

On photoinduced volume changes in chalcogenide glasses

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We proposed a new explanation of photo-induced volume changes in chalcogenide glasses. In our computer simulation we observed covalent bond breaking in the network caused by excited electrons, whereas holes contribute to the formation of inter-chain bonds. The interplay between photo-induced bond breaking and inter-chain bond formation leads to either volume expansion or shrinkage. In the non-ideal case, only a part of the processes is reversible and the total expansion includes the reversible and irreversible changes. Finally we investigate the structural properties of flatly and obliquely deposited chalcogenide thin films. Different void sizes can cause different photoinduced volume changes.

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1. Motivation

Chalcogenide glasses exhibit various changes in the structural and electronic properties during bandgap illumination, like photo-induced volume changes, photodarkening, and photo-induced changes in the phase state [1]. These phenomena do not occur in the crystalline chalcogenides, nor in any other amorphous semiconductors. A size effect can be observed: photodarkening cannot be induced in As_2S_3 films which are thinner than 50 nm [2]. The microscopic structural changes are facilitated by two factors common to chalcogenide glasses: the low average coordination number and the structural freedom of the non-crystalline state. During the illumination, some of the films can expand (a-Se, a- As_2S_3 , a- As_2Se_3 , etc.), while the other sets of glasses shrink (a- GeSe_2 , a- GeSe_2 , etc.) [3-4].

Recently, real-time *in situ* measurements of photo-induced volume changes in chalcogenide glasses were carried out by Ikeda and Shimakawa [5]. They recorded *in situ* variation of the surface height during illumination in a-Se, a- As_2Se_3 , a- As_2S_3 and a- GeSe_2 thin films. A group of films was deposited with an angle of 80° between the normal to the substrate and the direction of the incidence of the evaporated atoms, these are called obliquely deposited samples. Another group was deposited at normal incidence to the substrate, these are flatly deposited ones. During illumination, they observed a volume expansion in flatly deposited films and a volume contraction in the obliquely deposited case. Our main goal in this paper is to provide a possible explanation of these different effects.

2. Computer simulation background

In our Molecular Dynamics [MD] simulation on a-Se [6, 7], we assumed that immediately after a photon

absorption the electron and the hole become separated in space on a femtosecond time scale [8]. This effect is applied in copy machines, where the cylinder is made from selenium. Therefore, excited electrons and created holes can be treated independently. We ran two sets of simulations: first, to model the excited electron creation, we put an extra electron into the LUMO (Lowest Unoccupied Molecular Orbital), and second, we annihilated an electron in the Highest Occupied Molecular Orbital, HOMO (hole creation). We neglect the Coulomb interaction between electrons and holes. In our approach, excitons do not play any role during the photoinduced volume changes.

2.1. Electron excitation

When an additional electron was put on the LUMO in the majority of cases, a covalent bond between two-fold and three-fold coordinated atoms was broken ($\text{C}_2+\text{C}_3 \Rightarrow \text{C}_1+\text{C}_2$). This effect causes a macroscopic volume expansion. Release of excitation restores all bond lengths to their original value.

2.2. Hole creation

More interesting results were obtained during hole creation. We observed that inter-chain bonds were formed after creating a hole, and they cause a contraction of the sample. This always happens near to atoms where the HOMO is localized. Since the HOMO is usually localized in the vicinity of a one-fold coordinated atom, the inter-chain bond formation often takes place between a one-fold coordinated atom and a two fold-coordinated atom ($\text{C}\{1,0\}+\text{C}\{2,0\} \Rightarrow \text{C}\{1,1\}+\text{C}\{2,1\}$, where the second number means the number of inter-chain bonds). However, sometimes we also observed the formation of

inter-chain bonds between two two-fold coordinated atoms ($C\{2,0\}+C\{2,0\} \Rightarrow C\{2,1\}+C\{2,1\}$).

3. Macroscopic models

3.1. Ideal (reversible) case

The light induced volume expansion and volume shrinkage in amorphous selenium simultaneously exists, so that they are additive quantities. 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). The time dependent thickness change is equal to

$$\Delta(t) = d_e(t) - d_h(t) = \beta_e n_e(t) - \beta_h n_h(t) \quad (1)$$

Assuming $n_e(t) = n_h(t) = n(t)$ we get

$$\Delta(t) = (\beta_e - \beta_h) n(t) = \beta_\Delta n(t) \quad (2)$$

where β_Δ is a characteristic constant of the chalcogenide glasses related to the photo-induced volume (thickness) change. The sign of this parameter governs whether the material shrinks or expands. The number of electrons excited and holes created is proportional to the time during illumination ($n_e(t) = n_h(t) = G(t)$). Their time independent generation rate G depends on the photon absorption coefficient. Recombination is a reverse process. The number of electron-hole recombination events depends on the time and on the number of excited electrons and holes. A rate equation for this dominant process can be written as follows

