MOLECULAR DYNAMICS STRUCTURE SIMULATIONS OF AMORPHOUS SELENIUM PREPARED BY DIFFERENT METHODS

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Two different preparation methods, liquid-quenching and evaporation of amorphous selenium have been investigated by molecular dynamics simulations. We applied a classical empirical threebody potential of selenium to describe the interactions between atoms. Our particular aim was to determine how the structural changes occur due to the different preparation methods. Our simulation shows that a significant difference can be observed in the homogeneities.

1. Introduction

Basically, there are two different ways to produce non-crystalline materials: liquidquenching and evaporation. The quenched materials are usually named glasses and the amorphous forms are prepared from gas phase onto substrates. The principal advantage of rapid quenching compared to evaporation is that the method can provide large volume of samples. There might be differences in the physical properties of samples produced by different ways because these states are non-equilibrium states [1]. Our particular aim was to determine how the structural changes occur due to the different preparation methods. In order to obtain an answer for this question we performed molecular dynamics simulations.

Molecular dynamics (MD) needs a local potential to describe the interaction between atoms. Our atomic networks contained about 1000 selenium atoms interacting via classical empirical three-body potential [2]. The parametrization of this potential is based on fitting the structures of small Se clusters determined by DFT calculations and experimental data due to crystalline phase.

2. Computer simulation of preparations

We have developed a MD computer code (ATOMDEP program package) to simulate the real preparation procedure of disordered structures. Only a brief summary of our simulation technique is given here (for details, see Ref.4). A crystalline lattice cell containing 324 selenium atoms was employed to mimic the substrate. There were 108 fixed atoms at the bottom of the substrate. The remaining atoms could move with full dynamics. The simulation cell was open along the positive z direction and periodic boundary conditions were applied in x, y directions. Kinetic energy of the atoms in the substrate was rescaled at every MD step ($\Delta t = 1$ fs) in order to keep the substrate at a constant temperature. In this kind of simulation there is no *ad hoc* model for energy dissipation of incoming atoms.

In the deposition process the frequency of the atomic injection was 300 fs^{-1}. This ux is orders of magnitude larger than the deposition rate commonly applied in experiments but we compensate this disadvantage with a low substrate temperature. After bombarding (no more

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incoming atoms) there were 30 ps periods for structure relaxations in each case. During the bombardment and the relaxation procedure substrates remained similar to the crystal lattice arrangement. Three different structures have been constructed by the technique mentioned above at the temperature of 100 K. The average bombarding energies of Se0.1eV, Se1eV, and Se10eV models were 0.1 eV, 1 eV and 10 eV, respectively. A snapshot of a typical network can be seen in Fig. 1
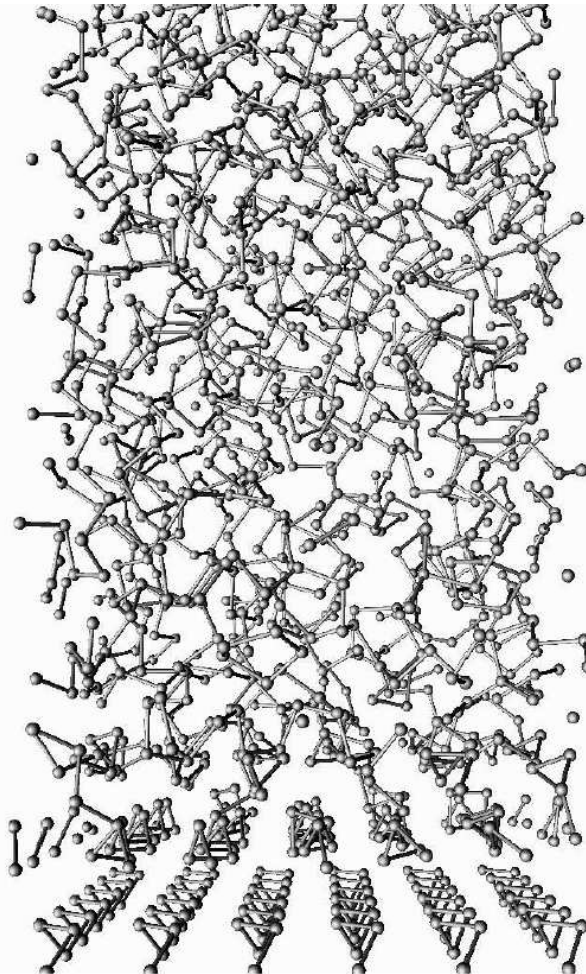

Fig. 1. Snapshot of the final amorphous structure grown with 1 eV bombarding energy at 100 K. There are 324 substrate atoms at the bottom of which 108 were held fixed to mimic the bulk crystal.

