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Invited Paper

LIGHT-INDUCED VOLUME CHANGES IN AMORPHOUS SELENIUM. MOLECULAR DYNAMICS SIMULATION; SAMPLE PREPARATION AND EXCITATION

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We investigated the photo-induced changes in chalcogenide (selenium) glasses by self-consistent tight-binding molecular dynamics simulations. Our aim was to prepare realistic glassy networks which mimic the real thin film structures. The samples, prepared by a 'cook and quench' method, were used in a systematic study of the response to light induced excitation. Light-excitation was modeled by transferring an electron from the HOMO to the LUMO state.

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1. Introduction

Photo-darkening and photo-expansion in chalcogenide glasses have recently attracted considerable interest, due to their scientific importance and potential applications [1]. Although amorphous selenium is considered as a model material for chalcogenide glasses, there are very few experimental studies of light-induced volume changes in the literature. Recently, Ikeda and Shimakawa published an *in-situ* measurement on a-Se [2]. Density functional theory computer simulations of this phenomenon have a drawback, in that studying photo-exciting phenomena consumes much computing power, so that only limited system sizes and simulation times are allowed for such calculations. This difficulty has recently been overcome by applying tight-binding (TB) models for selenium and other chalcogenide glasses [3-6]. We have developed a molecular dynamics (MD) computer code (the ATOMDEP program package) to simulate the real preparation procedures for amorphous structures. In recent works, the growth of amorphous carbon [7] and silicon [8,9] films were simulated by this TB-MD method. The computer code is convenient for investigating photo-induced volume changes.

In a recent TB-MD simulation [4], the local bonding topology of the glassy network was found to play an important role in the response to light excitation. Therefore, realistic glassy sample preparation should be an initial stage. We have developed a technique for this purpose.

2. Simulation details

2.1. Molecular dynamics method and atomic interaction

For integrating the Newton equations in the MD simulation, we used the well-known velocity Verlet algorithm. The time step was chosen as 2 fs, since we are interested in sample

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preparation at 20 K, where the atomic velocities are relative small. Shorter time steps must be applied at higher temperatures, i.e. 1 fs is usually used for the case of selenium at room temperature. The TB model which we applied is considered to be a realistic description for the glassy phase, since the obtained structure has about 90% two-fold coordinated atoms [5]. The first version of TB model used [4] had a problem in that the charge transfer was too high. That was why the two-fold coordinated atoms comprised only about 50% in the glassy phase. This problem was corrected by a Hubbard term [4,5,10], which punishes the system if charge transfer occurs. This term could be taken into account in a MD calculation via perturbation theory [5] or with a self-consistent field (SCF) method [3,10]. We chose the latter. The excitation-caused light could then be treated more transparently, and for a reasonable accuracy [0.01 electron/atom] only a few SCF and MD steps were needed. First, we constructed a tight-binding Hamiltonian, and then diagonalized it. After obtaining a solution, we added the Hubbard terms and recalculated the Hamiltonian matrix. The procedure was repeated until the necessary convergence was reached. The Hamiltonian matrix changed only slightly in one MD step, due to the small atomic movements. Therefore, we could use the eigenvectors from the previous MD step as the starting point in the self-consistency cycle. A convergence problem occurred when we tried to use the SCF method. The solution oscillated, and did not converge if the Hubbard parameter was the optimized value, 0.875 eV. To solve this issue we introduced a damping to the SCF cycles by linearly combining the new solution with the previous one. This method slowed down the convergence speed, but eliminated the oscillations as well.

2.2. Sample preparation

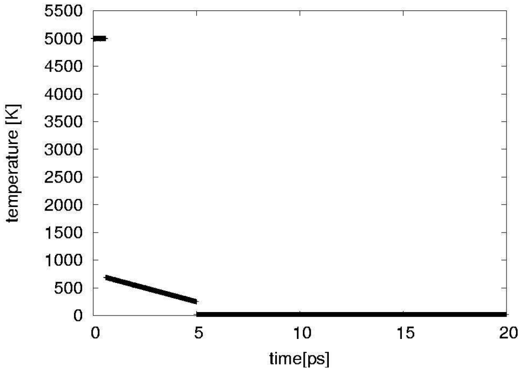

Fig. 1. Temperature as a function of time during the sample preparation.

