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STRUCTURAL MODELLING OF REVERSIBLE PHOTODARKENING IN $a$-$As_xSe$

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Abstract: Reversible photodarkening in amorphous $As$-$Se$ films is attributed to photopolymerization. The difference between $As$-rich and $Se$-rich films is due to the initial predominantly molecular structure of the former and to the structural instability under heat of the latter.

INTRODUCTION. Well annealed $a$-$As_x(S,Se)_y$ films with $x \leq 4$ display reversible photodarkening (PD). The shift of the absorption edge increases in time and reaches saturation values which depend on the level of irradiation and on temperature for a given wave length of the incident light. By lowering the level of irradiation incomplete photobleaching (PB) occurs; raising the temperature above a critical value induces total thermal bleaching (TB) \cite{1}. PD is accompanied by only minor changes in the X-ray diffraction pattern \cite{2}.

All recently proposed models \cite{1,3,4} rightly suppose that PD is due to a metastable structural modification. They let, however, many questions open. What is the reversible structural change which narrows the optical gap without markedly modifying the X-ray diffraction pattern? Why is this happening mainly in $As$-rich $a$-$As-(S,Se)$ films? The Leningrad group had suggested earlier \cite{5} that photopolymerization is somehow involved, but opted later \cite{1} for another model. We shall try to show that PD is due to light-induced polymerization of initially predominantly molecular films.

THE STRUCTURE OF $As$-$(S,Se)$ CRYSTALS AND GLASSES. Fig.1 shows that crystals containing only $As$-$(S,Se)$ bonds are layered. Elemental crystals are either molecular and metastable or polymeric and stable. $As$-$(S,Se)$ compounds with comparable numbers of $As$-$As$ and $As$-$(S,Se)$ bonds form stable molecular crystals consisting of cradle-shaped molecules similar to those encountered in the vapour.

The sudden change in structure between $x=4$ and $x=6$ shows up clearly in fig.1. The polymeric crystals $\varepsilon$-$As$; $As_4Se_6; hex. Se$ and $\varepsilon$-$As$; $As_4S_6$; cubic S, respectively, lie on the same straight lines. The molecular crystals $As_4Se_4; \alpha$-$Se$ and $As_4S_4; \alpha$-$S$ lie deeper on nearly parallel lines. The glassy $As$-$Se$ system displays a density jump similar to that seen in the crystals. There are no $As$-$S$ glasses beyond 43 at.% $As$. The left- and right-branch of the curves extrapolate linearly to the density of glassy $As$. It can be inferred from these data that the structure of annealed $As$-$(S,Se)$ glasses and $a$-films is predominantly molecular for $x \leq 4$ and polymeric for $x \geq 6$. The instability of $As_4$ and $As_4(S,Se)_6$ molecules in the solid phases is due to the high distortion of their bond angles ($\neq As=60^\circ$ in $As_4$ and $\neq S=114^\circ$ in $As_4S_6$). They relax in the layered $\varepsilon$-$As$ and $As_4S_6$ crystals to 960 and 990, respectively. For $x=4$ both free molecules and those included in crystals are equally relaxed ($\neq As=98^\circ ; \neq S=101^\circ$).
OPTICAL PROPERTIES AND POLYMERIZATION.

Fig.1 shows that polymer phases are denser than equivalent molecular ones. If PD is due to polymerization, it must result in both densification and an increase in refractive index, as it indeed does /6/.

Fig.2 displays the conventional position of the absorption edge for $\alpha=100$ and 10 cm$^{-1}$ vs. composition in the glassy As-Se system and some crystals. By comparing molecular $\alpha$-Se, as-deposited $\alpha$-As$_4$Se$_6$ and yellow As with polymeric hex.Se, annealed $\alpha$-As$_4$Se$_6$ and $\alpha$- or $\varepsilon$-As, one arrives at the conclusion that polymerization always narrows the energy gap, thus inducing PD. The curve corresponding to polymeric glasses extrapolates into polymeric $\alpha$-As, while the curve corresponding to molecular glasses extrapolates towards molecular yellow As. Thus, in essence, PD means moving from curve 1 towards curve 2 in fig.2. The higher the As content, the bigger the highest possible absorption edge shift (table 1).

<table>
<thead>
<tr>
<th>Film composition</th>
<th>Model $\Delta E$/eV</th>
<th>Experimental $\Delta E$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$_3$Se$_2$</td>
<td>0.34</td>
<td>0.24</td>
</tr>
<tr>
<td>As$_4$Se$_4$</td>
<td>0.18</td>
<td>0.13</td>
</tr>
<tr>
<td>As$_4$Se$_6$</td>
<td>0.03</td>
<td>0.02</td>
</tr>
</tbody>
</table>

LIGHT-INDUCED POLYMERIZATION. When light temporarily expels an electron from a lone-pair orbital (fig.3a), a valence-alternation pair (VAP) of induced stability /7/ can be generated in a favourable environment found in disordered materials (fig.3b). One needs a second photon, in the same place and within a sufficiently short time, to form a dimer. Neutralization occurs by recombination with the expelled electrons. The two-photon process of photopolymerization does not involve major changes in medium-range order because longer, non-bonded distances are replaced by strained, but shorter bonded distances and vice-versa (fig.3c). The resulting polymer is an excited metastable state separated from the monomer ground state by an energy barrier expected to be the higher, the stiffer the new polymer structure, i.e. the more trivalent As the system contains.

