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Photoinduced volume changes in obliquely deposited a-Se

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The structures and the photoinduced volume changes of obliquely deposited amorphous selenium were studied using Molecular Dynamics computer simulation. Obliquely deposited a-Se thin films contain larger voids than the flatly deposited ones. Our computer simulations confirmed that the preparation method strongly determines the photoinduced changes of the chalcogenide glasses. We described in detail for the first time the complex atomic rearrangements occurring on photoexcitation in porous samples, which are reversible and irreversible photo contraction/expansion, bond breakings and formations (both inter- and intrachain). A model for the kinetics of the photoinduced volume changes of flatly and obliquely deposited chalcogenide thin films is presented.

1 Introduction

Chalcogenide glasses are truly remarkable materials as they show a plenty of exploitable physical properties and phenomena. One of the most interesting properties is that they are sensitive to band gap light illumination causing a variety of photoinduced changes like volume change, photo-crystallisation and amorphisation, photo darkening etc. [1-3]. From several experiments [4-6] we can conclude that obliquely deposited chalcogenide thin films show more enhanced photoinduced changes during band gap light illumination. Obliquely deposited chalcogenides present also giant photo contraction [7].

Recently Ikeda and Shimakawa published their experimental results on photoinduced volume changes due to flatly and obliquely deposited *a*-As_2Se_3 films [8]. Primary conclusion was that the flatly deposited sample showed photoinduced volume expansion, while the other shrank during the illumination. After switching off light the volume remained the same at the second case. In order to understand these controversial results we carried out atomic scale MD computer simulations to study the atomic arrangement and the photoinduced volume changes of flatly and obliquely deposited *a*-Se thin films. As well-known the model material of chalcogenide glasses is the amorphous selenium.

Flatly deposited amorphous chalcogenide glasses had been already studied by Hegedüs et al. [9]. The simulation methods and the obtained structures of obliquely deposited *a*-Se thin films are discussed in the second section. In the following section models for the kinetics of the photoinduced volume changes in flatly and obliquely deposited chalcogenide thin films are presented.

2 Obliquely deposited thin films

2.1 Structure

As a first stage a set of our Molecular Dynamics (MD) computer code was ran to grow amorphous samples in different angles of depositions. A classical empirical three-body potential was applied to calculate the atomic interactions [10]. The simulation technique is described in details in Ref. [11]. Several samples were prepared with average angles between the normal to the substrate and the direction of the randomly directed incidence atoms of 0°, 20°, 45°, and 60°. In order to find the differences between the films structure the radial distribution functions, the densities, and the coordination number distributions were calculated. On base of radial distribution functions we did not distinguish among thin film structures. The first neighbor peaks appeared at 2.35 Å, while the second neighbor ones were at 3.5 Å. The coordination number distributions of different samples were analyzed next. About 90% of the atoms had coordination number of 2. The remaining atoms had coordination number of 1, and 3. The number of these coordination defects increased by 3% if the average angle of incidence was varied from 0° to 60°.

Increasing the deposition angle in the interval of 0°–60° the density of thin films decreased monotonically, as it is displayed in Table 1.

Table 1 Densities of amorphous selenium thin films.

Angle of deposition (°)	0	20	45	60
Density (*g/cm*^{3})	4.50	4.40	4.38	4.20

This correlation suggests that the structure of obliquely deposited films is more porous because larger voids could be found inside the atomic structures. To confirm this supposition, a void size analysis of the samples has been performed using the Voronoi–Delaunay approach [13]. Voids with larger volume than 6 Å^3 were found in the obliquely deposited thin films as it is presented in Fig. 1.

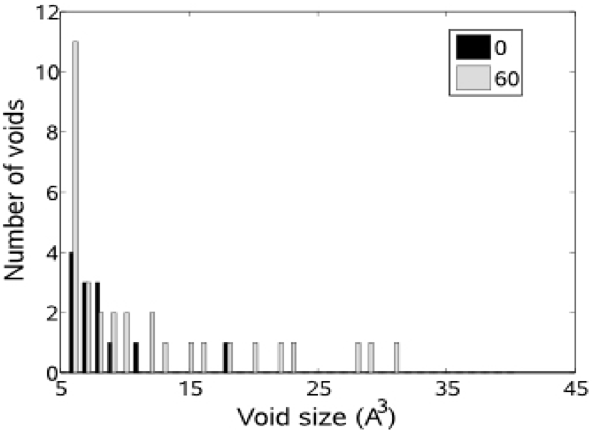

Figure 1 Distribution of large voids of two different samples.

These results confirm that the preparation method strongly determines the structure of the glasses.

