Chalcogenide Letters Vol. 9, No. 2, February 2012, p. 79 - 84

OPTICAL MEMORY IN CHALCOGENIDE GLASSES

V.K. MALINOVSKY*, N.V. SUROVTSEV

Institute of Automation and Electrometry Siberian Branch of the Russian Academy of Sciences 630090, Acad. Koptug Pr. 1, Novosibirsk, Russia

Some glasses are light-sensitive, being possible candidates for optical memory. Chalcogenide glasses display the highest photoinduced effects among other materials, their photosensitivity does not involve chemical reactions. In spite of the long history of experimental and theoretical studies, there are still no well-accepted models for photoinduced changes in chalcogenide glasses. In the present work it is demonstrated that a simple approach, implying photoinduced local heating, allows one to explain basic features of photoinduced changes in chalcogenide glasses. The model uses the feature that glasses at nanometer scales are inhomogeneous, consisting of nanoregions. The structure of covalent glasses at nanometer scales in a certain sense is similar to the crystalline-like order, which in the case of chalcogenide glasses implies the existence of polarization dichroism of absorption. In the framework of the model, photo-induced changes (both scalar and vector ones) occur in each single act of light absorption. They are related to reconstruction of nanoregions owing to local heating and subsequent quenching. Vector changes (in addition to scalar changes) occur because of selective absorption predominantly in those nanoregions whose maximum absorption axis coincides with the direction of polarization in the light wave.

(Received November 30, 2011; Accepted February 15, 2012)

Keywords: Glasses nanoregions; Photoinduced phenomena; Optical memory

1. Introduction

The idea of creating an optical computer was extremely popular approximately 40 years ago. One of the main components of the new elementary base was expected to be a material whose optical properties had to be changed many times within a short time with minimum energy expenses. Active searching for such materials and studying photo-induced phenomena in these materials were started that time and are still urgent at present.

It seems that the greatest changes in optical properties are observed in the case of illumination of chalcogenide vitreous semiconductor (ChVS) films. Light-induced changes in ChVS optical properties are either scalar (shift of the absorption edge toward lower energies) or vector (emergence of macroscopic polarization dichroism and birefringence). A usual trend to explain photo-induced properties of chalcogenides and their compounds is considering specific bistable defects, which were called the valence alternation pairs (VAPs) [1]. Origination of VAPs is associated with the structure of the outer shells of atoms forming the compound. All possible VAP types in chalcogenides and also in compounds with tetrahedral coordination of atoms were analyzed in detail in [2].

A critical viewpoint of models proposed to explain photo-induced effects in chalcogenide glasses was presented recently by Fritzsche [3], one of the founders of the science of photo-induced transformations in ChVS. He believes that there are two kinds of effects inducing changes in ChVS optical properties. Effects of the first type are related to reconstruction of bistable centers, whereas effects of the second type are associated with reconstruction of the entire glass structure.

---

*Corresponding author: lab21@iae.nsk.su

In our work we present a model, which assumes reconstruction of the entire glass structure after the photon absorption, but the model does not involve the language of switching of specific bistable centers. Such a model approach was proposed in [4] previously and assumed nanoscale inhomogeneities in the glassy structure. Now more information is known about the glassy structure, and we will briefly review the basic statements of the model. Is the assumption of nanometer inhomogeneities still valid and how are they manifested in experiments? What is the mechanism of photo-structural changes? Is the photon energy enough to heat a nanoregion above the glass transition temperature?

2. On the structure of glasses

In contrast to crystals, atom positions in glasses are not ideally ordered, and there is no long-range translational order. But does it mean that there is no any ordering in atom positions in the glasses? Extremely different descriptions of the glassy structure as microcrystallites (microcrystallite glass theory [5]) and as a continuously random network [6] are known. Now it seems that the glass structure neither contains perfect nanocrystallites separated by a loose network nor possesses absolute homogeneity in terms of density or elastic constants. Hypothesis of nanometer inhomogeneities of glass-formers is known to be useful in description of many glass-former properties [7].

It is clear that the dense structure of condensed matter dictates a certain order at least for the nearest-atom positions. Directed bonds of covalent glass seem to extend the local order to some intermediate range. We will use the name “nanoregions” for the distinctive structure organization of atoms at the nanometer scale. The problem of “nanoregions” belongs to the problem of the intermediate order in the glassy structure. The ordering domain covers, according to estimates of different authors, from several tens to one hundred of atoms and has a scale of ~ 1 nm. Because of a small scale, the substance remains X-ray amorphous, but is there any experimental evidence of the intermediate order in the glassy structure?

Experimental data testifying to the existence of nanoregions in glasses are somewhat indirect. These data include:

a) pre-peak in the radial distribution function obtained from X-ray structural data [8]. The pre-peak width was found to be related to the characteristic size D. The value of D is approximately estimated from 1 to 4 nm for various glasses;

b) excess heat capacity $C(T)$ and a "plateau" in the temperature dependence of thermal conductivity $\chi(T)$ in the interval $T = 10 - 20$ K, which are observed in all glasses and amorphous materials. According to the models developed in [9, 10], the low-temperature anomalies are related to the correlation radius of the structure $R_c \sim 1$ nm. In [11], these features of $C(T)$ and $\chi(T)$ are attributed to quasi-local vibrations of atomic groups;

c) low-frequency peak (boson peak) found in Raman scattering spectra of light in all amorphous materials [12]. The maximum frequency of the boson peak allows determining the correlation radius of the structure [13]. It was demonstrated [14] that the boson peak has a universal shape for a large number of glasses with different chemical compositions and corresponds approximately to one value $R_c \sim 1$ nm. If the characteristic size of nanoregions is somewhat different in different glasses, then these differences have to be simultaneously observed in experiments with structural factor measurements and in estimates based on the low-frequency Raman scattering of light. Indeed, it was shown [15] that the estimates based on the structural factor and on the Raman scattering are the same with a good precision. Moreover, if one can change the characteristic size of the nanoregions in a chemically unchanged substance, then one have simultaneously to change the boson peak position and the width of the pre-peak in structural measurement. Experiments performed with vitreous SiO_2 modified by high pressures confirmed this rigorous correspondence [16].

