

Photoinduced Volume Changes of Obliquely and Flatly Deposited Amorphous AsSe Films Universal Description of the Kinetics

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Recently, we have constructed structural models for flatly deposited amorphous Se (a-Se) and using these configurations we have developed atomic scale model of photoinduced volume changes in this type of films. In this paper the same work on obliquely deposited thin film is presented. Universal description for the kinetics of photoinduced volume change in chalcogenide glasses is proposed based on our results. Our model containing reversible (transient) and irreversible (metastable) parts for kinetics fits well the experimental results of both obliquely and flatly deposited a-AsSe thin films. Finally, we make a brief comment on stretched exponential function which could also provide a quite good fit to experimental data. © 2011 The Japan Society of Applied Physics

1. Introduction

Chalcogenide glasses consisting of S, Se, and Te exhibit various changes in structural and electronic properties during illumination such as photo-induced volume change, photodarkening, etc.^{1–3} These photostructural changes are unique to glasses and are not observed in crystalline phases or in tetrahedrally coordinated amorphous semiconductors.⁴ Films can either expand (a-As₂S₃, a-As₂Se₃, etc.) or shrink (a-GeSe₂, a-GeS₂, etc.)⁵ or both (see §6). Several investigations have been carried out in order to provide an explanation of the photoinduced phenomena.^{6–10} Recently, Ikeda and Shimakawa have developed an *in situ* system for the simultaneous measurement of photoinduced volume changes and photodarkening to analyse the correlation between them.¹¹ A theoretical description of light-induced metastable defects creation, photodarkening and photo-induced volume expansion in amorphous chalcogenides were reviewed by Singh.¹²

Time scale of these processes is minutes. These effects are much slower than data storage devices utilizing the properties of phase change materials.¹³ Data storage is effected by fast, reversible phase changes between crystalline and amorphous states of chalcogenide alloy systems, such as In–Sb–Te, Ge–Sb–Te, and Ag–In–Sb–Te, Ge–Sb–Te.¹⁴ In the recent years, interest in amorphous Se, the model material of chalcogenide glasses has been increased by its application as a good flat panel X-ray image detector.¹⁵

Some years ago we proposed a description of the photo-induced volume changes based on tight-binding (TB) molecular dynamics (MD) simulations on amorphous selenium.¹⁶ Our proposed mechanism for photo-induced kinetics is supported by the first *in situ* surface height measurement on flatly deposited amorphous selenium by ref. 17.

2. Model

After photon absorption excited electrons and holes become separated in space on a femtosecond time scale in our model.¹⁶ Consequently, they can be treated independently in our finite-size cluster calculations. Furthermore, excitons are not considered in this explanation. Two sets of TB-MD simulations were run: first, to model the excited electron creation we put an extra electron into the lowest unoccupied molecular orbital (LUMO), and next, we annihilated an electron in highest occupied molecular orbital (HOMO)

modeling hole creation. When an additional electron was put on the LUMO in the majority of cases a covalent bond between a two-fold and a three-fold coordinated atom was broken ($C2 + C3 \Rightarrow C1 + C2$). Our localization analysis revealed that the LUMO was localized at this site before bond breaking. Release of excitation restores all bond lengths to their original value. More interesting results were obtained during hole creations. We observed that inter-chain bonds were formed after creating a hole and they cause contraction of the sample. This always happens near to atoms where HOMO is localized. Since 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 ($C1,0 + C2,0 \Rightarrow C1,1 + C2,1$, where the second subscript means the number of inter-chain bonds). However, sometimes we also observed the formation of inter-chain bonds between two two-fold C2 coordinated atoms ($C2,0 + C2,0 \Rightarrow C2,1 + C2,1$).

3. Kinetics of Volume Change in Flatly Deposited a-Se

The volume expansion caused by bond breakings and shrinkage due to inter-chain bond formations are additive values, i.e., the expansion d_+ is proportional to the number of excited electrons while the measure of shrinkage d_- is increasing by the number of created holes. The total volume change is equal to $D = d_+ - d_-$. Assuming that the number of excited electrons is equal to the number of created holes $n_e(t) = n_h(t) = n(t)$ we get the time dependent volume change, $D(t)$:

$$D(t) = B_D n(t), \quad (1)$$

where B_D is a characteristic constant of the chalcogenide glass sample related to photo-induced volume change. The sign of this parameter governs whether the material shrinks or expands.