Rapid cooling of liquid phase is frequently applied to construct glassy structures. The system is usually cooled down to room temperature by a rate of 10^{11}-10^{16} K/s in computer simulations although this rate is some orders of magnitude smaller in the experimental techniques. In order to retrieve information on the rapid cooling, we prepared a model (SeQuench) in the following way. Temperature of a deposited film (Se1eV) was increased up to 900 K as an initial state (liquid phase), while the substrate temperature remained the same. After this melting, the trajectories of the selenium atoms were followed by full dynamics for 100 ps. The substrate temperature kept at 100 K leads to the cooling of the film above the substrate. This technique can be considered as the computer simulation of real splat cooling, where small droplets of melt are brought into contact with the chill-block.

3. Comparison of the structural properties

3.1. Radial distribution functions

The radial distribution function is one of the key properties used to characterize noncrystalline materials since it can be obtain through experimental and computer simulation ways. In order to ignore the effect of the rough surface on the top of the grown film we identified two different cells: bulk and total sample. The top side position of the bulk was by 5 Å below the atom having the largest z coordinate and bulk does not contains substrate atoms at the bottom. The average bond length in our a-Se models is 2:37 ± 0:004 Å. We considered 2.8 Å as an upper limit of bond length. A detailed analysis shows that the average distance between twofold coordinated _rst-neighbor selenium atoms (Se2-Se2) is equal to 2.35 Å, while in case of Se2-Se3 and Se3-Se3 those values are 2.41 Å and 2.47 Å, respectively.

In Fig. 2 radial distribution function of our Se1eV model is shown along with the corresponding partial inter- and intra-chain radial distribution functions. All the other models provide similar radial distribution functions. First and second neighbor peak positions are similar to trigonal crystalline case but peaks are broadened because of torsion inside the chains. There is a characteristic inter-chain distance in α crystalline phase at 3.43 Å which is completely disappeared from the radial distribution function. Note that the second peak is composed from inter- and intra-chain contributions.
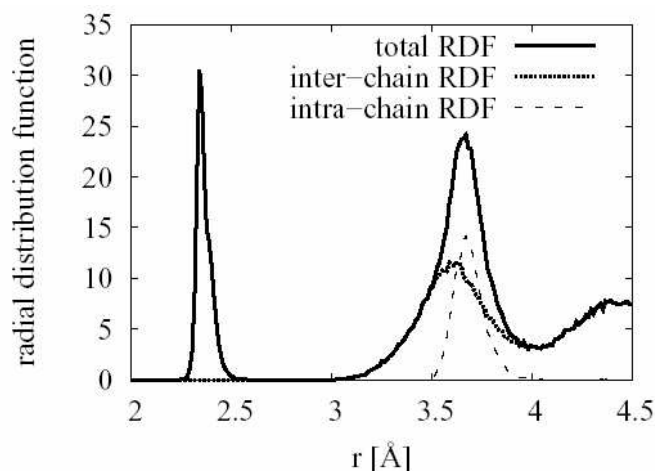

Fig. 2. Radial distibution function of the representative Se1eV model is displayed with the corresponding partial inter-chain and intra-chain radial distribution functions. Note that the second neighbour peak is partly due to the large number of inter-chain distances.

The average coordination number in a-Se is sligthly higher than two as can be seen in Table 1.

There is no fourfold coordinated selenium atom but we found threefold coordinated atoms (defects) in every models. In quenched sample (SeQ) 8 % of Se atoms were threefold coordinated while in the deposited samples this ratio is higher.

Table 1. Name of the model, number of bulk and total atoms, avarage bond length, number of atoms with different coordination numbers (Z) and bulk density are shown in this table.