2.2 Photoinduced volume change

Does the difference between structures lead to distinct photoinduced changes in the amorphous selenium thin films? To study the photoinduced structural changes in these amorphous samples further MD simulations were ran using a TB model Hamiltonian [14]. This TBMD computer code was developed by Hegedüs et al. [9, 15]. It was assumed that immediately after the photon absorption the electron and the hole become separated in space on a femtosecond timescale [16]. Therefore excited electrons and created holes were treated independently. Two different types of simulation methods were carried out: one to model the excited electron creation with placing an extra electron into the lowest unoccupied molecular orbital (LUMO). A second one to simulate the hole creation by removing an electron from the highest occupied molecular orbital (HOMO). In this approach excitons do not play any role during the photoinduced volume changes and the Coulomb interactions between electrons and holes were also neglected. To mimic voids our simulations were carried out on *a*-Se samples which contained two large ellipsoid voids. The sample preparation is presented in details in Ref. 12. The height (thickness) of the films in the *z* direction was analysed.

Similar to the flatly deposited *a*-Se thin films a part of the obliquely deposited thin films showed photo expansion as a result of a covalent bond breaking presented in Fig. 2 and photo contraction due to interchain bond formation [9]. Besides these photoinduced changes multiple reversible and irreversible "exotic" cases were obtained.

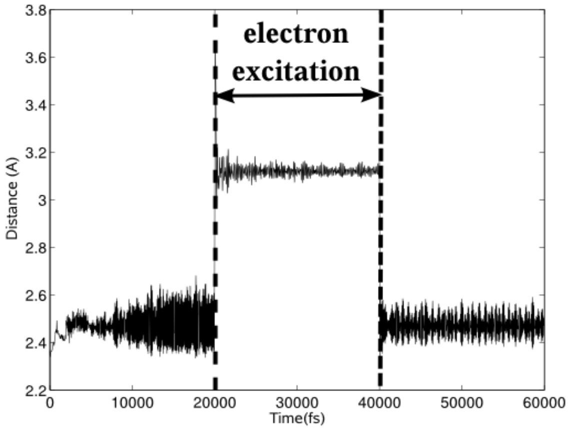

Figure 2 Electron excitation induced reversible covalent bond breaking.

Analysing on microscopic level these *a*-Se samples a lot of irreversible and reversible covalent bond breakings and formations were observed. On atomic level in the sample showing reversible photo contraction we found reversible covalent bond breaking on the surface of a void which collapsed during electron creation.

For example as a result of an electron excitation an irreversible photo contraction caused by an irreversible covalent bond breaking has been observed (Fig. 3).

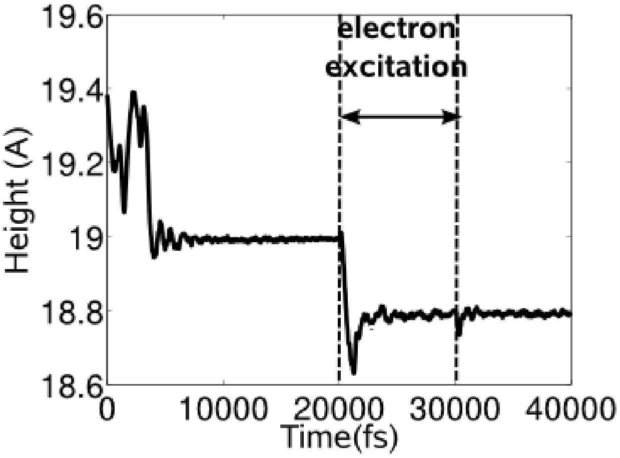

Figure 3 Electron excitation caused macroscopic irreversible photo contraction.

Under the hole creation process irreversible photo contraction was found as a result of irreversible covalent bond formation. As a result of the hole creation on macroscopic level reversible and irreversible photo contractions were also found. On microscopic scale mostly irreversible and reversible interchain bond formations and creations were found. Surprisingly in these void containing samples appeared covalent bond creations and formations too causing ring development, bond alternations [17], and chain slips.

From these MD simulations can be concluded that due to the presence of voids the *a*-Se samples on macroscopic level show diverse photo induced volume changes. Complex structural changes could be witnessed on the microscopic level as the results of covalent and interchain bond breakings and formations.

3 Macroscopic models. Kinetics of volume changes

3.1 Ideal, reversible case (a-Se)

Our model of light induced volume expansion in pure amorphous selenium has been already published [18]. The expansion in thickness d_e is proportional to the number of excited electrons n_e ($d_e = \beta_e n_e$), while the shrinkage d_h is proportional to the number of created holes n_h ($d_h = \beta_h n_h$), The parameter β_e (β_h) is the average thickness change caused by an excited electron (hole). Assuming $n_e(t) = n_h(t) = n(t)$ ($n_e(t)$, and $n_h(t)$ are sums of stepwise functions) the macroscopic time dependent thickness change is equal to $\Delta(t) = (\beta_e - \beta_h)\, n(t) = \beta_\Delta n(t)$. The number of electrons excited and holes created is proportional to the time during illumination. A rate equation for this process can be written as follows

$$dn_e/dt = G - C\, n_e(t)\, n_h(t), \qquad (1)$$

where G and C are the time independent generation rate and the recombination rate, respectively. Using $\Delta(t) = \beta\Delta\ n(t)$, we obtain an equation for the time dependent volume change, namely

