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# Thickness oscillation effect in photoexpansion and photocontraction of amorphous selenium

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Thickness oscillations under light irradiation or by switching-off the light have been revealed in amorphous selenium films. The explanation was given in the frame of a theory that takes into account the balance between the expansion of the inter-chain distance due to electrical charging and better ordering of chains due to freedom of chains to accommodate into the structure as a result of the diminishing or increasing of the spatial hindrance.

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## 1. Introduction

Specific photodarkening (PD) and photoinduced volume changes (PVC) are produced in amorphous chalcogenides and they attracted considerable interest due to their scientific importance and potential applications [1]. These phenomena together with other photoinduced phenomena were investigated in many papers along the years [2-22]. Correlations between PD and PVC have been reported in recent years [23,24]. However, PD and PVC were measured individually in all previous experimental works. To understand the dynamics and correlations of PD and PVC in chalcogenide glasses, *in-situ* simultaneous measurements are required, since they will provide the important information about the time evolution of the changes.

We have developed a real-time *in-situ* surface height measuring system based on phase-shifting interferometer (PSI) and performed the *in-situ* measurements of PVC in chalcogenide glasses [25]. This new technique overcomes the drawbacks of conventional thickness measuring systems based on the spectral analysis of interference fringes [26, 27].

A real-time computer controlled spectroscope to measure the PD and put these two components together as an *in-situ* simultaneous PD and PVC measuring system has been reported [28]. The surface height map of the sample and the spectroscopic analysis of the transmission data were obtained at a maximum rate of every 1/4 second. The authors of [28], Ikeda and Shimakawa found that the time evolution of PVC seems to be different from that of PD. It is therefore expected that there is no one-to-one correlation between PD and PVC, which is contrary to the expectations of most researches in the field [29]

## 2. Experimental

### 2.1 Sample preparation

The films of amorphous selenium (thickness, $d$ ~ 500 nm) were deposited onto sapphire substrates (13 mm in diameter and 0.5 mm in thickness) by the conventional thermal evaporation method in vacuum (~ $1\times10^{-6}$ Torr) at room temperature. The films were deposited at normal incidence to the substrate (so-called flat deposition). The samples were mounted onto an aluminum block to reduce the temperature rise during illumination.

### 2.2 Measurements and results

The time evolutions of both the PVC and PD in *a*-$As_2Se_3$ film, and the surface height maps that is obtained by the surface height measuring system described in [28]. The surface height increased by 8.5 nm ($\Delta d/d \approx 1.7$ %) after 1200 seconds of illumination and reached an equilibrium state, while the change in the optical absorption is still taking place. When the illumination was turned off (after illumination of 1500 s), the surface height decreased around 1 nm and 500 cm$^{-1}$, respectively, from those values just before stopping the illumination.

PD and photoinduced volume expansion (PVE: increase of surface height) are observed during and after illumination. Transient PD and transient PVE [30] must be involved during illumination, since after stopping illumination, slight decreases of $\Delta h$ are observed. The remaining increases of $\Delta h$ after the cut off of illumination are the so-called metastable PD and metastable PVE [30], respectively. We have analyzed the PD and PVC during the illumination by nonlinear fitting using the Marquardt-Levenberg algorithm [31]. Both the PD and PVE are presented by the following stretched exponential function:

$$y = A\left[1-\exp\left\{-\left(\frac{t}{\tau}\right)^{\beta}\right\}\right] \qquad (1)$$

where $y$ is the measured value ($\Delta h$) at time $t$, and $A$ is a constant (equal to the total amount of change), $\tau$ and $\beta$ are, the effective reaction time and the dispersion parameter, respectively.

The time evolution of $\Delta h$ is very close to an exponential function ($\beta$ is close to 1), while the change in $\Delta\alpha$ at 2.1 eV is given by a typical stretched exponential function ($\beta = 0.71$). The effective reaction time $\tau$ for $\Delta h$ are 280 s. The above results suggest that there is no one-to-one correspondence between PD and PVE as pointed out in an earlier work [32]. Therefore, by simultaneous measurement of PD and PVC in amorphous selenium differences in the growth kinetics for PD and PVC have been pointed out. Differences in both the effective reaction times and the dispersion parameters for PD and PVC suggest that the origins of PD and PVC are not the same.

