Photo-induced volume changes in selenium. Tight-binding molecular dynamics study

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Available online 9 April 2004

Abstract

Tight-binding molecular dynamics simulations of photo-excitations in small Se clusters (isolated Se_8 ring and helical Se chain) and glassy Se networks (containing 162 atoms) were carried out in order to analyze the photo-induced instability in amorphous selenium. In the cluster systems after taking an electron from the highest occupied molecular orbital to the lowest unoccupied molecular orbital a bond breaking occurs. In the glassy networks photo-induced volume expansion was observed and at the same time the number of coordination defects changed significantly due to illumination.
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PACS: 73.61.Jc

1. Introduction

The photo-induced structural changes during illumination in chalcogenide glasses [1,2] can be classified into two groups, those which are irreversible and which can be reversed. A further possible sorting is the following: there are defect related metastabilities and there are structure related one. Several investigations have been carried out in amorphous selenium (a-Se) in order to provide an acceptable explanation of these phenomena [3–7]. Present capacity of fast computers allow us to simulate the photo-induced structural changes, i.e. to follow the time development of these phenomena by molecular dynamics (MD). Our particular aim was to determine how the structural changes occur in a-Se due to illumination. We performed tight-binding molecular dynamics simulations to study the dynamics of a Se_8 ring, a linear chain and glassy Se networks before, during and after the illumination.

2. Simulation method

We have developed a MD computer code (ATOM-DEP program package) to simulate the real preparation procedures of amorphous structures (growth by atom-by-atom deposition on a substrate and rapid quenching). In our recent work [8], the growth of amorphous carbon films were simulated by this MD method. This computer code is convenient to investigate photo-induced volume changes as well if the built-in atomic interaction can handle the photo-excitation. Standard velocity Verlet algorithm was applied in our MD simulations in order to follow the atomic scale motion. We chose $\Delta t = 1$ or 2 fs for the time step, depending on the temperature. These values are the typically used time steps for such simulations. To control the temperature of the systems we applied the velocity-rescaling method.

For calculating the inter-atomic forces in a-Se we used tight-binding (TB) [9] and self-consistent tight-binding (SCF-TB) [10] models. The TB parametrization [9] has been introduced for disordered selenium following the techniques developed by Goodwin et al. [11]. It was thoroughly tested by molecular dynamics calculations in liquid and amorphous phases and the results were compared to experiments and to ab initio calculations. The

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agreement with experiments and ab initio calculations are rather good apart from the fact that the number of coordination defects in the solid and liquid phases are higher than the experimentally measured values. The authors improved their TB Hamiltonian by including the Hubbard correction [10]. This implies that either the algorithm have to be made self-consistent or perturbation theory must be applied. Our choice was the first alternative. The convergence for SCF-TB calculations was controlled by the charge differences on the atomic sites. Convergence criteria were considered to be satisfied if the deviation of atomic charges between the actual and the previous iterations was less than 0.01 electron/atom.

3. Sample preparation

3.1. Cluster geometries

Crystalline forms of selenium consist of chains and eight-membered rings. Typical bond lengths are around 2.35 Å while most of the bond angle values are around 103°. It is very likely that these local arrangements can be found in non-crystalline forms of selenium as well. The initial configuration of the eight-membered ring in our simulation has bond lengths of 2.38 Å and bond angles of 102°. Dihedral angles are equal to 100° (see Fig. 1, top panel). For the eighteen-membered selenium chain (with 1-dimensional periodic boundary condition) these values are: 2.36 Å, 100°, and 98°, respectively. Every Se atom had two first-neighbors, i.e. there was no coordination defect.

3.2. Glassy structure

Glassy selenium networks having 162 atoms (with three-dimensional periodic boundary conditions) were prepared by 'cook and quench' technique (from 3000 to 20 K). The average quenching rate was 4×10^{12} K/s. In our simulation after quenching the periodic boundary
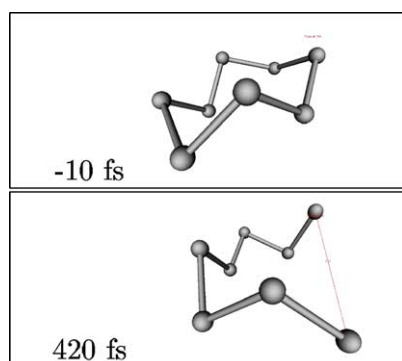

