

PHOTODARKENING AND LIGHT INDUCED ANISOTROPY IN CHALCOGENIDE GLASSES

I. Janossy, A. Jákli and J. Hajtó*

Central Research Institute For Physics, H-1525 Budapest 114, P.O.B.49, Hungary

(Received May 15, 1984 by A. Zawadowski)

A unified description of photodarkening and light induced anisotropy in chalcogenide glasses is presented in terms of bistable atomic configurations

It is a well established fact, that certain amorphous chalcogenide semiconductors show structural changes under light illumination¹. There is an irreversible part of the structural changes which occurs in vapour deposited films, prior to any heat treatment^{2,3}. On the other hand in melt-quenched glasses or in well-annealed evaporated films so-called reversible structural changes occur. Light illumination, well below the glass transition temperature leads to changes of a number of physical parameters within the illuminated spot, such as optical constants, density etc. Heat treatment near the glass transition temperature restores the initial structure and all parameters become the same as before the illumination. This cycle can be repeated a lot of times.

Photostructural changes are most easily observed through the variation of the absorption coefficient, α . During reversible photostructural changes light irradiation always leads to an increase of α (photodarkening). Furthermore it is observed, that when the illumination is carried out with polarized light, the irradiated spot becomes anisotropic^{4,5,6}. The optical axis of the anisotropic structure is determined by the direction of the polarization of the illuminating light beam. The optical axis can be reoriented a lot of times into any direction by rotation of the direction of the polarization. The induced anisotropy can be erased by unpolarized or circularly polarized light⁶.

To illustrate the effects mentioned above, in Fig.1 we present experimental results obtained for an annealed GeSe₂ film. The absorption coefficients were determined from reflection and transmission measurements, using a dye laser. The film thickness was chosen to be large enough to avoid interference effects. (The dichroism data presented in Ref.(6) may be influenced by interference effects). The anisotropy of the absorption coefficient (dichroism) de-

termined as $\alpha_{\parallel} - \alpha_{\perp}$, is negative and is around 10% of the photodarkening (α_{\parallel} and α_{\perp} are the absorption coefficients for a light beam with polarization parallel and perpendicular to the polarization of the illuminating light beam, resp.).

Photodarkening has been explained by assuming that in chalcogenide glasses local bistable atomic configurations are present^{1,7}. A similar assumption was made by us to account for the light induced anisotropy⁶. The aim of the present letter is to provide a unified description of photodarkening and induced

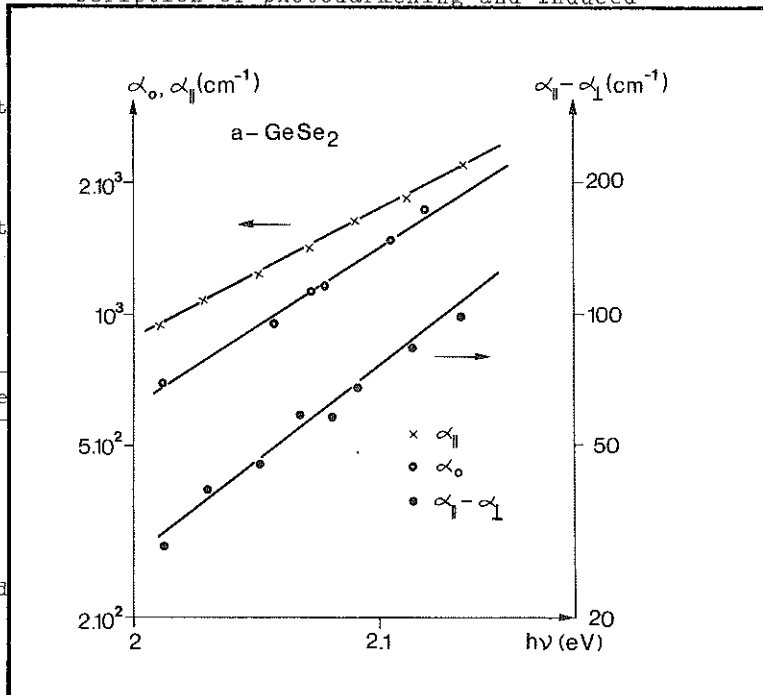


Fig.1 Experimental results for a-GeSe₂. Film thickness 20 μm. α_0 : absorption coefficient after annealing. α_{\parallel} and α_{\perp} : absorption coefficients after illumination at $\lambda=600$ nm, for 4^h , at power density $12W/cm^2$.