## 2.2 Processing of the PD and PVE curves. Characterization of the thickness oscillation

The photo-induced expansion of amorphous selenium films was measured in situ for the first time using optoelectronic interference enhanced by image processing. We have represented at a larger scale both resulting curves for expansion during illumination and shrinkage after switching off the illumination (Fig. 1). It is observed a gradually increase of thickness (due to volume expansion of the film) followed by a gradually decrease (after switching of the light incident on the film). The noise on the curves seems to be enough large. Therefore, in order to see the possible deviations from the exponential increase or decrease of the monitored thickness parameter, we carefully processed the curves. The noise was eliminated using a Fourier transformation procedure. Firstly the continuous component was subtracted from both curves. The strings of the experimental points so adjusted (Fig. 2) were processed by a Fourier transformation. The spectra of harmonic oscillations for both strings of data are represented in Fig. 3.

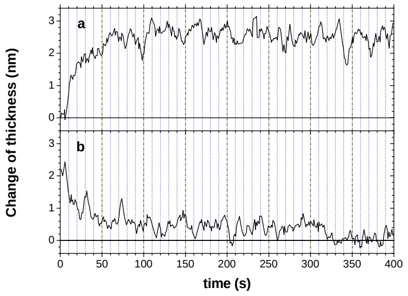

*Fig. 1. Measured photoinduced changes in amorphous selenium. Upper panel: expansion due to illumination (a). Lower panel: shrinkage after switching off illumination.*

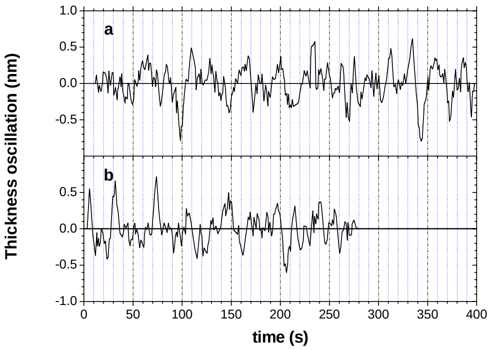

*Fig. 2. The curves from figure 1 transformed by subtracting the continuous component (average increase (a) and decrease (b)).*

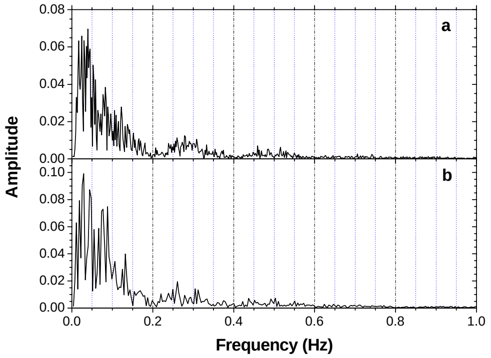

*Fig. 3. Frequency spectrum for the data of Fig. 2.*

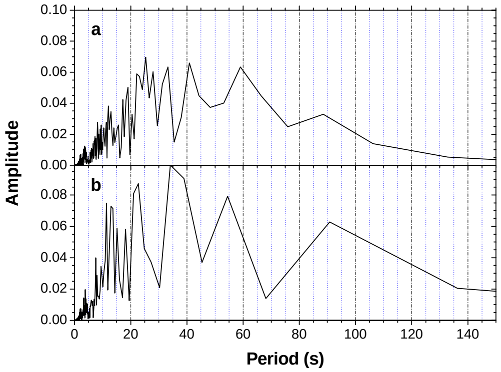

*Fig. 4. The periods of the oscillations as obtained from the frequency spectrum.*

By transforming the frequency spectrum into a period spectrum, we got period spectra that point out oscillations of well-defined time-length situated at 40 s, 60 s and 85 s.