$$dn_e/dt = G - C n_e(t) n_h(t), \quad (3)$$

where C is the recombination rate. Using $n_e(t) = n_h(t) = n(t)$ and $\Delta(t) = \beta_\Delta n(t)$, we obtain an equation for the time dependent volume change, namely

$$d\Delta(t)/dt = G \beta_\Delta - (C/\beta_\Delta) \Delta^2(t). \quad (4)$$

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

$$\Delta(t) = (G'/C')^{1/2} \tanh((G'C')^{1/2} t). \quad (5)$$

In the steady state case ($t = \infty$)

$$\Delta(t = \infty) = (G'/C')^{1/2} = a. \quad (6)$$

$\Delta(t=\infty)=a$ is a well-known value from experiments ($\Delta(t) = a \tanh((G'C')^{1/2} t)$). After the light is turned off. Eq. (4) reduces to ($G = 0$)

$$d\Delta(t)/dt = -C' \Delta^2(t) \quad (7)$$

with the solution

$$\Delta(t) = a / (a C' t + 1). \quad (8)$$

We have only one fitting parameter and two different curves to fit using this parameter! Fig. 1 displays the best fit for the photoinduced volume expansion of a-Se glass during illumination. The dashed line shows the measured volume including fluctuations while the solid line was drawn using our model. The horizontal dashed line is the upper limit of the volume expansion ($\Delta(t = \infty)=a$). The measured volume shrinkage of a-Se (dotted line) and the fitted curve (solid line) are shown after switching off the illumination in Fig. 2.

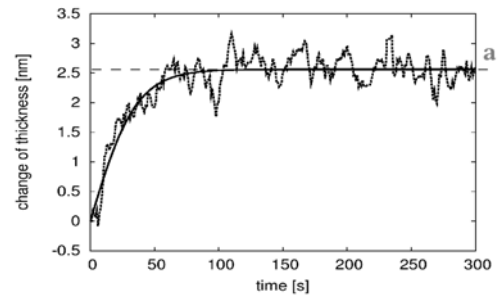


Fig. 1. Time development of the measured volume expansion in amorphous Selenium (dotted line) and its fit using our model (solid line).

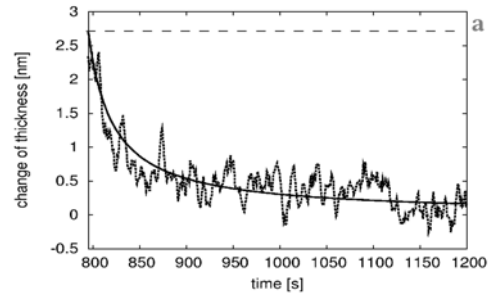


Fig. 2. The measured shrinkage of a-Se (dotted line) and the fitted curve (solid line) after switching off the illumination.

3.2. Non-ideal, irreversible (metastable) case (a-As₂Se₃)

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 a flatly deposited a-As₂Se₃ film is quite different from the ideal selenium case (see Fig. 3).

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 and irreversible changes, and it can be written as:

$$\Delta_{\text{total}}(t) = \Delta_{\text{rev}}(t) + \Delta_{\text{irr}}(t). \quad (9)$$

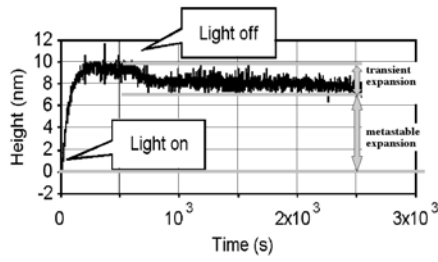


Fig. 3. The measured volume change on a flatly deposited $a\text{-As}_2\text{Se}_3$ film.

The reversible part follows Eqs. (4) and (7) during and after the illumination, with the corresponding solutions given in Eqs. (5) and (8), respectively.

