Comparative analysis of different preparation methods of chalcogenide glasses: molecular dynamics structure simulations

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Abstract

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

Chalcogenide glasses have been the subject of numerous experimental works in recent decades. Basically, there are two different ways to produce samples for experiments; liquid-quenching and evaporation. In the first case the initial phase of raw materials is liquid while in the latter case the starting compound is vaporized. Usually, the quenched materials are 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 may 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. Our atomic networks contained about 1000 selenium atoms interacting via classical empirical three-body potential [2]. Non-crystalline selenium has received particular attention since it is the model material of twofold coordinated covalently bounded chalcogenide glasses.

2. Simulation details

There are two main possibilities for structural modeling on the atomic scale. The first is Monte Carlo (MC) type methods. Traditional MC using a potential minimizes the total energy in an energy hyper-surface. Recently a new version of this method – the so-called reverse Monte Carlo (RMC) simulation – was developed which is also convenient for the investigation of amorphous materials. It is based on results of diffraction measurements. This method was applied for constructing large scale a-Si and a-Se models [3,4]. The second method, molecular dynamics (MD) also needs a local potential to describe the interaction between atoms. We have developed a MD computer code (ATOMDEP program package) to simulate the real preparation procedure of disordered structures.

2.1. Computer simulation of preparations

Amorphous and glassy structures are usually grown by different vapor depositions on substrates. In our recent MD work [5], the growth of amorphous carbon films was simulated by this method. Only a brief summary of our simulation technique is given here (for details, see Ref. [5]). A crystalline lattice cell containing 324 selenium atoms was employed to mimic the substrate. There were 108 fixed atoms at the bottom of the

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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 and 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 flux 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 incoming atoms) there were 30 ps periods for structure relaxations in each case. Three different structures [SeStr] have been constructed by the technique mentioned above at the temperature of 100 K. The average bombarding energies of SeStr0.1, SeStr1, and SeStr10 models were 0.1, 1 and 10 eV, respectively.

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 (melt-quench), we prepared a model (SeStrQ) in the following way. Temperature of a deposited film (SeStr1) 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.

2.2. The applied potential

Pair potentials cannot be used for covalently bonded structures because these types of potentials cannot handle the bond angles. We need at least three body interactions. For our simulation we applied a 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.

3. Structural properties

3.1. Pair correlation and bond angle distribution functions

There are several different crystalline forms of selenium. Basically, they consist of chains and eight-membered rings. Typical bond lengths are around 2.35 Å

while most of the bond angle values can be found around 103°. Snapshot of the amorphous SeStr1 network (bottom half part) is shown in Fig. 1. We considered 2.8 Å as an upper limit of bond length. Substrates remained similar to the crystal lattice arrangement during the bombardment and the relaxation procedure. The average bond length in our a-Se models is 2.37 ± 0.004 Å. A detailed analysis shows that the average distance between twofold coordinated first-neighbor selenium atoms (Se^2–Se^2) is equal to 2.35 Å, while in case of Se^2–Se^3 and Se^3–Se^3 those values are 2.41 and 2.47 Å, respectively (see Table 1). 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 (see Ref. [5]). 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. In Fig. 2 pair correlation functions of our SeStr1 model and an unconstrained RMC simulation [4] based on experimental data are shown in the interval of 1–5 Å. 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 pair correlation function.

A histogram of calculated bond angles in our model is displayed in Fig. 3. The main contribution to the bond
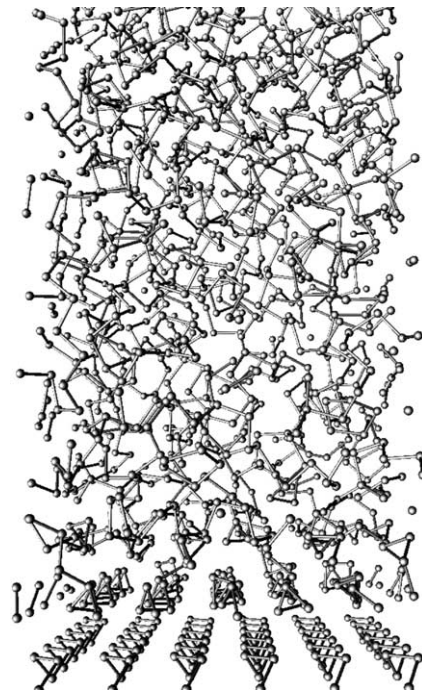

Fig. 1. A snapshot of the SeStr1 model in the interval of $z = 0$–20 Å. Substrates remained similar to the crystal lattice arrangement during the bombarding.

Table 1
Average and detailed bond lengths (Å) and densities (g/cm^3) of different models

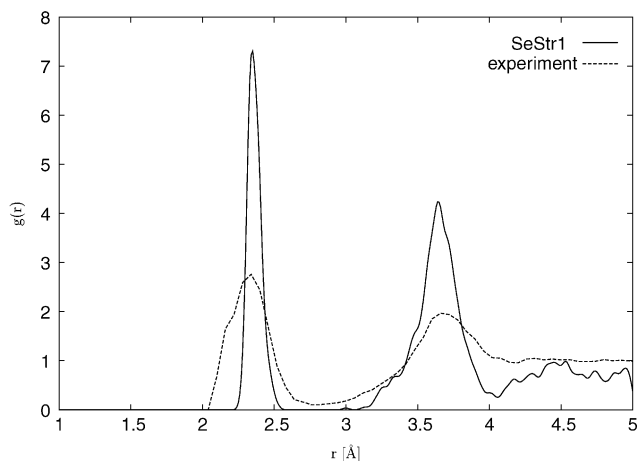| Name	Bulk atoms	Total atoms	Se–Se	Se^3–Se^2	Se^3–Se^3	Se^2–Se^2	Density
SeStr0.1	509	954	2.37	2.41	2.48	2.35	3.21
SeStr1	584	1016	2.37	2.41	2.47	2.35	3.73
SeStr10	373	822	2.37	2.41	2.46	2.35	4.34
SeStrQ	676	1118	2.37	2.41	2.49	2.35	3.95

