Thermooptical transitions during photostructural transformations in chalcogenide glassy semiconductors (CGS)

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The temperature threshold for photo-lightening in As_3Se_2 films is found. A configuration model is developed for two CGS structural states, between which thermo-optical transitions take place. The model explains both new and earlier known results from the study of photostimulated processes in CGS.

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Reversible photostimulated changes in the properties of CGS have long received the attention of researchers as an extremely interesting physical phenomenon and as the basis for creating unique light-detecting media.[1-3] Most researchers assume that reversible structural changes form the basis of photostimulated processes. The effect of light, causing a weakening of the interatomic bonds, leads to a structural transition in CGS from the ground state to some metastable state, accompanied by a darkening of the sample. Heating to temperatures close to the melting point causes a reversible transition (thermolightening).

Not long ago it was shown that lightening of pre-darkened CGS samples may also be carried out under the influence of the light which induced the darkening [4-7] To do this the illuminating should be carried out at temperatures which somewhat exceed the temperature of the initial light interaction (thermostimulated photo-lightening--TP).

These facts were used as an argument by Vlasov *et al.*[7] for rejecting the idea of photostructural transformations and in the setting up a model of "multiple-charge" centers. On the other hand, Zhdanov and Malinovskiĭ[8] suggested a model of an infinite number of CGS structural states, each of which corresponds to a definite temperature.

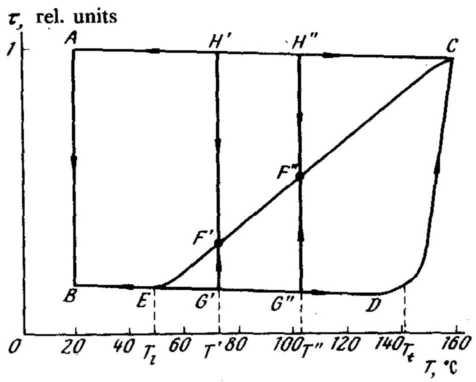

FIG. 1. Dependence of the transition (τ) for exposed and unexposed regions of glassy As_3Se_2 films on temperature.

In investigating TP we obtained fundamentally new results permitting us to apply a configuration model[9] of two stable states for CGS atomic centers, between which thermooptical transitions take place, in order to explain the reversible changes in CGS properties.

The experiments were carried out with CGS films composed of As_3Se_2 by evaporation in a vacuum, exposed to the light of a He-Ne laser ($\lambda = 633$ nm) at different temperatures. The transmission of the films was detected at the same wavelength.

The results of the investigation are given in Fig. 1. The line AB represents photodarkening at room temperature. The lines AC and $BEDC$ reproduce, respectively, the temperature variation (at a heating rate of 3 deg/min) of transmission for the exposed and unexposed portions of the film. $H'F'$ and $H''F''$ (photodarkening) and $G'F'$ and $G''F''$ (photolightening) correspond to a change in the transmission of the unexposed and exposed portions of the film under the effect of the light at temperatures T' and T''. $BEF'F''C$ thus shows steady-state values of the transmission of a sample subject to the effect of light at different temperatures. Clearly, the photolightening effect increases with the temperature and, what is very important, has a temperature threshold.

What turns out to be interesting is the fact that the final value for the film transmission (the points on the curve $BEF'F''C$) is determined by the effect of the light and temperature, and is independent of the initial state (H or G) of the film. This result is in good agreement with the data in Ref. 6. Section DC characterizes the thermal lightening of the film in darkness, which increases sharply at $T_t \approx 150\,^{\circ}$C.

The data given and, in particular, the existence of a TP temperature threshold, are difficult to interpret within the framework of the concepts described in Refs. 7 and 8. However, they may be understood on the basis of a configuration model for two stable states of the atomic centers: a ground state and a metastable state. For the As_3Se_2 material which we studied, by the ground state may be understood a structural state where all the arsenic atoms are chemically bound with their surroundings, while by the metastable state may be understood the state where the excess (in comparison with the stoichiometric composition) arsenic atoms appear to be torn out of the basic lattice of the substance.

The correlation of the centers in the ground and metastable states determines, as in a solid solution, the real structure of the substance along with its physico-chemical parameters, including optical transmission.

A certain equilibrium configuration coordinate Q, and equilibrium energy E^{10} correspond to the atomic center in the ground state and, respectively, Q_2 and E_{20} (Fig. 2) in the metastable state.

We shall assume that Q_1 and Q_2 are quite different, as is shown in Fig. 2. Possible thermal and optical transitions between the two states are designated by I_T and I_0, respectively.

In the case when the parabolas corresponding to the ground and metastable states differ significantly in terms of their slopes (Fig. 2), a situation is possible where at a low temperature the photon energy is adequate for a transition of the atomic center

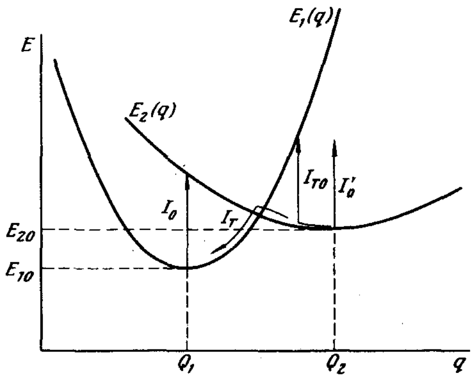

FIG. 2. Configuration diagram for CGS ground an metastable states.

from the ground to the metastable state, but is not adequate for the reverse transition. In this case the direct process dominates, leading to photodarkening.

A reversible optical transition is effectively "included" only for a temperature T_l (TP threshold), when the photon energy is absorbed by an atomic center having a certain thermal excitation. We shall designate such a transition as thermooptical, I_{TO}. For $T_l < T < T_t$ the population of the metastable state is determined only by the relationship between the direct and reverse thermooptical transition probabilities. At T_t an effective thermal transition of the atomic centers to the ground state begins (thermal resistance).

Therefore, on the basis of the model developed, it is possible to understand the existence of a TP temperature threshold, and also the fact that the steady-state value of the film transmission is independent of its initial state.

According to the model, the following condition must be satisfied for reverse themocouple transition (see Fig. 2):

$$E_2(q) + \hbar\omega = E_1(q),$$

i.e., by increasing the photon energy TP should begin at lower temperatures. Our control experiments for exposure to light with $\lambda = 480$ nm have confirmed this hypothesis: the TP threshold is shifted in this case to the region of lower temperatures by more than 20 degrees.

This model has also permitted us to predict a number of other facts verified experimentally (the effect of the light intensity on the final state of the sample, the departure from the law of interchangeability of the light intensity and the duration of its effect, etc.).

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