In order to reveal more clearly in the experimental data the existence of oscillations corresponding to the dominant period of 60 s we have applied a smoothing procedure by computer. The high frequency components corresponding to the noise have been cut and the remaining frequencies have been Fourier transformed back in the space of distances (real space). Fig. 4 shows the results.

It is quite remarkable that both expansion and compression of the thickness of amorphous selenium film exhibit a dominant oscillation with the period of 60 s. Thus, we have demonstrated the existence of specific oscillations in the amorphous selenium subjected to gap light irradiation and during relaxation after switching off the light incident on film.

The mechanism and theory of this new phenomenon will be discussed in the next section.

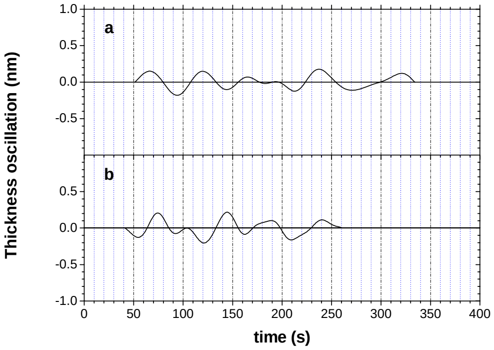

*Fig. 5. The experimental data from figure 2, smoothed, in order to evidence the fundamental oscillations of the thickness.*

## 3. Theory

Several attempts to explain the oscillatory phenomenon have been carried out.

The photo-excitation in selenium was explained by Hegedus et al. [33-36]. During absorption of a photon an electron of selenium is transferred from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUOMO). In fact the photo-excitation is the formation of electron-hole pairs. The bond breaking in selenium and the formation of coordination defects are expected. Hole and electron creation cause opposite effects: a hole shrinks the material while the electron expands the material. The total effect seems to correspond to volume expansion of the selenium.

Shimakawa and Ikeda [37] developed an *in situ* system for simultaneous measurement of photodarkening and photoinduced volume changes in amorphous chalcogenides and concluded that the origin of the two phenomena is different.

Sakaguchi and Tamura [22] explained the expansion in amorphous chalcogenides by the excitation of the lone pair electrons on chalcogens, that leads to the distortion of the bonds, thus weakening the bonding forces and changing the bond lengths (increase) in the surrounding atoms. The effect propagates and, as a general result, an expansion of the material is produced.

We suggest the following model for expansion, shrinkage and oscillatory behavior of the thickness during light excitation and during relaxation (after switching off the illumination).

The light excitation in selenium determines the expulsion of an electron from the lone pair. Thus one Se-Se bond is weakened or even broken. The excitation is especially active on highly distorted sites of the chain that are correlated with the VAP defects frequently occurring in the amorphous material [38]. The photo-excited electron is transferred to the neighboring Se chain on the high distorted position and an exciton electron-hole pair is formed. The energy of the new formed state is higher than that in the not-excited state. The covalent Se-Se bonds from the surrounding atoms are weakened and this is expressed by larger bonding distances. The increase of local bonding distances can propagate to the next surrounding atoms and finally spread to macroscopic distances. The process is amplified in time. Nevertheless, the opposite process is also in competition: the relaxation of the selenium chain configuration, towards a metastable state. Due to photo-excitation an increase of temperature is locally produced. This increase leads to more mobility of the chains which tend to take a more ordered, and, therefore, a denser atomic configuration. In the next step, further illumination is not efficient (the situation approaches to that of well ordered, crystalline chalcogenides, where the illumination cannot change the material structure and properties), while a gradual de-excitation process occurs. As a consequence, a new state with more disorder is formed and, this state can be again photo-excited to an expanded state and accumulates energy. The oscillation between expanded and compressed state is possible because the photo-excited process is a cooperative one. The macroscopic expanded state is observed only if the accumulation of photo-excitations overcomes a minimum threshold.

In order to explain mathematically the oscillation process we must take into account two variables: w - the number of photoexcited states per unit time, c1, induced in the material by illumination with continuous light (this is a function of time!) and the number of exciton states that are relaxed per unit time with a rate constant c2.