Fig. 2. Pair correlation functions of our SeStr1 model and of a model constructed by unconstrained RMC simulation [4] (experiments) are shown in the interval of 1–5 Å.
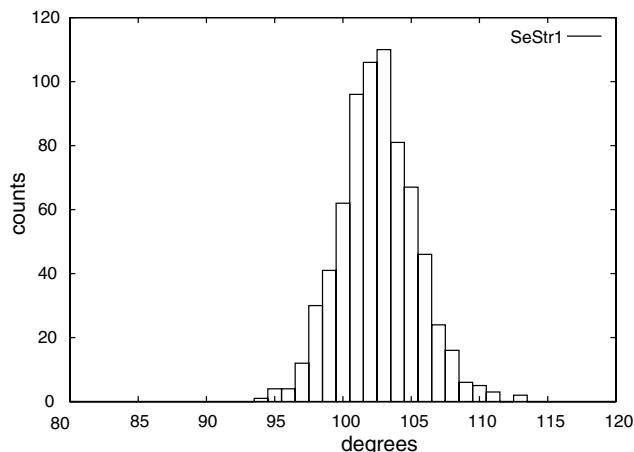

Fig. 3. Histogram of calculated bond angles. The main contribution to the bond angle distribution arises from angles between 95° and 110°. The average value in our simulation is 102.1°.

angle distribution arises from angles between 95° and 110°. In α-selenium the bond angle is 103.1° which is larger than the average value in our simulations (102.1°). Considering the local arrangements we can not distinguish between deposited and quenched models. The average coordination number in a-Se is approximately two as shown in Table 2. There is no fourfold coordinated selenium atom but we found threefold coordinated atoms (defects) in every models. In quenched sample (SeStrQ) 8% of Se atoms were threefold coordinated while in the deposited samples this ratio is higher.

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 1 contains these densities of different models which are between 3.21 and 4.34 g/cm^3. For crystalline α, β and

metallic selenium the densities are equal to 4.4, 4.35 and 4.8 g/cm^3 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 fluctuation of two models. In Fig. 4 five layer densities of both models are displayed as a function of time. 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.

4. Summary

We have developed a molecular dynamics computer code to simulate the preparation procedure of a-Se networks, which are grown by a vapor deposition

Table 2
Bond angles (°) and coordination numbers calculated inside bulks

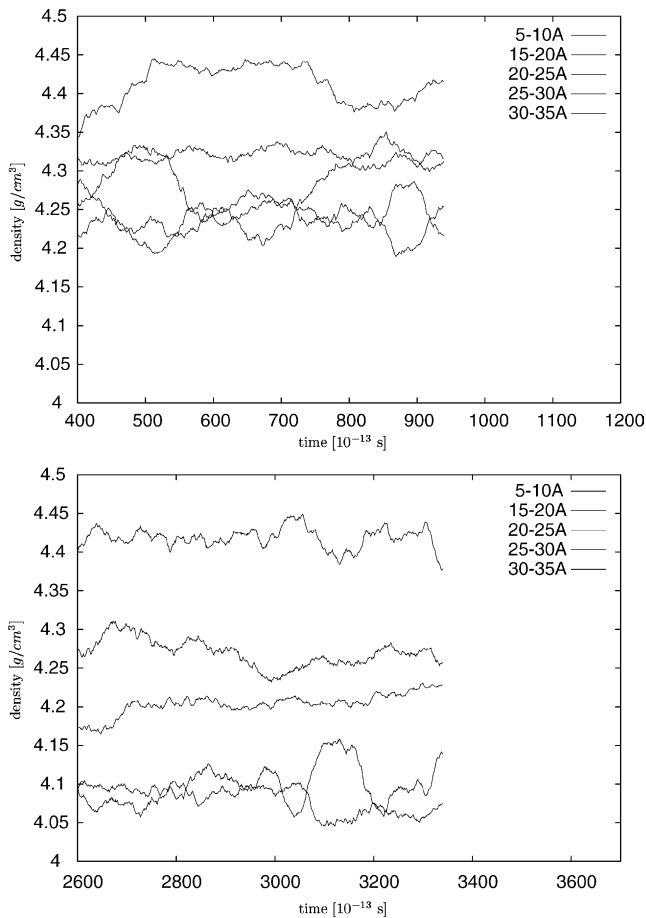| Name	Se–Se^3–Se	Se–Se^2–Se	Se–Se–Se	$Z = 1$	$Z = 2$	$Z = 3$	$Z = 4$
SeStr0.1	100.9	102.69	102.08	2	432	75	0
SeStr1	100.97	102.68	102.2	1	516	67	0
SeStr10	101.08	102.68	102.25	1	332	40	0
SeStrQ	100.93	102.39	102.09	0	622	54	0

Fig. 4. Density developments of five $\Delta z = 5$ Å thick layers prepared by rapid quenching (top panel) and deposition (bottom panel). A significant difference was observed in the local density fluctuations of the two models.

technique and prepared by rapid cooling in order to make a comparison between the atom-by-atom deposition on a substrate and the melt-quenching preparation techniques. The most important difference we have found between the models prepared at various conditions, is in local density. Bond length and bond angle distributions are very similar in both cases.

Acknowledgements

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