion there is only one independent parameter left to be fit.

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/cm²) and decreased as soon as the light was turned off. Fig. 5(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. 5(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. 2a in Ref. 9). To explain the difference we must take into account a large number of metastable changes in the local atomic arrangement [15,16]. The total expansion includes the transient (trans) and metastable (met) changes:

$$\Delta(t) = \Delta_{trans}(t) + \Delta_{met}(t), \quad (6)$$

During and after the illumination the transient part follows Eqs. (3) and (5) ($\Delta_{trans}(t) = \Delta(t)$). The solutions are the same. After illumination there is no volume change caused by metastable microscopic effects. During illumination the

metastable expansion is governed by the

$$\frac{d\Delta_{met}(t)}{dt} = G_{met} - C_{met}\Delta_{met}(t) \quad (7)$$

differential equation. The solution in this case is given by

$$\Delta_{met}(t) = \frac{G_{met}}{C_{met}}(1 - e^{-C_{met}t}). \quad (8)$$

We can measure the steady-state volume expansions (transient and metastable), so here we have two independent parameters to fit. The best fit is displayed in Fig. 6. 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. Rate equation model with one independent fitting parameter reproduces the time development of photo-induced volume change in a-Se and two independent parameters are needed to describe the photo-expansion in a-AsSe.

Acknowledgments

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