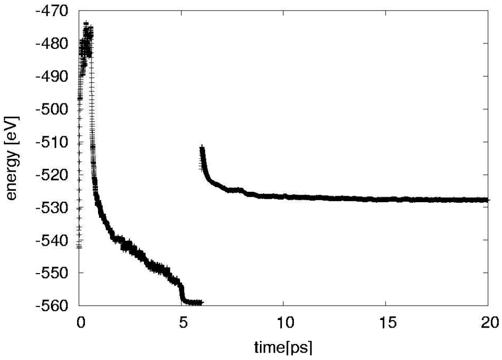

Fig. 2. A typical curve of the potential energy of the sample during preparation, vs. time.

To mimic real thin film structures, we fabricated rectangular parallelepiped shaped glassy networks, for which we applied periodic boundary conditions (PBC) in two dimensions [x,y]. The samples were open in the z direction. When we illuminate the cell, it could expand or shrink into the open direction. The volume changes of the sample could be derived by measuring the distance between atoms at the two open ends. Th initial simulation cell geometry was a rectangular box of size 12.78x12.96x29.69 (xyz in Å). The 162-atom sample had an initial density of 4.33 g/cm^3.

Our 'cook and quench' sample preparation procedure was as follows: first we set the temperature of the system to 5000 K for the first 300 MD steps. During the following 2200 MD steps, we decreased linearly the temperature from 700 K 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 relaxed the sample for 500 (1 ps) MD steps. The closed box was opened in the z-direction at the 3000th MD step. We thus obtained two surfaces, and the number of one-fold coordinated atoms and the potential energy increased. This final topology corresponded to a thin-film structure. This is why the temperature would also have increased if we did not rescale the velocities of the atoms. One problem still remained: the localised vibration modes at the surface were excited by the opening procedure. This caused an inhomogenity in the temperature distribution: the sample had higher temperatures at the ends. Therefore, we homogenously redistributed the atomic kinetic energies according to the Maxwell-Boltzmann distribution, to speed up the thermalization process. We did this three times at the 4000th, 6000th, and 7000th MD steps. The Hubbard parameter, U was also changed during quenching. By increasing U, one can expect a greater tendency to form a nearly fully two-fold coordinated structure, which is claimed to be the situation for selenium [5]. Therefore, we set the Hubbard parameter to be 5 eV during the quenching in the first 4000 MD steps. After the opening procedure, during the relaxation phase, at the 4000th MD step we restored U from 5 eV to 0.875 eV, which is the optimized value according to Lomba *et al.* [5]. This means that during the opening procedure we had a relatively high value of the Hubbard parameter. This helped to avoid coordination defects created by the opening of the sample. The system was relaxed for at total of 40,000 MD steps (80 ps), at 20 K. We used the velocity-rescaling method to keep the temperature at the desired value.

The preparation procedure can be better understood by examining Figs. 1-4. The initial structure was a bulk glassy selenium network. As in the first phase (0-0.6 ps) the temperature was set to 5000 K in the first MD step, the potential energy abruptly increased from -540 eV to -480 eV (Fig. 2). This means that the initial bonding topology was completely destroyed since at high temperature all the bonds break immediately. It can be seen in Fig 3. as well. The relative number of onefold coordinated atoms is about 40% during the first 0.6 picoseconds. The number of threefold coordinated atoms was 10%. At 0.6 picoseconds, where the temperature was set to about 700 K, this situation changes drastically, the percentage of one-fold and threefold coordinated atoms decreased to 20-25% and 1-2%, respectively. At this point the potential energy decreased by 60 eV within less than 0.1 ps. In the second phase (0.6-5 ps), as we reduced the temperature from 700 K to 250 K the number of one-fold coordinated atoms decreased simultaneously from 20% to 5% and number of threefold coordinated atoms did not change.

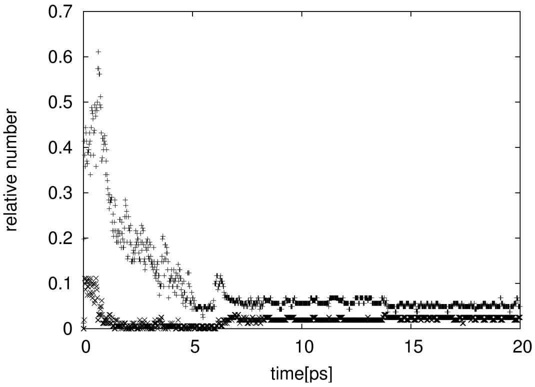

Fig. 3. Time development of the relative numbers of 3-fold (x) and 1-fold (+) coordinated atoms during sample preparation. Two atoms were considered to be bonded when their distance was less than 2.7 Å.