The system of equations written in the one-dimensional case and describing the excitation of lone pair electrons and relaxation of electron-hole pairs are:

$$
\begin{aligned}
&\frac{1}{c}\cdot\frac{\partial I(t,x)}{\partial t}-\frac{\partial I(t,x)}{\partial x}=(\alpha_0+\beta\cdot N_a)\cdot I(x,t)\\
&\frac{\partial N_c}{\partial t}=-\frac{N_c}{\tau_0}+(\alpha_0+\beta\cdot N_a)\frac{I(t,x)}{h\nu}\\
&\frac{\partial N_a}{\partial t}=\frac{\theta\cdot N_c}{\tau_o}-\frac{N_a(N_a-N_v^0)}{\tau\cdot N_a^0}
\end{aligned}
\qquad (1)
$$

Where: I = light beam intensity

$N_{eh}$ = non-equilibrium electron-hole concentration

$N_{eh}{}^{o}$ = equilibrium e-h concentration

$\theta$ = the number of e-h pairs generated by a light quantum

$\alpha_o$, $\beta$ = constants

$N_h{}^{o}$ = hole concentration

$N_e{}^{o}$ = lone pair electron concentration

If one supposes that light intensity I(t,X) transmitted through the amorphous film is proportional to the change in thickness (due to the effect of eh pair generation) then I~d (d=thickness)

An analytical model for quasi-linear solutions has been developed [39].

The equation which describes the evolution of the optical field transmitted through the films, related to the thickness d modification is:

$$\hat{\mathrm{L}}\mathrm{w}(\mathrm{u}) = 0 \rightarrow \frac{\partial}{\partial \eta}\left[\frac{\partial^2 \mathrm{w}}{\partial \eta^2} - \mathrm{C}_1\frac{\partial \mathrm{w}}{\partial \eta} - \mathrm{D}_1\right] = 0 \qquad (2)$$

It results:

$$\frac{\partial^2 \mathrm{w}}{\partial \eta^2} - \mathrm{C}_1\frac{\partial \mathrm{w}}{\partial \eta} - \mathrm{D}_1 = \mathrm{k}_1 \qquad (3)$$

where $k_1$ is the integral constant.

The characteristic equation associated to (31) is:

$$\mathrm{r}^2 - \mathrm{C}_1\mathrm{r} - (\mathrm{D}_1 + \mathrm{k}_1) = 0 \qquad (4)$$

where solutions are:

$$\mathrm{w}(\eta) = \mathrm{k}_2 e^{r_1\eta} + \mathrm{k}_3 e^{r_2\eta} + \mathrm{w}' \qquad (5)$$

Using the initial conditions:

$$\left.\mathrm{w}(\eta)\right|_{\eta=0} = \mathrm{w}(0) = \mathrm{w}_0 + \mathrm{w}'$$
$$\left.\frac{d\mathrm{w}(\eta)}{d\eta}\right|_{\eta=0} = \varphi_\mathrm{w} \qquad (6)$$

the solution $r_{1,2}$ of the characteristic equation can be written the form:

$$\mathrm{r}_{1,2} = \frac{\mathrm{C}_1}{2} \pm \sqrt{\left(\frac{\mathrm{C}_1}{2}\right)^2 + (\mathrm{D}_1 + \mathrm{k}_1)} \qquad (7)$$

One searches solutions of the form:

$$\mathrm{w}(\eta) - \mathrm{w}' = \mathrm{k}_2 \cdot e^{r_1\eta} + \mathrm{k}_3 e^{r_2\eta} \qquad (8)$$

with $k_2$ and $k_3$ as integration constants.