Fig. 1. Two snapshots of bond-breaking process caused by photo-excitation in the Se_8 ring. Top panel displays the ring structure before excitation. An electron from the HOMO is excited to the LUMO at $t = 0$ fs. Bottom panel shows the configuration after 420 fs.
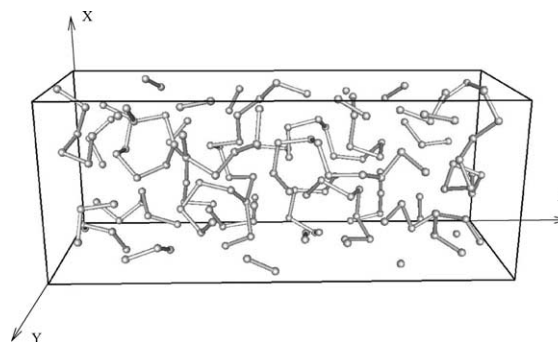

Fig. 2. One of the glassy networks constructed with rapid cooling technique. It contains 162 Se atoms with periodic boundary condition in x and y directions.

constraint in the z-direction was released and the system was allowed to relax for another 100 ps. In this way the system was able to change its volume in the z-direction. Four models have been prepared with different initial topologies and densities. The snapshot of one of our models can be seen in Fig. 2.

4. Results

4.1. Photo-excitation of small Se clusters

Before illumination (photo-excitation) the individual ring and the chain were relaxed for 4 ps at $T = 500$ K. During this period the structures were stable. When a photon is absorbed an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) is transferred. This is a simple model of photo-excitation when an electron is shifted from the valence band to the conduction band (electron-hole pair creation). In our study electron–hole pair recombination was also simulated by taking back the electron from the conduction band to the valence band. The lifetime of the excitation was 200 fs.

After excitation one bond length in the ring started to increase and bond-breaking occurred. Two snapshots of this process can be seen in Fig. 1. A similar result was published [12] by a Japanese group for S_8. They performed MD simulation within the framework of density functional theory in the local density approximation. In our second MD simulation we investigated the linear chain structure. The same procedure was performed to model the excitation. An electron from HOMO to LUMO was transferred. Very similar result was obtained; a bond inside the chain was broken immediately after a HOMO electron was excited.

4.2. Photo-excitation of glassy Se networks

The excitation procedure for the glassy networks was different from the method applied for small clusters. The

hole procedure was carried out at the temperature of 20 K. Instead of a single electron excitation, five electrons were transferred from the valence band to the conduction band. The first excited electron was taken from the HOMO, the second excited electron was taken from the level below it and so on. A difficulty applying this procedure appeared during the simulation. The HOMO and the LUMO levels shifted into the middle of the gap after excitation and even level crossing was observed. After that point the result obtained by MD simulation was uncertain and useless. It could cause incorrect conclusions. To avoid this problem we applied the following calculation method: we separately calculated the influences of electron and hole creation and annihilation.

Our systems were open only along the z-direction and periodic boundary conditions were applied in the other two directions. To measure the length (i.e. volume) of the sample we have proceeded in the following way. We have considered 40 atoms in z-direction closest to the either ends of the sample. But we neglected those 10–10 atoms at the ends of these clusters, which had the largest (smallest) z coordinated to avoid the surface effects. The length of the sample was defined as the average z coordinates of 30 rest atoms at the left end of the sample minus the average z coordinates of 30 rest atoms at the right end.

The total length of four samples with average density of 4.5 g/cm^3 is shown in Fig. 3. Arrows demonstrate the electron excitations and deexcitations. Only one excitation out of five caused volume decrease. The total influence is volume expansion. In the opposite process three out of five decrease, one increases the length. Final conclusion is that photo-induced volume expansion occurred during illumination and remained after finishing illumination. A typical atomic scale rearrangement after one photo-induced electron excitation is shown in Fig. 4.

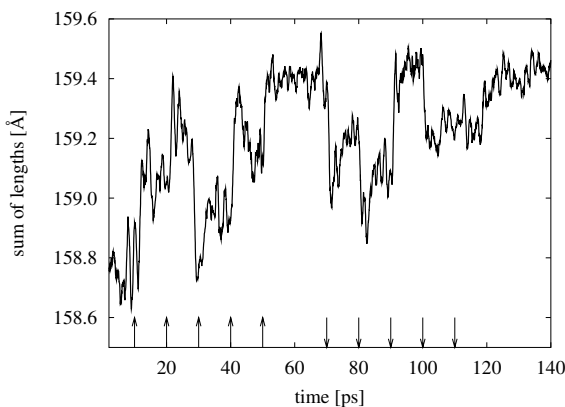More interesting is the number of coordination defects. Basically, selenium atoms have two nearest-
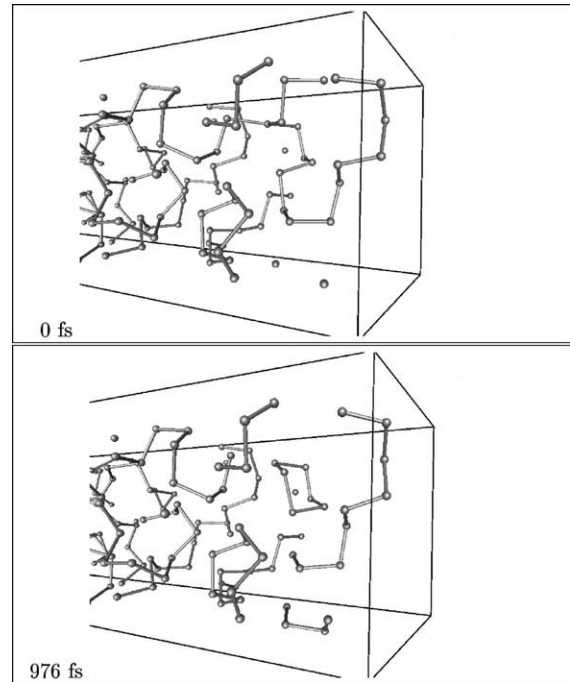

