LIGHT-INDUCED VOLUME CHANGES IN GLASSY SELENIUM
II. KINETICS OF VOLUME EXPANSION

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Based on our previous molecular dynamics simulations we present an universal macroscopic model, which can simultaneously explain the photo-induced volume expansion and shrinkage. It is supported by the recent surface height measurements on amorphous selenium.

1. Introduction

Chalcogenide glasses exhibit various changes in structural and electronic properties like photo-induced volume change, photo-darkening, defect creation, and photo-induced change in the phase solid during illumination. These phenomena are unique to chalcogenide glasses and they cannot be found in crystalline chalcogenides or in any other amorphous semiconductors. Photo-darkening cannot be induced in As_2S_3 films which are thinner than 50 nm [1]. Materials showing photo-induced volume change can be classified into two different groups: films can either expand or shrink [2]. Several investigations have been carried out in order to provide an acceptable explanation of the photo-induced phenomena, but a general theory is still missed. Based on our tight-binding (TB) molecular dynamics (MD) simulations we propose a new description of the photo-induced changes in a-Se and we compare it with the first in-situ real time measurement.

2. Macroscopic model

The results of our previous molecular dynamics simulations [3, 4] (part I of this paper was published in [3]) confirm that light induced volume expansion and volume shrinkage in amorphous selenium simultaneously exists which are quantities. The expansion in thikness d_e is proportional to the number of excited electrons $n_e (d_e = A_e n_e)$, while the shrinkage d_h is proportional to the number of created holes $d_h (d_h = A_h n_h)$. The parameter $A_e (A_h)$ is the average thickness change caused by an excited electron (hole). The time dependent thickness change is equal to

$$\Delta(t) = d_e(t) - d_h(t) = A_e n_e(t) - A_h n_h(t).$$

(1)

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

$$\Delta(t) = (A_e - A_h) n(t) = A_\Delta n(t)$$

(2)

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where A_Δ is a characteristic constant of the chalcogenide glasses related to photo-induced volume (thickness) change and it is a unique parameter for each glass. 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. Their generation rate G depends on the photon absorption coefficient and the number of incoming photons. After photon absorption, the excited electrons and holes migrate within the amorphous sample and then eventually recombine. A phenomenological equation for this dominant process can be written as

$$\frac{dn_e(t)}{dt} = G - Cn_e(t)n_h(t) \tag{3}$$

where C is a constant. Using $n_e(t) = n_h t(t) = n(t)$, $G^* = GA_\Delta$, $C^* = G/A_\Delta$, we obtain an equation for the time dependent volume change , namely,

$$\frac{d\Delta(t)}{dt} = G^* - C^*\Delta^2(t) \tag{4}$$

Solution of this nonlinear differential equation is given by

$$\Delta(t) = \sqrt{\frac{G^*}{C^*}}\tanh\left(\sqrt{G^*C^*}t\right). \tag{5}$$

Recently, the photo-induced expansion of amorphous selenium films was measured *in situ* for the first time using optoelectronic interference, enhanced by image processing [5]. Fig. 1 shows the measured time evolution of the surface height in the interval of 0-400 s. The best fit according to Equation 5 gives $G^* = 0.072\,\text{nms}^{-1}, C^* = 0.011\,\text{nm}^{-1}\text{s}^{-1}$, as seen in Fig. 1
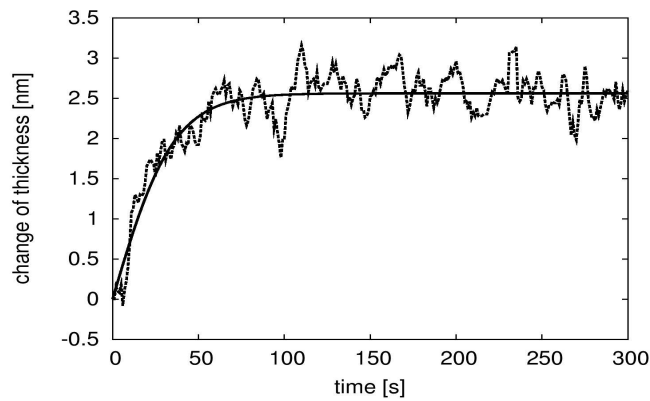

Fig. 1. Time development of volume expansion in amorphous selenium (dashed line) and its theoretical description (solid line). Illumination starts at t=0 s.

After the light is turned off equation 4 reduces to (*G = 0*)

$$d\Delta(t)/dt = -C^*\Delta^2(t) \tag{6}$$

with the solution

$$\Delta(t) = a/(aC^*t+1) \tag{7}$$

Fig. 2 displays the measured decay and the fitted theoretical curve with $C^* = 0.013 nm^{-1}s^{-1}$ and a = 2.16. Although the slight difference in the value of C in the above two fits is within the error bar, this discrepancy might be expected because we have also rarely found irreversible changes in the local atomic arrangements in our TB-MD simulations.
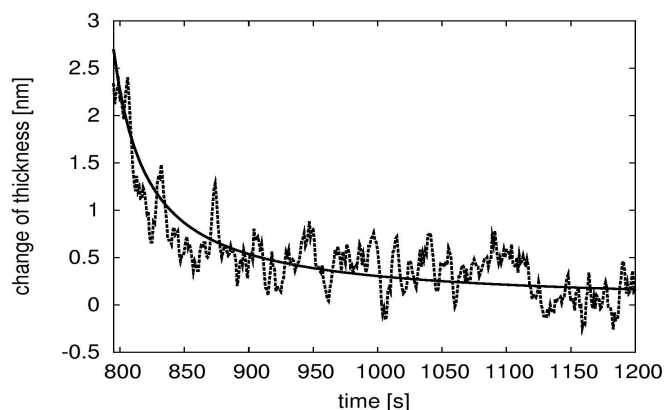

Fig. 2. Recovery after illumination of amorphous selenium (dashed line). Light was switched off at t = 800 s. Solid line corresponds to our theoretical model.

3. Conclusion

We have proposed a comprehensive explanation of photo-induced volume changes in chalcogenide glasses, which can simultaneously describe photo-induced shrinkage and expansion. This phenomenon is unique to amorphous chalcogenides because of the two-fold coordination of the chalcogenide atoms, which provides structural flexibility. Covalent bond breaking occurs in systems with 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. Our comprehensive microscopic explanation of the photo-induced volume change is in an excellent agreement with the first *in situ* surface height measurements in amorphous selenium.

References

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