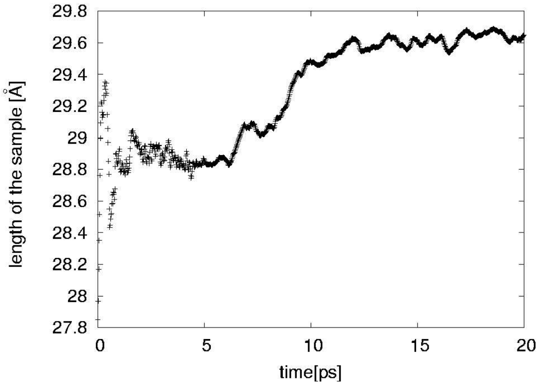

Fig. 4. Length of the sample during preparation.

The cooling rate during this phase was $9.7*10^{13}$ K/s. At 5 ps, another sudden 5 eV decrease can be observed in the potential energy (Fig. 2), the temperature was set from 250 K to 20 K. After this, the system was equilibrated for another 1 ps, and the network was opened by releasing the PBC in the z-direction. Examining the potential energy (Fig. 2), an immediate increase from -560 eV to -510 eV can be seen. This corresponds to breaking approximately 10-20 bonds at the surface. Subsequently, a quick recovery occured, involving about a 5-10 eV decrease in the potential energy in 0.5 picoseconds and then another 5-10 eV decrease on a longer time scale (10-100 picoseconds). The first corresponds to forming new bonds, as one sees in the change of coordination numbers (Fig. 3), while the second corresponds to a large scale structural change, i.e. volume expansion (Fig. 4.).

During last five picoseconds the sample became stable and the volume no longer changed significantly. If we only changed the initial velocities of the atoms during the first MD step we got completely different structures at the end of preparation. Therefore, this kind of sample preparation method allows us to fabricate topologically different glassy networks under the same physical conditions. For a 162 atom system, one SCF step on a 1200 MHz computer took about 2-3 seconds. The visualization of the structures and of the time development of the system was carried out by self-written Java software, JGLMOL which is freely available [11].

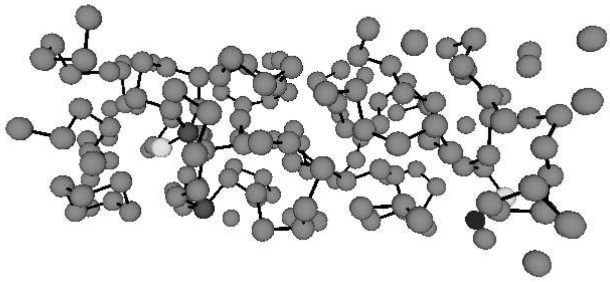

Fig. 5. Snapshot of a final glassy selenium network. The darker atoms mean 3-fold coordination, and the brighter ones 1-fold. The sample could expand in vertical direction, since at the left and right ends we did not apply periodic boundary conditions.

2.3. The prepared samples

Samples prepared at 20 K had densities from 3.95 to 4.19 g/cm^3. The number of coordination defects ranged from 3 to 12%. Most of these defects were located on the surfaces. The structure mainly consisted of branching chains, but some rings could also be found. The samples were accepted if the volume fluctuation was less than 0.5 % after 60 picoseconds. We prepared altogether 30 samples, and 17 were considered to be stable and useful for further studies.

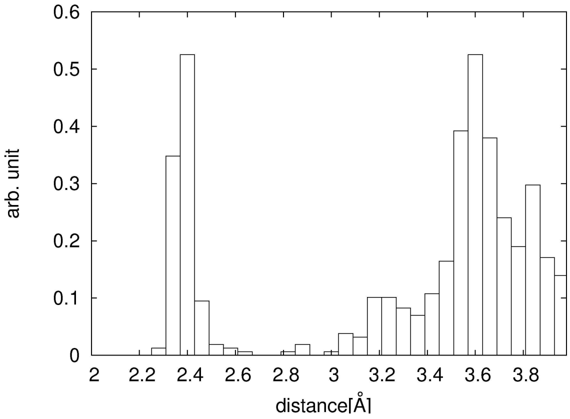

Fig. 6. Radial distribution function at 20 K.