* present address: University of Edinburgh Department of Electrical Engineering Edinburgh, EH9 3JL U.K.

anisotropy by generalizing the previous models.

The existence of bistable configurations (or double-well potentials) is assumed in a number of glasses in order to explain the linear heat capacity and related phenomena observed at low temperatures⁸. We emphasize however that the bistable configurations which are responsible for photostructural changes should differ from those which cause e.g. the linear heat capacity in the following respect. In the latter case there is a continuous distribution of the height of the potential barriers separating the two minima, thus tunneling transitions occur even at very low temperatures. In case of photostructural changes we assume, that the potential barriers have a more or less well-defined height, and this is large enough to prevent thermal transitions even at room temperatures. Such transitions can occur only near the glass transition temperature.

The concept of bistable centres was applied to describe photodarkening quantitatively by Kolobov et.al.⁷. In this model it is assumed that after heat treatment all the bistable atoms sit in the deeper energy minimum. Light irradiation at room temperature makes possible transitions from the ground state to the metastable configuration of the given centre. The transition consists of two steps: an incoming photon excites an electron and this induces the relaxation of the surrounding atoms to a new (metastable) equilibrium position. Of course the inverse process, i.e. transition from the metastable state to the ground state can also occur in a similar way. After a long illumination an equilibrium establishes, i.e. the rate of transitions from the ground state equals to that of the inverse transitions. Denoting by w_{12} the probability of the first transition and by w_{21} that of the inverse one, the equilibrium fraction of the atoms in the metastable state (n_2) is

$$n_2 = \frac{w_{12}}{w_{12} + w_{21}} \quad /1/$$

The probabilities w_{12} and w_{21} are proportional to $(\mu_1 E)^2$ and $(\mu_2 E)^2$ where μ_1 and μ_2 are the dipole matrix elements for the electronic excitations in the stable and metastable configurations resp.; E is the field strength of the irradiating light beam. Denoting the proportionality factors by A_1 and A_2 we can write.

$$w_{12} = A_1 (\mu_1 E)^2 ; \quad w_{21} = A_2 (\mu_2 E)^2 \quad /2/$$

It is reasonable to assume that not only the magnitude of μ_1 and μ_2 differs but their directions too. We shall show that this circumstance leads to light induced anisotropy.

Although, for the time being there is no generally accepted microscopic model of bistable atomic configurations, it is evident that these should be anisotropic. We found convenient to ascribe an "orientation" to the bistable centres in the following way. Let us choose as "reference" centres those bistable configurations for which μ_1 and μ_2 lie in the XY plane and the bisector of μ_1 and μ_2 coincides with the X axis. The orientation of a given bistable centre can be characterized by the orthogonal transformation, Ω which transforms a reference centre to the given one. Ω can be expressed with the help of 3 independent parameters, e.g. by the Euler angles⁹. Assuming a uniform distribution of orientations, the number of bistable centres with orientation between Ω and $\Omega + d\Omega$ in unit volume is $N/8\pi^2 \cdot d\Omega$, where N is the total number of the centres per unit volume. /In terms of the Euler angles $d\Omega = \sin\theta d\theta d\phi dy/$.

In the present paper we assume for simplicity that all bistable centres are identical, apart from their orientations. In a reference centre the dipole matrix elements are $\mu_1^{(0)}$ and $\mu_2^{(0)}$; in a centre with orientation Ω these are $\mu_1 = \Omega \mu_1^{(0)}$ and $\mu_2 = \Omega \mu_2^{(0)}$.

The isotropy of the amorphous film after annealing originates from the uniform distribution of the orientations. However after illumination, n_2 depends on the orientation of the bistable centre with respect to the polarization direction of the light beam. From Eqs./1/ and /2/

$$n_2(\Omega) = A_1 (\mu_1 E)^2 / (A_1 (\mu_1 E)^2 + A_2 (\mu_2 E)^2) \quad /3/$$

The dependence of n_2 on the orientation implies macroscopic² anisotropy of the illuminated spot.

If the density of the bistable centres is small enough, it can be assumed that these give independent contributions to the change of any physical parameter. In this case the dielectric tensor is

$$\underline{\epsilon} = \epsilon_0 \underline{1} + \frac{N}{8\pi^2} \int n_2(\Omega) \underline{\mu} \underline{\mu} \underline{v}_0 \underline{v}_0^{-1} d\Omega \quad /4/$$

where ϵ_0 is the dielectric permittivity of the annealed sample.