Name	Bulk atoms	Total atoms	Se – Se	Z = 1	Z = 2	Z = 3	Z = 4	Density [g/cm^3]
Se0.1eV	509	954	2.37	2	432	75	0	3.21
Se1eV	584	1016	2.37	1	516	67	0	3.73
Se10eV	373	822	2.37	1	332	40	0	4.34
SeQ	676	1118	2.37	0	622	54	0	3.95

3.2. Density

The structures of different models consist almost of the same number of atoms. For realistic density calculations one should consider only bulk densities. Table I contains the densities of different models which are between 3.21 g/cm3 and 4.34 g/cm3. For crystalline α, β, and metallic selenium the densities are equal to 4.4 g/cm3, 4.35 g/cm3 and 4.8 g/cm3 which are larger than the values we obtained for a-Se, i.e. our molecular dynamics simulation provided lower dense structures. In order to investigate the homogeneity we divided the structures prepared by deposition and by rapid quenching into $\Delta z=5$ Å thick layers. A significant difference was observed in the local density uctuation of two models. In Fig. 3 the number of atoms in five different layers in both models are displayed in function of time.
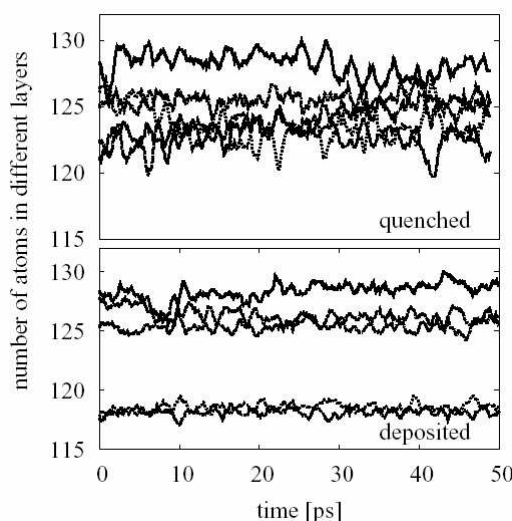

Fig. 3. Time development of number of atoms in five $\Delta z = 5$ Å thick layers in samples prepared by rapid quenching (top panel) and deposition (bottom panel). We conclude that large and stable voids are present in the deposited sample.

It can be concluded that sample prepared by rapid quenching is more homogeneous than the deposited counterpart. This is an observable difference we obtained for two different preparation techniques.

3.3. Comparison with experimentally determined bond angles and bond lengths

To compare the local arrengements obtained by molecular dynamics simulations to experiments we have additionally analysed the structure of molecules containing -Se-Se- and -Se-Se-Se- fragments. This systematic analysis of structural data has been carried out using the Cambridge Structural Database (CSD) [6], which is the world's largest database of experimentally determined crystal structures containing the results of X-ray and neutron diffraction studies. CSD is designed as a critically evaluated numerical resource, containing three-dimensional atomic coordinates.

In Fig. 4 the bond length distributions in the simulated Str1eV model and the corresponding distribution of 551 molecules containing -Se-Se- bonds are compared. The shape of the two curves are surprisingly similar, however the experimentally determined bond lengths are shifted to lower values with 0.1 Å compared to values obtained from the Se1eV model.
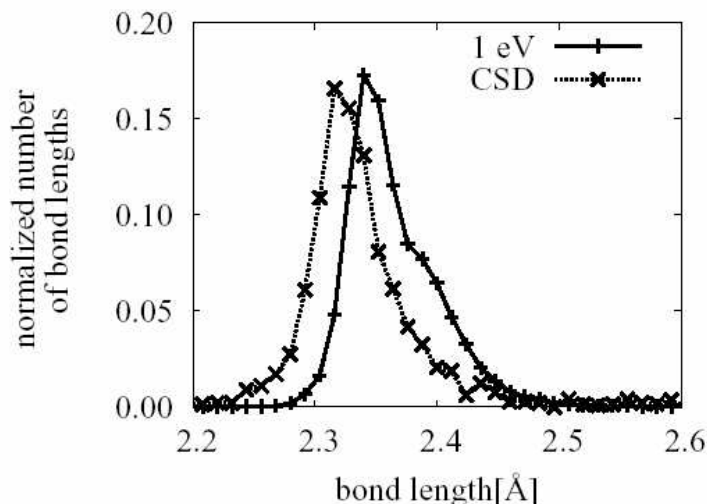
Fig. 4. Differences between the bond length distribution in the simulated Str1eV model and
the corresponding distribution obtained using 551 different molecular structures
which contained {Se{Se{ bonds.