The integration constants will be written down as functions of the initial conditions defined by (34):

$$k_2 = \frac{\left(\sqrt{\left(\frac{C_1}{2}\right)^2 + D_1 + k_1} - \frac{C_1}{2}\right)\cdot(w_o - w') + \varphi_w}{2\sqrt{\left(\frac{C_1}{2}\right)^2 + (D_1 + k_1)}} \qquad (9)$$

$$k_3 = \frac{\left[\left(\sqrt{\left(\frac{C_1}{2}\right)^2 + D_1 + k_1} + \frac{C_1}{2}\right)\cdot(w_o - w') - \varphi_w\right]}{2\sqrt{\left(\frac{C_1}{2}\right)^2 + (D_1 + K_1)}}$$

Then, in a straightforward way one gets the optical field:

$$\mathrm{w}(\eta) - \mathrm{w}' = e^{\frac{c_1}{2}\eta}[\mathrm{w}(0) - \mathrm{w}'] \cdot \sqrt{1 - \omega_{f1}^2} \cdot \mathrm{ch}\left[\omega_f \eta + \varphi_{w_1}\right] \qquad (10)$$

with:

$$\omega_{f_1} \rightarrow i\omega_{f_1}$$
$$\varphi_{w_1} \rightarrow i\varphi_{w_1} \qquad (11)$$

Becomes:

$$\mathrm{w}(\eta) - \mathrm{w}' = e^{\frac{c_1}{2}\eta}[\mathrm{w}(0) - \mathrm{w}'] \cdot \sqrt{1 + \omega_{f1}^2} \cdot \cos\left[\omega_f \eta + \varphi_{w_1}\right] \qquad (12)$$

$$\omega_{f_1} = \left[\frac{\varphi_w - \frac{C_1}{2}(w_0 - w')}{(w_0 - w')\sqrt{\left(\frac{C_1}{2}\right)^2 + D_1 + k_1}}\right]$$

$$\omega_f = \sqrt{\left(\frac{C_1}{2}\right)^2 + D_1 + k_1} \qquad (13)$$

$$\varphi_{w_1} = \arg th(\omega_{f_1})$$

$$\eta = \frac{t}{\tau_0} - \frac{n}{c}\cdot\frac{x}{\tau_0}$$
$$C_1 = \tau_1 v_0(1 - 2\tau_1) - 1 \qquad (14)$$
$$D_1 = V_0[\tau_1 - (2 + B)\cdot\tau_1^2]$$

A bifurcation point of the system is given by the nature of the characteristic equation (7):

- for real solutions: $\left(\frac{C_1}{2}\right)^2 + D_1 + k_1 \geq 0$ (hyperbolic solutions exist);
- for complex solutions: $\left(\frac{C_1}{2}\right)^2 + D_1 + k_1 \leq 0$ (harmonic solutions exist).

This means that the complex solutions describe the oscillation property of the light intensity transmitted through sample and correspondingly of the thickness parameter.

In the case of switching off the light, the intensity transmitted through sample is substituted in the equations by the rate of relaxation of e-h pairs while θ will be the number of exciton states newly formed as a consequence of the energy released by the e-h relaxation.

## 4. Discussion

From the results presented above and from the theory that takes into account the balance between the photo-excited and relaxed charge carriers there was demonstrated that both optical transparency and thickness of the amorphous selenium films change periodically during illumination, or by relaxation after switching off the illumination. The period of oscillation is enough large: 60 s.

The oscillatory phenomena are satisfactory explained by the competition of two non-equilibrium processes that take place into the amorphous film: electron photo-excitation from the lone pairs of the chalcogen and electron-hole relaxation as a whole. These processes are interfering and, therefore, periodical oscillations, of thickness due to excitation and relaxation of lone-pair that governs the spatial arrangement of the atoms are produced.

## 5. Conclusions

Thickness oscillations of the selenium film have been revealed. The oscillations in the PD and PVE are due to the competition of two processes: formation of electron-hole pairs by photo-excitation of the lone pair electrons in selenium and relaxation of the exciton state (electron + hole complex) with the recovery of the structural distortions that occur during photo-excitation. The theory takes into account the balance between the expansion of the inter-chain distance due to electrical charging and better ordering of chains due to freedom of chains to accommodate into the structure as a result of the diminishing or increasing of the spatial hindrance.

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