$$d\Delta(t)/dt = G\,\beta_\Delta - (C/\beta_\Delta)\,\Delta^2(t). \qquad (2)$$

The solution of this nonlinear differential equation is given by (using: $G' = G\,\beta_\Delta$; $C' = C/\beta_\Delta$)

$$\Delta(t) = (G'/C')^{1/2} \tanh((G'C')^{1/2}\, t). \qquad (3)$$

In the steady state case $(t = \infty)$ $\Delta(t = \infty) = (G'/C')^{1/2} = a$, where a is a measurable value. After the light is turned off Eq. (3) reduces to ($G = 0$)

$$d\Delta(t)/dt = -C'\,\Delta^2(t) \qquad (4)$$

with the solution

$$\Delta(t) = a / (a\, C'\, t + 1). \qquad (5)$$

We have only one fitting parameter (only C' because $G'/C' = a^2$) and two different curves to fit using this parameter!

3.2 Non-ideal, irreversible (metastable) case (a-As$_2$Se$_3$)

In the ideal case we assumed that each original local structure was reconstructed after the electron-hole recombination. However, the result of a measured volume change on flatly deposited a-As$_2$Se$_3$ film is quite different from the ideal a-Se network. To explain the difference we must take into account a large number of irreversible (metastable) changes in the local atomic arrangement i.e. after turning off the light a part of local configuration remains the same. The total volume change includes both the reversible (transient) and irreversible (metastable) changes and it can be written as:

$$\Delta_{total}(t) = \Delta_{rev}(t) + \Delta_{irr}(t). \qquad (6)$$

The reversible part follows Eqs. (3) and (5) during and after the illumination, respectively.

Let us consider the irreversible component. During illumination, the generation rate of irreversible microscopic change is time dependent. An upper limit exists for the maximum number of electrons and holes causing irreversible changes and denoted by $n_{e,irr,max}$ and $n_{h,irr,max}$. To simplify the derivation let us assume that $n_{e,irr,max} = n_{h,irr,max}$. In this approach one can write the electron generation rate as:

$$G_e(t) = G_{e,irr}\,(n_{e,irr,max} - n_e(t)). \qquad (7)$$

Note that there is no recombination term in Eq. (7). The irreversible expansion is governed by:

$$d\Delta_{irr}(t)/dt = G_{irr} - C_{irr}\Delta(t)\ . \tag{8}$$

Equation (11) then leads to the solution:

$$\Delta_{irr}(t) = (G_{irr}/C_{irr})\ (1 - \exp\{-C_{irr}\, t\})\ . \tag{9}$$

Again, at steady state case ($t = \infty$) we get $\Delta(t = \infty) = (G_{irr}/C_{irr}) = b$ and b is a measurable value. Now we have only two fitting parameters (a and b)! After illumination there is no volume change caused by the irreversible microscopic effects.

This model is a good explanation of a measured volume change on flatly deposited a-As_2Se_3 but the result of obliquely deposited film is seems to be quite different from that where volume shrinkage was observed. This is not so! Obliquely deposited films contain large number of voids and these structural defects cause shrinkage during light illumination. If we consider that most of these processes are irreversible (metastable) i.e. the sign of (G_{irr}/C_{irr}) in Eq. (9) is negative (shrinkage) we get again an excellent fit the measured data as it is displayed in Fig. 4.

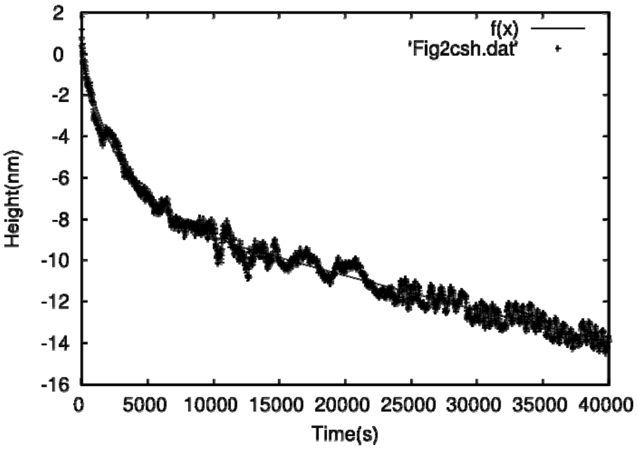

Figure 4 Electron excitation caused macroscopic irreversible photo contraction. Solid line is the best fit to the experimental data (symbols).

4 Conclusions

Using Molecular Dynamics computer simulation the structures and the photoinduced volume changes of obliquely deposited amorphous selenium were studied. We obtained that the obliquely deposited a-Se thin films contain larger voids than the flatly deposited ones. Our computer simulations confirmed that the preparation method strongly determines the photoinduced changes of the chalcogenide glasses. We proposed an explanation of photo-induced volume changes in different chalcogenide glasses. Our comprehensive microscopic explanation of the photo-induced volume change is in an excellent agreement with the first in situ surface height measurements in a-Se and a-As_2Se_3 [8].

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