To analyse bond angles we investigated molecules containing –Se-Se-Se- fragments, we
have found an interesting correlation in the experimental data: larger bond angles correspond to
smaller bond lengths on avarage. This can be seen in Fig. 5. Each point represents a measured bond
angle as a function of bond length. The majority of the points fall in the expected region, i.e. around
2.35 Å and 102°. The minimum bond length is 2.09 Å while the maximum is 2.58 Å. The bond
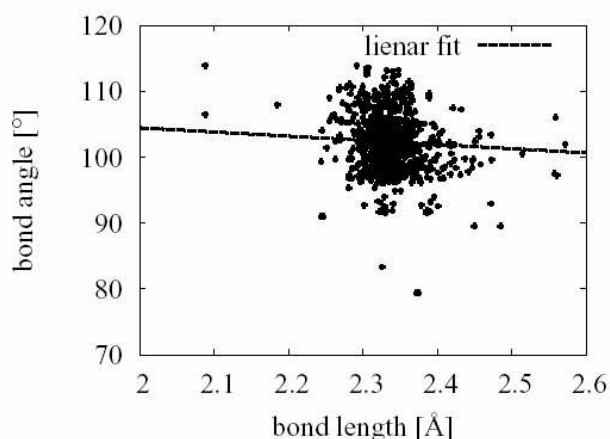angles lie inside the interval 79-114°.

Fig. 5. Bond lengths and bond angles of –Se-Se-Se- fragments in molecules whose structure
was determined by diffraction measurements (CSD). Bond angles depend on
bond lengths: larger bond lengths tend to reduce corresponding bond angles.

A histogram of calculated bond angles in one of our model along with the corresponding
histogram obtained using the CSD is displayed in the Fig. 6. The main contribution to the bond
angle distribution arises from angles between 95° and 110° in our model which is in a very good
agreement with the experimental histogram. In α selenium the bond angle is 103:1° which is larger
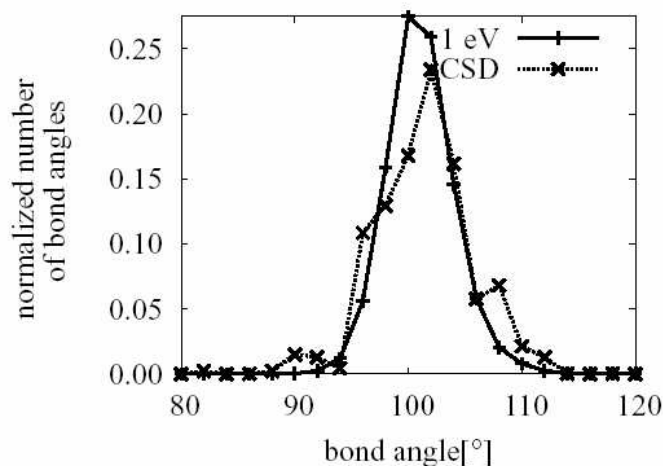than the average value in our simulations (102:1°).

Fig. 6. Comparison of distributon of bond angles in a simulated model (Str1eV) and in molecules containing –Se-Se-Se- fragments found in the Cambridge Structural Database (CSD).

4. Summary

We have developed a molecular dynamics computer code to simulate the preparation procedure of a-Se networks. We have grown three models by a vapor deposition technique and additionnally prepared one model with simulated rapid cooling. This enabled us to to make a direct comparison between the atom-by-atom deposition and melt-quenching preparation techniques. The most important difference we have found between the models prepared at various conditions, was in the local density. Rapid quenched models were more homogeneous than their deposited counterparts. Furthermore, we observed an increase in bulk density due to higher bombarding energies in the deposited models. Bond angles and bond lengths were compered with experimentally determined values obtained using the Cambridge Structural Database, the world's largest database of experimentally determined crystal structures. Bond lengths were larger in the simulated models compared to experimental values, however, bond angle distributions were in perfect agreement with diffraction data.

References

[1] K. Morigaki, Physics of Amorphous Semiconductors, World Scienti_c Publishing Co. 1999.
[2] C. Oligschleger, R. O. Jones, S. M. Reimann, H. R. Schober, Phys. Rev. B **32**, 1340, (1986).
[3] S. Kugler, L. Pusztai, L. Rosta, P. Chieux, R. Bellissent, Phys. Rev. B **48** 7685 (1993).
[4] K. Kohary, S. Kugler, Phys. Rev. B **63**, 193404, (2001).
[5] P. Jovari, R. G. Delplane, L. Pusztai, Phys. Rev. B **67**, 172201, (2003).
[6] F. H. Allen, O. Kennard, R. Taylor 1983 Accts chem. Res. 16 146.