Let us consider the irreversible component. During illumination, the generation rate of the irreversible microscopic change is time dependent. An upper limit exists for the maximum number of electrons and holes causing irreversible changes, 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 case, one can write the electron generation rate as:

$$G_e(t) = G_{e,irr} (n_{e,irr,max} - n_e(t)). \quad (10)$$

Note that there is no recombination term in Eq. (10). Following Eq. (4), we obtain the result that the irreversible expansion is governed by:

$$d\Delta_{irr}(t)/dt = G_{irr} - C_{irr} \Delta(t). \quad (11)$$

Equation (11) then leads to the solution:

$$\Delta_{irr}(t) = (G_{irr}/C_{irr}) (1 - \exp\{-C_{irr} t\}). \quad (12)$$

Again, in the steady state case ($t = \infty$), we get

$$\Delta(t = \infty) = (G_{irr}/C_{irr}) = b. \quad (13)$$

where $\Delta(t=\infty)=b$ is a measurable value.

Now we have only two fitting parameters (a and b)! Using Eq. (12) and Eq. (8), the best fit of the total volume expansion ($\Delta_{total}(t)$), with reversible and irreversible parts ($\Delta_{rev}(t)$ and $\Delta_{irr}(t)$) is displayed in Fig. 4.

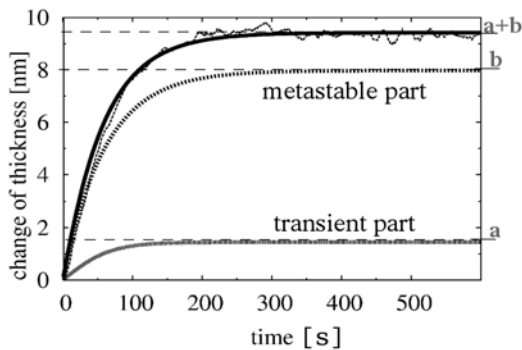


Fig. 4. Time development of the volume expansion of $a\text{-As}_2\text{Se}_3$. The thin solid line is the measured curve and the thick solid line is the fitted line. The lower dashed curve is the best fit of $\Delta_{rev}(t)$ while upper one is that of the irreversible part $\Delta_{irr}(t)$ ($\Delta_{total}(t) = \Delta_{rev}(t) + \Delta_{irr}(t)$).

After illumination, there is no volume change caused by the irreversible microscopic effects. Fig. 5 shows the shrinkage after switching off the illumination, which is a similar fit to that obtained in the reversible case.

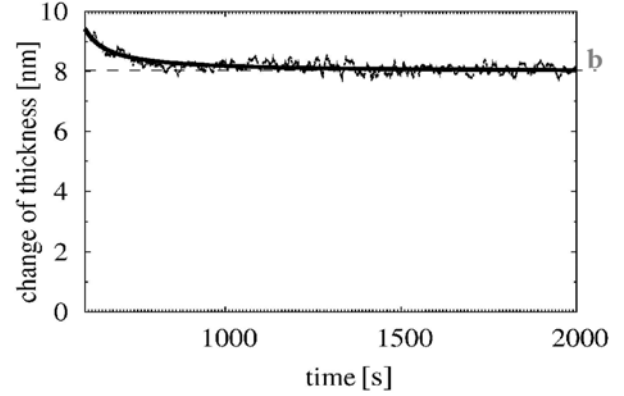


Fig. 5. The measured decay (thin solid line) and the fitted theoretical curves (thick solid line) for the shrinkage as a function of time after the illumination has stopped.

This model is a good explanation of a measured volume change on flatly deposited $a\text{-As}_2\text{Se}_3$, but the result for an obliquely deposited film is quite different from that (Fig. 6) in which volume shrinkage was observed. In order to understand this discrepancy, we performed an additional computer simulation for structures using a different preparation method.

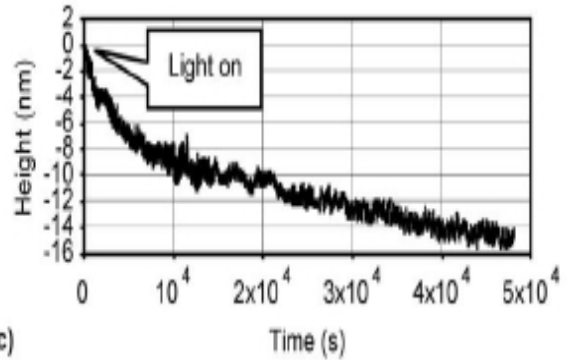


Fig. 6. Time evolution of the surface height for obliquely deposited $a\text{-As}_2\text{Se}_3$ [Ref.5 Fig 2c].

4. Sample preparation

We have developed a MD computer code [9] to simulate the thermal evaporation growth process of flatly and obliquely deposited a-Se. A classical empirical three-body potential was used to calculate the atomic interactions [10]. Our simulation technique was the following. A trigonally crystalline lattice, containing 324 selenium atoms was employed to mimic the substrate.