\underline{v}_0 is a symmetric tensor, which gives the change of $\underline{\epsilon}$ during a transition from the stable state to the metastable one in a reference centre. \underline{v}_0 contains 6 independent parameters, which could be determined only on the basis of a microscopic model. As we shall see below, in fact only 3 parameters enter in the expression for $\underline{\epsilon}$, which we shall consider here as phenomenological coefficients.

The imaginary part of $\underline{\epsilon}$ at optical frequencies determines the absorption coefficients. For symmetry reasons the illuminated spot becomes optically un-

iaxial, so the equilibrium form of $\underline{\epsilon}$ can be written as

$$\epsilon_{ij} = \epsilon_{\perp} \delta_{ij} + (\epsilon_{\parallel} - \epsilon_{\perp}) e_i e_j \quad /5/$$

where ϵ_{\perp} and ϵ_{\parallel} denote the dielectric permittivity perpendicular and parallel to the unit vector \underline{e} ; \underline{e} lies in the direction of the polarization of the irradiating light beam. Evaluating the integral in Eq. /4/ we get

$$\text{Tr} \underline{\epsilon} = \epsilon_{\parallel} + 2\epsilon_{\perp} = 3\epsilon_0 + N \text{Tr} v_0 f_0(\beta, M) \quad /6.a/$$

$$\epsilon_{\parallel} - \epsilon_{\perp} = N (v_0^{xx} - v_0^{yy}) f_1(\beta, M) + v_0^{xy} f_2(\beta, M) \quad /6.b/$$

Here β is the angle between $\underline{\mu}_1$ and $\underline{\mu}_2$; $M^2 = A_1 \mu_1^2 / (A_2 \mu_2^2)$; the f functions are given in Figs.2 and 3. Eq./6.a/ describes photodarkening, while Eq./6.b/ gives the induced anisotropy.

We note that while v_0 is a function of the wavelength at which the optical constants are measured, the f functions depend on the wavelength at which the illumination is carried out. According to our model, the dependence of photodarkening and induced anisotropy on the wavelength of illumination/measured at fixed wavelength/ gives information on the wavelength dependence of the parameter $M = (A_1 \mu_1^2 / (A_2 \mu_2^2))^{1/2}$. As f_0 is more or less linear in M , from photodarkening measurements the relative variation of M with wavelength can be estimated. On the contrary f_1 and f_2 are far from linear, so anisotropy measurements /in conjunction with photodarkening measurements/ provide information on the absolute value of M .

To demonstrate this possibility, we compared the photoinduced changes

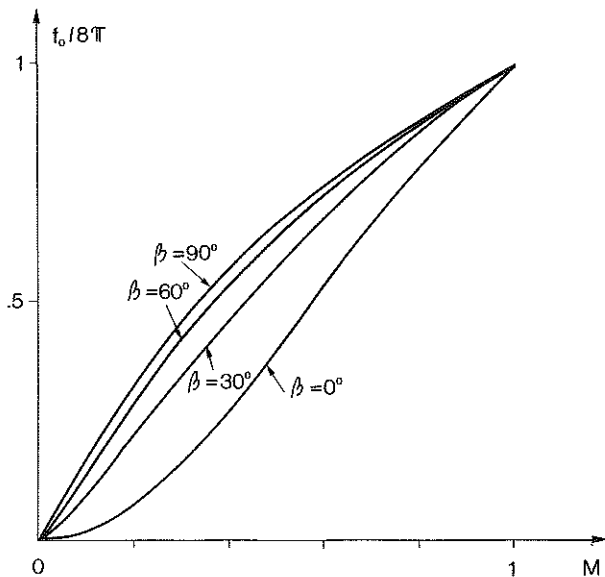


Fig.2 f_0 as a function of M and β .