The number of excited electrons and created holes is proportional to illumination time. Their generation rate G depends on the photon absorption coefficient and the number of incoming photons. After photon absorption, excited electrons and holes migrate within the amorphous sample and then eventually they recombine. As a consequence, the phenomenological equation for this dominant process can be written

$$\frac{dn_e(t)}{dt} = G - Cn_e(t)n_h(t), \quad (2)$$

where the coefficient C is related to the recombination probability. Substituting the expressions $n_e(t) = n_h(t) = n(t)$ and eq. (1) into eq. (2), we obtain an equation for the time dependent volume change during illumination $D(t)$, namely,

$$\frac{dD(t)}{dt} = GB_D - \left(\frac{C}{B_D}\right)D^2(t). \quad (3)$$

Solution of this nonlinear rate equation is equal to

$$D(t) = B_D\sqrt{\frac{G}{C}} \tanh(\sqrt{GC}t). \quad (4)$$

Measured volume changes for flatly and obliquely deposited a-AsSe show significant difference.¹⁷⁾ In order to understand this unexpected behavior we performed further MD simulations on obliquely deposited a-Se thin films. In the following section the structures of two types are analyzed.

4. Structure Analysis of Obliquely Deposited a-Se

Using MD simulations we modeled the thermal evaporation growth process of a-Se thin films in order to create obliquely deposited samples. A classical empirical three-body potential was used to describe the atomic interactions.¹⁸⁾ This relatively simple potential allows us to build up large atomic networks with about 1000 atoms. As a substrate, 324 Se atoms in crystalline arrangement were considered. 108 out of 324 atoms were fixed at the bottom part of the substrate layer to mimic the bulk crystal. The rest 216 Se atoms could move freely. The MD time step was 1 fs and the surface temperature of the substrate was 300 K. In every 125th MD step an atom was injected into the simulation cell. 1 eV was chosen for average bombarding energy.¹⁹⁾ Injected atoms were usually bound to the substrate growing the amorphous sample. Some non-bound atoms left the simulation box. Periodic boundary conditions were applied into the x and y directions. The problem of thermostatting was resolved by the velocity rescaling method. Four different samples were grown in angles of 0, 20, 45, and 60° to the normal of the substrate. Densities, radial distribution functions, coordination number distributions, and void size distributions of obtained structures were investigated. The radial distribution functions were identical for every sample. The first neighbor peak was found at 2.35 Å, indicating the normal Se–Se covalent bond length. The second neighbor peak appeared at 3.5 Å. The densities of the four different samples are given in Table I. Monotonic decrease of the densities can be observed in function of the increasing angles of incidence. Densities of the samples decrease because large voids appear in the oblique samples. The number of coordination defects increased with 3% when the angle of incidence was varied from 0 to 60°. The final conclusion of the analysis was that oblique samples of about 1000 atoms contain large voids and have a more porous structure than flatly deposited ones.

5. Photoinduced Volume Change of Obliquely Deposited a-Se

Previously used classical empirical three-body potential is not sufficient for modelling the photoinduced effects because

Table I. The density of amorphous Se samples (g/cm³), grown in angles of incidence 0, 20, 45, and 60°.

	Angle of incidence (deg)			
	0	20	45	60
Density	4.50	4.40	4.38	4.20

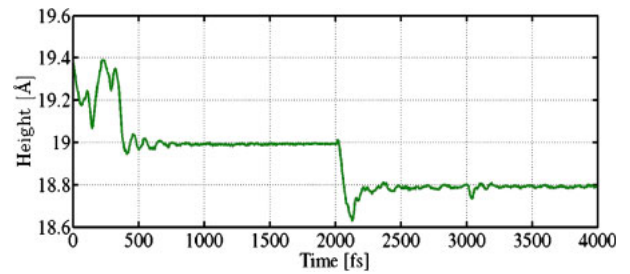


Fig. 1. (Color online) Time evolution of the thickness of a sample where irreversible volume contraction took place (MD simulation).