There were 108 fixed atoms at the bottom of the substrate and the remaining 216 atoms could move with full dynamics. The simulation cell was open along the positive z axis, and periodic boundary conditions were applied in the x and y directions. The velocity Verlet algorithm was used to follow the motion of atoms. The time step was chosen to be 1 fs. The frequency of the atomic injection was $f=1/125 \text{ fs}^{-1}$ on average. The kinetic energy of the atoms in the substrate was rescaled at every MD step, to keep the substrate at a constant temperature. We prepared several samples with angles of 0° , 20° , 45° and 60° between the normal to the substrate and the direction of the incidence of the randomly injected atoms. The surface temperature of the substrate was 300 K, while the average bombarding energy was 1 eV. We prepared only a-Se samples. Binary component glass preparation is much more difficult, because of at least three different interactions [11].

5. Analysis

We analyzed the samples in order to obtain information about the differences in their structures. In the first step, we calculated the radial distribution functions [RDF] (see Fig. 7).

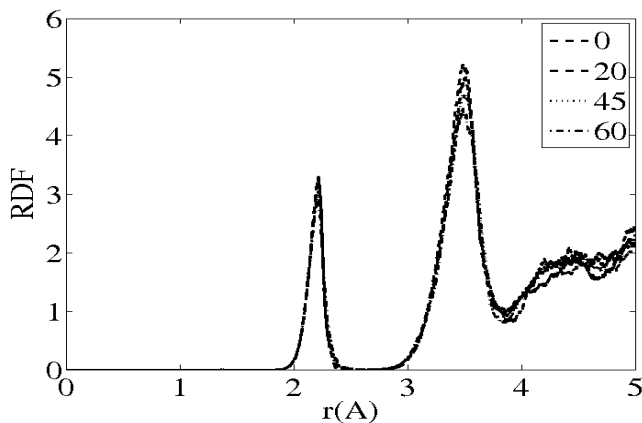


Fig. 7. Radial distribution functions of different samples.

The first neighbour shell peak appears at 2.35 \AA , and the second neighbour shell is at 3.5 \AA . The experimental measurements provide 2.33 \AA and 3.70 \AA for these values [12]. There are no relevant differences between the RDFs due to different samples.

We analyzed the coordination number distribution of the samples (Fig. 8). Most of the atoms ($>90\%$) had a coordination number 2. There are atoms with coordination number 3 ($\sim 10\%$) and very few with coordination number

1. It is relevant that the number of coordination defects increases with an increasing angle of incidence.

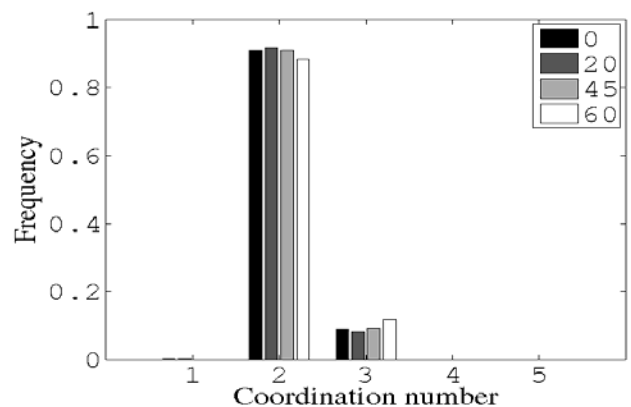


Fig. 8. Coordination number distribution of samples.

We calculated the density of the different samples (Fig. 9) and found a correlation between the angles of incidence and densities. If we increase the angle from 0° to 60° , the densities of the samples decreased.

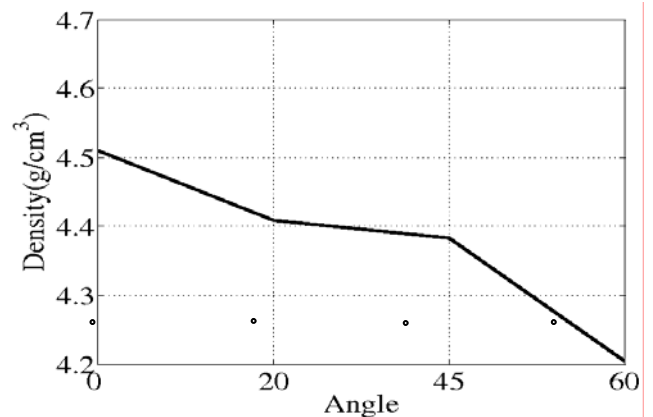


Fig. 9. The density of flatly (•) and obliquely (-) deposited samples.