The radial distribution function is displayed in Fig. 6. The first peak is located at 2.4 Å, which corresponds to the crystalline bond length. This value agrees with classical MD simulations [12] and RMC simulations, and is consistent to experiments [13]. Peaks at 3.6 and 3.9 Å correspond to the intrachain second-neighbour distances. (See the bond-angle distribution, where the bond angles range from 91^o to 108^o, Fig 7.). We examined the origin of this bond-angle distribution, since it is much broader than the results obtained by classical molecular dynamics simulation [12]. We concluded that atoms which have smaller bond angle than 100^o have about 15 % more atoms which are closer together than 3.4 Å. To correctly identify the length changes, we studied five different types of graph. In the case of every sample, we calculated the lengths by leaving out 10, 20, 30, 40 or 50 atoms at both open ends of the network. In this way, we were able to observe whether surface effects play a role in the expansion, and where the volume changes occurred. These graphs did not differ significantly during the sample preparation.

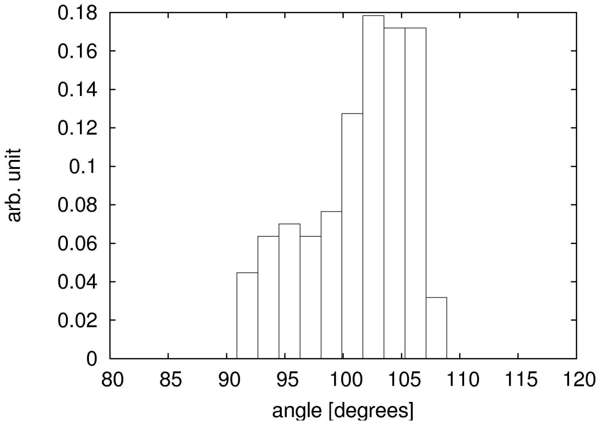

Fig. 7. Bond angle distribution function at 20 K.

3. Photo excitation of small Se clusters

When a photon is absorbed, an electron is transferred from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This is a simple model of photo-excitation, in which an electron is shifted from the valence band to the conduction band (electron-hole pair creation). In our earlier study [3], electron-hole pair recombination was also simulated by returning the electron from the conduction band to the valence band. Our results suggest photo-induced bond breaking and a change in the number of coordination defects under these conditions.

Next, we made a more detailed investigation. In order to study the influence of individual hole creation (annihilation) or individual electron creation (annihilation), we removed (put) an electron from the HOMO or we put (removed) an extra electron into the LUMO. We made two simultaneous series of simulations on 17 different samples. The total influences on the volume changes are shown in Fig. 8.

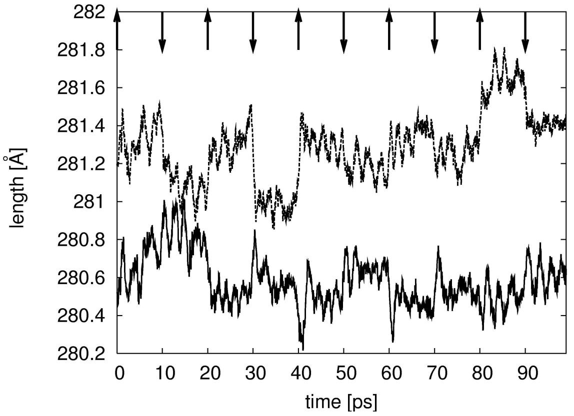

Fig. 8. Total lengths of samples during five excitations. Upper (bottom) curve belongs to the electron (hole) creation. Arrows pointing upwards (downwards) mean creation (annihilation).

The arrows demonstrate the electron (hole) excitations and de-excitations. The lifetime of the excitation was 10 ps. The results obtained are interesting: hole and electron creation caused opposite effects. A hole shrinks the sample while an electron expands it, but the total effect was that photo-induced volume expansion occurred during illumination and remained after termination of the illumination.

4. Conclusions

Tight-binding molecular dynamics simulations of photo-excitations in glassy Se networks (containing 162 atoms) were carried out in order to analyse the photo induced instability in amorphous selenium. The investigation of this effect needs correct sample preparation. It means that samples must be stable and less than 10 % coordination defects should be present. After examining 17 different clusters at a temperature of 20 K, we conclude that hole creation causes shrinkage, while electron creation has the opposite effect.

Acknowledgements

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