The polymer can be dissociated by irradiation. Breaking one of the newly created bonds will liberate enough energy to break the second bond too, thus restoring the molecular configuration. Depolymerization
by light is therefore an one-photon process. If \( n/N \) is the ratio between the excited and the total number of dimerization sites and the absorption edge shift \( \Delta \alpha \) is admitted to be proportional to \( n \),

\[
\frac{dn}{dt} = g(N - n)\alpha^2 I^2 - r \Delta \alpha I,
\]

where \( I \) is the flux of incident photons of energy \( h\nu \), \( \alpha \) is the number of photons absorbed per unit of time in the bleached thin film of unitary thickness and absorption coefficient \( \alpha \), \( g \) and \( r \) are quantum efficiencies. If \( h\nu \) lies not too far above the absorption edge \( h\nu_0 \), so that \( a_h = k(h\nu - h\nu_0)^2 \), \( \Delta \alpha = S n = 2a\Delta\varepsilon/(h\nu - h\nu_0) \).

Knowing that the relative transmissivity of the film \( \tau/\tau_0 = \exp(-\Delta \alpha) \), one easily obtains for the time dependence of PD at temperatures where no TB yet occurs

\[
\frac{\tau}{\tau_0} = \exp(-\Delta \alpha) = \exp \left( -\Delta \alpha_M \left[ 1 - \exp \left( -B I^2 t/\Delta \alpha_M \right) \right] \right)
\]

and of PB under reduced irradiation \( i \), after PD for a time \( t_1 \),

\[
\frac{\tau}{\tau_0} = \exp \left( -\alpha_M \left[ 1 - \exp \left( -B I^2 t_1/\Delta \alpha_M \right) \exp \left[ -B I^2 (t - t_1)/\Delta \alpha_M \right] \right] \right)
\]

where

a) \( A = rS/\alpha^2 \); b) \( B = gSN\alpha^2 \); c) \( \Delta \alpha_M = NS/(1+A/1) \); d) \( \Delta \alpha_m = NS/(1+A/1) \).

Eqs. (2), (3) and (4c) are compared with experimental results taken from /8/ in figs. 4 and 5, the material containing 60 at.% As. The model also accounts qualitatively for the changes in microhardness and solubility accompanying PD as well as for the induction of dichroism and bi-refringence by linearly polarized light /9/.

**Fig. 3. Phases of photodimerization.**

**Fig. 4. Maximal decrease in transmissivity \( \Delta \tau \) vs. intensity of incident light \( I \).**

**Fig. 5. Kinetics of PD and PB.**

PHONON ASSISTED PB occurs when an already darkened film is heated under irradiation to a temperature \( T \) at which no TB yet happens in the
dark. A higher $\tau/\tau_0$ is reached which can also be obtained by irradiating an initially bleached film at the same temperature $T$ /1/. This is due to the lack of stability of the intermediate non-equilibrium VAP (fig.3b) which can easily be destroyed by lattice vibrations before the arrival of the second photon involved in dimerization. This results in a dependence of $g$ on $T$ of the form

$$g = g_0/\exp \left[ \lambda I(\exp w/kT -1) \right]^{-1},$$

(5)

where $w$ is the height of the energy barrier preventing the decay of the VAP, thus diminishing $\Delta M$ and raising $\tau_m/\tau_0$. A comparison between the calculated and the experimental $T_m/\tau_0$ vs $T$ curves is offered in fig.6.

Fig. 6. Phonon-assisted PB. --- calc.; --- exp. /8/. A$\delta_4[S,Se]$ FILMS. After thorough annealing at $T_a>\tau_g$, these films still display some reversible PD, but no PB. Partial PB occurs at any $T>T_o$ at which PD was achieved. Total PB occurs at $T_a$. This is due to the instability of their structure to heating. The vapour of A$\delta_4[S,Se]$ at $T_a$ contains no A$\delta_4[S,Se]$ molecules, but A$\delta_4[S,Se]$ and A$\delta_4[S,Se]$ molecules /10/. Annealing at $T_a$ thus induces separation into A$\delta_4[S,Se]$ molecules and a (S,Se)-rich network. This structure freezes-in at cooling into a non-equilibrium state. Light reestablishes the ground state inducing PD by polymerization, because both As-richer and Se-richer glasses have larger optical gaps than A$\delta_4$ (fig.2); it can however not induce bleaching. Heating progressively depolymerizes the structure, thus inducing after cooling a higher transmissivity. Thermally induced changes in the ring/chain ratio could explain the similar low-temperature PD and PB phenomena in a-Se.

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