This fact suggests that "larger" voids could be found in the obliquely deposited films. To investigate this supposition, we made a void size analysis for the samples, by the Voronoi-Delaunay approach [13]. The Voronoi diagram of a set of atoms $i=1, N$ is a decomposition of the space into N regions (called Voronoi polyhedra) associated with each atom, such that every point of a Voronoi region is closer to the associated atom than to any other atom in the system. Atoms whose Voronoi polyhedras share a face are considered to be contiguous. A set of four atoms contiguous to each other forms a tetrahedron, which is called the Delaunay tetrahedron (DT) in three-dimensional space (see Fig. 10 in 2D).

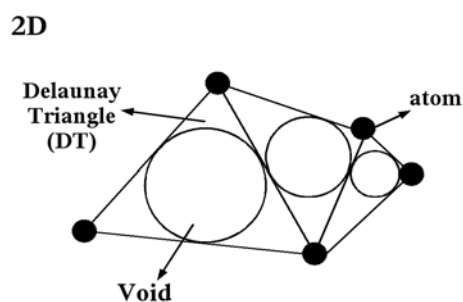


Fig. 10. The Delaunay triangle in two-dimensional space and the approximation of voids with a Delaunay-triangle incircle.

We applied the Delaunay-tetrahedrons in sphere volume as a measure of the void volume. The results show that in obliquely deposited samples, larger voids could be found.

The void size distribution from 3 \AA^3 to 6 \AA^3 follows a logarithmic distribution (Fig. 11).

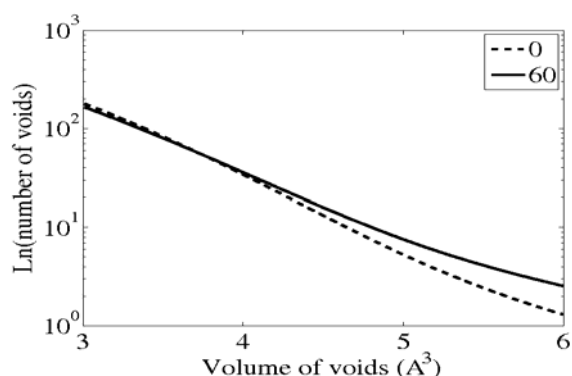


Fig. 11. Void size distribution from 3 \AA^3 to 6 \AA^3 .

The number of voids, having larger volumes than 6 \AA^3 , increases as a function of the angle of incidence (Fig. 12).

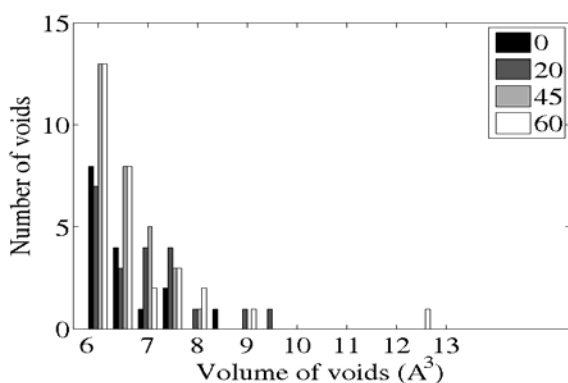


Fig. 12. Void size distribution for voids bigger than 6 \AA^3 .

A possible scenario for the photo-induced volume contraction of obliquely deposited films is the following: the primary effect in these materials is the void collapsing. Bond breaking probably destroys voids, decreasing their sizes. The flatly deposited films, because of the lack of the larger voids, avoid this effect.

6. Conclusions

We proposed a new and a universal explanation of photo-induced volume changes in chalcogenide glasses.

1. During illumination in void-free a-Se samples, we got covalent bond breaking with excited electrons, whereas hole creation contributed to the formation of inter-chain bonds. The interplay between the photo-induced bond breaking and inter-chain bond formation led to either volume expansion or shrinkage.
2. Our microscopic explanation is convenient in describing the time development of the macroscopic photo-induced volume change. Our model is confirmed by the first *in-situ* surface height measurements. There is only one fitting parameter.
3. Furthermore, in the non-ideal case, only a part of the microscopic processes is reversible and the total expansion includes the reversible (transient) and irreversible (metastable) microscopic changes. There are two fitting parameters in this case, which provide excellent fits to measured data.
4. Finally, we investigated the structural properties of flatly and obliquely deposited chalcogenide thin films. Small void sizes can cause photoinduced expansion in the flatly deposited relatively dense case, while the larger voids probably support shrinkage, eliminating these voids in the obliquely deposited case.

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