in this case quantum mechanical nature of the atoms must be taken into account. This reason leads us to prepare new amorphous selenium samples with voids using tight-binding molecular dynamics simulations.^{20,21)} Applying the “cook and quench”²²⁾ technique 25 different a-Se samples have been prepared by TB-MD. Two overlapping ellipsoid voids have been created inside these samples.²³⁾ Our new model films contain only about 100 Se atoms. Height (thickness) of these films in the z -direction was measured. The bonding configuration was also investigated. When an extra electron was created in the most cases reversible volume expansion were observed. The volume expansion was generated by a reversible covalent bond breaking. In void free (flatly deposited) samples Hegedüs *et al.* found the same behavior.¹⁶⁾ We observed several other interesting volume changes during the electron creation processes. These changes were irreversible volume expansion, reversible and irreversible volume contraction and two step volume contraction. In every case a covalent bond breaking occurred. When reversible volume change took place the covalent bond breaking process was reversible. In case of irreversible volume changes the covalent bond breaking process was irreversible inducing other irreversible changes in the bonding network. The most interesting cases were the irreversible volume contractions. There irreversible covalent bond breakings induced irreversible changes in the bonding network thus causing void size reduction. Figure 1 displays time evolution of the film thickness at a sample where irreversible volume contraction was observed. The irreversible changes in the bonding environment caused the collapse of a void. During hole creation processes various photoinduced volume changes like totally or partially reversible and irreversible volume contraction and expansion occurred. Analyzing the samples on microscopic level various changes were detected. In the bonding configuration appeared covalent and interchain bond formations and bond breakings, chain deformations and slips, photoinduced covalent bond shift, and ring formations.²⁴⁾

6. Kinetics of Volume Changes in Flatly and Obliquely Deposited a-AsSe

Measured photoinduced volume changes in obliquely and flatly deposited a-AsSe are quite different i.e., the first one shrinks while the other expands.¹⁷⁾ To explain this difference we must take into account a large number of irreversible changes in the local atomic arrangement. The total expansion includes reversible (transient) and irreversible (metastable) changes:

$$D(t) = D_{rev}(t) + D_{irr}(t). \tag{5}$$

Reversible part follows the previously described time development. After illumination there is no volume change caused by irreversible microscopic effects. During illumination the irreversible expansion/shrinkage is governed by

$$\frac{dn_e(t)}{dt} = G(N_0 - n_e(t)), \tag{6}$$

where G describes the excited electron-hole generation and N_0 is the maximum number of sigma bonds due to the irreversible bond breakings. After some algebra we get

$$\frac{dD_{irr}(t)}{dt} = G_{irr} - C_{irr}D_{irr}(t) \tag{7}$$

differential equation. The solution in this case is given by

$$D_{irr}(t) = \left(\frac{G_{irr}}{C_{irr}}\right)[1 - \exp(-C_{irr}t)] \tag{8}$$

expression. The total change

$$D(t) = D_{rev}(t) + D_{irr}(t) = B_D \sqrt{\frac{G}{C}} \tanh(\sqrt{GC}t) + \left(\frac{G_{irr}}{C_{irr}}\right)[1 - \exp(-C_{irr}t)]. \tag{9}$$

Fits for flatly deposited a-AsSe are displayed in Fig. 2. Expressions, tanh and (1 - exp), have positive prefactors i.e., during the illumination the sample expands. In the other case the result opposite i.e., the obliquely deposited porous sample shrinks. We can describe this process by the same mathematical expression. The only difference is that both expressions [tanh and (1 - exp)] have negative prefactors. The best fit for obliquely deposited a-AsSe is shown in Fig. 3. Negative prefactors mean that both reversible and irreversible bond breakings cause macroscopic shrinkage in porous materials.

7. Additional Remark

Our additional remark is the following: instead of Debye type normal exponential relaxation several times stretched exponential functions are fitted to the measured data in disordered systems. Usually these curves fit quite well²⁵⁻³⁰⁾ but sometimes the physical understandings of these approaches are absent. In our case we also tried to fit stretched exponential function and we obtained relatively good correlation as you can see in Fig. 4. This example demonstrates that two different processes sometimes could be fitted by one stretched exponential function!