Fig. 4. Bond breakings and topological rearrangement inside the cluster due to illumination in a-Se.

neighbors. Average numbers of onefold-coordinated and threefold-coordinated atoms can be seen in Fig. 5. (Practically, the number of twofold coordinated atoms remained the same in our simulations.) During illumination the number of one-coordinated defects was increasing while it was opposite for threefold coordinated selenium atoms. During the deexcitation the inverse process occurred. It is striking that there are more threefold defects and less onefold coordinated atomic sites at the end of the simulation compared to initial configuration. All these observations suggest the atomistic explanation of volume changes in chalcogenide systems.
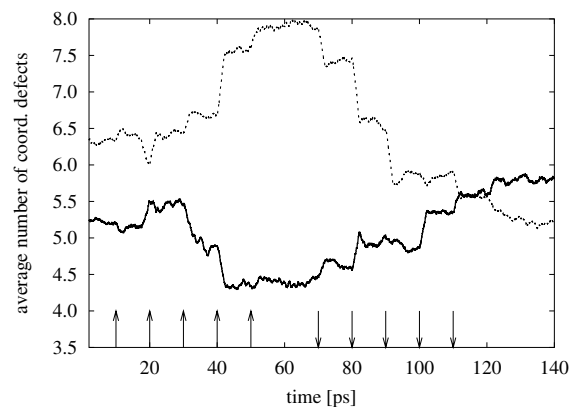

Fig. 3. Total length of four samples with average densities of 4.5 g/cm^3. The arrows represent the electron excitations (up arrow) and recombinations (down arrow) during the simulations.

Fig. 5. Average numbers vs. time of onefold coordinated (dashed line) and threefold-coordinated (solid line) atoms in 162 Se atom glassy networks.

5. Summary

We have developed a molecular dynamics computer code to investigate the time development of ring and chain-like structures after photo-excitation. Furthermore, we investigated the photo-induced volume change in glassy networks. Our results suggest photo-induced bond breaking and the change of the number in coordination defects in these conditions. This might be an explanation of photo-induced volume changes in a-Se and other chalcogenide glasses.

Acknowledgements

References

[1] K. Shimakawa, A. Kolobov, S.R. Elliott, Adv. Phys. 44 (1995) 475.
[2] K. Morigaki, Physics of Amorphous Semiconductors, World Scientific, 1999.
[3] H. Fritzsche, Solid State Commun. 99 (1996) 153.
[4] A.V. Kolobov, H. Oyanagi, V.V. Poborchii, K. Tanaka, Phys. Rev. B 59 (1999) 9035.
[5] X. Zhang, D.A. Drabold, Phys. Rev. Lett. 83 (1999) 5042.
[6] A. Ganjoo, Y. Ikeda, K. Shimakawa, J. Non-Cryst. Solids 266–269 (2000) 919.
[7] V. Palyok, I.A. Szabo, D.L. Beke, A. Kikineshi, Appl. Phys. A 74 (2002) 683.
[8] K. Kohary, S. Kugler, Phys. Rev. B 63 (2001) 193404;
K. Kohary, PhD thesis, Marburg-Budapest, 2001.
[9] D. Molina, E. Lomba, G. Kahl, Phys. Rev. B 60 (1999) 6372.
[10] E. Lomba, D. Molina, M. Alvarez, Phys. Rev. B 61 (2000) 9314.
[11] L. Goodwin, A.J. Skinner, D.G. Pettifor, Europhys. Lett. 9 (1989) 701.
[12] F. Shimojo, K. Hoshino, Y. Zempo, J. Phys.: Condens. Matter 10 (1998) L177.