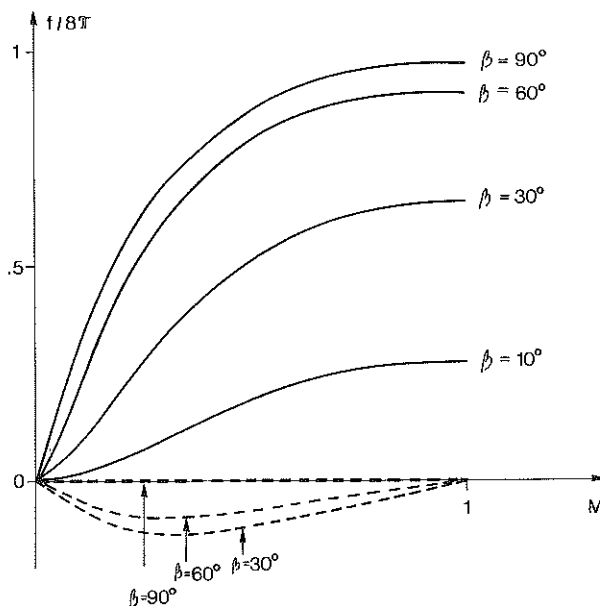


Fig.3 solid line: $f_2(M, \beta)$; dashed line $f_1(M, \beta)$.

in GeSe, at the wavelengths $\lambda_1 = 632$ nm and $\lambda_2 = 488$ nm (the optical constants were always measured at 488 nm). The first wavelength corresponds to a photon energy which is smaller than the optical gap, while for λ_2 the photon energy exceeds the gap. We found that photodarkening induced by λ_2 is approximately 40% larger than that for λ_1 . On the other hand we found that the two wavelengths induce approximately the same anisotropy, although the error of measurements in this case was rather large /10-15%. In any case, the difference between the anisotropies seems to be considerably smaller than that of the photodarkening. The results described above are consistent with the assumption that $M(\lambda_2) \approx 1$ and $M(\lambda_1) \approx 0.5$. /We assume that

$v_0^{xx} - v_0^{yy}$ is not considerably larger than v_0^{xy} . In this case the anisotropy is determined essentially by f_2 /Fig.3//.

The description of photostructural changes presented above implies that to every wavelength and state of polarization of the illuminating light there belongs an equilibrium (usually anisotropic) structure, which is determined by the n_2 / Ω distribution. Whatever is the initial structure, light irradiation establishes the equilibrium configuration belonging to the given wavelength and polarization. This fact makes possible to switch the amorphous film reversibly between different structures by changing the polarization / see reorientation experiments^{6/} or the wavelength. In accordance with this consideration, we

found in GeSe_2 that if a spot was first illuminated at the wavelength λ_2 , subsequent irradiation at λ_1 bleached the spot, i.e. α decreased by 40%.

As a summary, we think that the description of photostuctural changes in terms of bistable atomic configurations explains the main features of the phenomena. There is of course a number of way to improve the present model. E.g. it may be assumed that two electrons per centre can be excited to induce atomic rearrangements. These electrons may be the two bonding electrons

between a Se atom and the two neighbouring Ge atoms. A calculation, where we assumed that the magnitudes of the dipole matrix elements are equal for the two bonding electrons and that these are perpendicular to each other, gave very similar results to those presented in Fig. 2. Furthermore it seems likely that there is a distribution not only for the orientation of the bistable centers, but for other parameters like M and β too. This circumstance is important for the kinetics of photoinduced changes ⁶.

REFERENCES

- 1 K. TANAKA, Journ. of Non Cryst. Solids 35-36, 1023 (1980)
- 2 J.P. de NEUFVILLE in B.O. SERAPHIN (ed), Optical properties of Solids (North-Holland, Amsterdam, 1975/p.437)
- 3 S. RAJOGOPALAN, K.S. HARSHAVARDHAN, L.K. MALHOTRA and K.L. CHOPRA, Journal of Non-Cryst. Solids 50, 29 (1982)
- 4 V. G. ZHDANOV, B.T. KOLOMIETS, V.M. LYUBIN and V.K. MALINOVSKI, Phys. Stat. Sol. (a) 52, 621 (1979)
- 5 J. HAJTO and P.J.S. EWEN, Phys. Stat. Sol. (a) 54, 385 (1979)
- 6 J. HAJTO, I. JANOSSY and G. FORGACS, J. Phys. 15, 6293 (1982)
- 7 A.V. KOLOBOV, B.T. KOLOMIETS, B.T. KONSTANTINOV and V.M. LYUBIN, Journ. of Non-Cryst. Solids 45, 335 (1981)
- 8 W.A. PHILLIPS (ed), Amorphous Solids, Low-Temperature Properties (Topics in Current Physics Vol. 24, Springer-Verlag Berlin, 1981).
- 9 G.A. KORN and T.M. KORN Mathematical Handbook for Scientists and Engineers (MC.Graw-Hill. New York, 1961) p.413