8. Conclusions

Our MD structure investigations show that increasing deposition angle leads to lower density of the obliquely

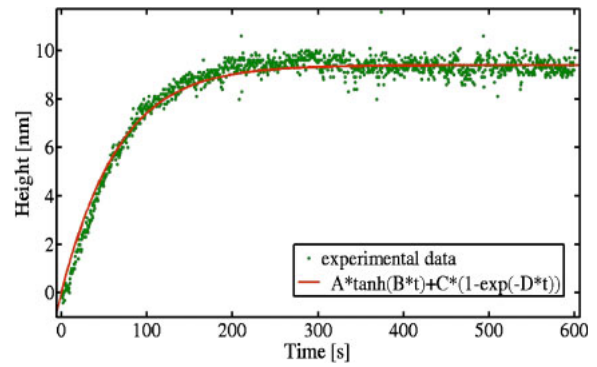


Fig. 2. (Color online) Volume changes in function of time of flatly deposited a-AsSe thin film. Symbols are the measured volume changes during the illumination and solid line is the best fit [$D(t) = 1.6 \times \tanh(10^{-2} \times t) + 7.8 \times p[1 - \exp(-1.5 \times 10^{-2} \times t)]$].

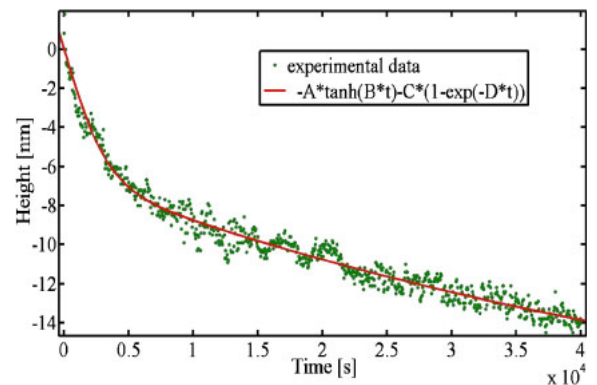


Fig. 3. (Color online) Volume changes in function of time of obliquely deposited a-AsSe thin film. Symbols are the measured volume changes during the illumination and solid line is the best fit of a $D(t) = (-6.4) \times \tanh(3 \times 10^{-4} \times t) + (-15.2) \times [1 - \exp(-1.6 \times 10^{-5} \times t)]$ function. The prefactors of tanh and (1 - exp) have negative signs!

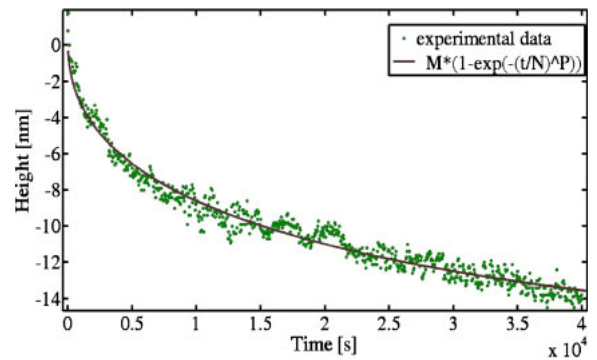


Fig. 4. (Color online) Volume changes of the same obliquely deposited a-AsSe thin film fitted by the $D(t) = (-20) \times \{1 - \exp[-(t/3.17 \times 10^4)^{0.5}]\}$ stretched exponential function.

deposited film. This rule can be explained by the presence of larger voids in the samples. TB-MD simulations of photo-induced volume changes showed more varieties of microscopic and macroscopic levels than we had earlier obtained for void free cases. We described in detail these complex atomic rearrangements occurring on photoexcitation in porous samples, which are reversible and irreversible

photocontraction/expansion, bond breaking and formations. Obliquely deposited chalcogenides are more sensitive to the illumination than flatly deposited samples because voids provide more degrees of freedom for atomic positions. We developed a universal macroscopic model which is able to describe the photoinduced expansion as well as the shrinkage in chalcogenide glasses prepared by different methods.

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