Thus, there is experimental evidence for the existence of nanoregions, within which a strong correlation of atomic positions exists. It was assumed in [17] that photo-induced effects in chalcogenide glasses are related to transformation of nanoregions. Is the size of this nanoregion the same as the above-made estimates? The idea of nanoregions transformed under photon absorption is as follows [17].

The reconstructed volume V_r can be determined from the assumption that the transition from one state (e.g., annealed state) to another occurs independently in each nanoregion. The idea is that if each nanoregion absorbs one and only one photon, the measured number of absorbed quanta N_f needed to transform the chalcogenide glass volume V_s allows one to find $V_r = V_s / N_f$. In reality, the measured quantity is the curve of the photo-induced change versus the number of absorbed quanta [17]. This dependence, being extrapolated to small numbers of absorbed quanta, when a probability of a nanoregion to absorb more than one photon is negligible, provides the possibility of estimating V_r.

With this idea in mind, we can write the optical density of ChVS films during photo-darkening

$$D = (1 - \alpha)\, D_o + \alpha D_1,$$

where D_o and D_1 are the optical densities of the initial and final states, and α is the fraction of the final state in a unit volume of the film, whence it follows that

$$\alpha\,(N) = \frac{D(N) - D_o}{D_1 - D_o},$$

where N is the number of absorbed photons. Thus, N_f can be found from intersection of the tangent line to the curve $D(N)$ at the limit $N \to 0$ and D_1, providing the estimate V_r.

Such measurements were performed on As_2S_3 films in ref. [17]. It was found that $V_r \sim 10^{-22}$ cm^3. In that work it was noted that V_r is weakly temperature-dependent far below the glass transition temperature T_g and significantly increases as the temperature approaches T_g. The linear size of the estimated V_r is 0.5 nm. Thus, the estimated value of the nanoregion size is of the same order as the assumption made.

3. Why do ChVS optical properties change?

Thus, what occurs in the glass nanoregion during absorption of a light quantum? What for and how is its energy spent? Several models were proposed to answer these questions. The most logical and complete explanation of experimental data is provided by the model of local heating or "thermal flashes" [17]. Our version of this model has the following features. An electron excited by light with energy above the absorption edge (~ 3 eV) has a high probability to recombine in a non-radiative manner and/or transfer significant part of its energy to phonon creation. For an estimation, we believe that about $Q \sim 1$ eV is emitted as high-frequency phonons, and the time of the non-radiative transition in a strongly anharmonic matrix is small ($\tau < 10^{-11}$ s). This assumption is supported by the fact that the Stokes shift of the luminescence line ~ 1 eV occurs in $\tau_{St} < 10^{-11}$ s after the excitation [18]. The initial spectrum of phonons has a noticeably non-Planck form (see, e.g., experimental data [19]), then high-frequency phonons decompose into phonons with lower frequencies, and the Planck and equilibrium distributions are gradually reached.

The nanometer inhomogeneity structure of glasses has a consequence that the energy of high-frequency phonons excited by photo-induced electrons is localized in nanoregions. Therefore, light quantum absorption leads to local heating of a nanoregion. For the time of heat localization, the nanoregion is converted to a state with an effective temperature T_{eff}. If $T_{eff} > T_g$, the viscosity drastically decreases, and the nanoregion properties become similar to liquid properties. New configuration locations of atoms are easily formed, which may lead to breakdown and switching of bonds. It should be emphasized that no specific light-induced turning of atomic groups is meant here: the atoms occupy new positions in a purely statistical aspect. The disordering region necessary for bond breakdown or switching includes approximately 100 atoms. It is of interest that this number is almost independent of the chemical nature of materials [20].

Owing to subsequent rapid cooling of the nanoregion (rapid with respect to usual times of cooling of a macroscopic sample after annealing at T_g), the nanoregion structure is fixed in the disordered state corresponding to a fictive temperature above T_g of well-annealed glass. The sample becomes darker because the forbidden band width is smaller in a more disordered state.

The local heating model predicts that the changes arising in glasses under the action of light have to be similar to the changes that occur during thermal quenching [21]. The analogy between these two processes has been frequently emphasized by various researchers. Experiments show that the light action, as well as quenching of annealed glasses, reduces the optical width of the forbidden band, increases the absorption coefficient and sample thickness, decreases the viscosity, etc. Moreover, the maximum values of photo-induced changes are observed in compositions that are most sensitive to thermal treatment.

4. Changes in ChVS optical properties during long-time irradiation

After long-time irradiation of the sample, its optical properties seem to cease changing: photo-induced darkening reaches a saturated level. The absorption edge does not move any longer. Nevertheless, absorption of light quanta is continued. What is the absorbed energy spent for?

We performed experiments with polarized light and found [4] that an initially isotropic film after its irradiation by polarized light transforms to a uniaxial crystal with a rather high birefringence index ($\Delta n \sim 10^{-3}$). If the sample is irradiated until its saturation with one polarization direction in the light wave and then the polarization plane is turned by $\pi/2$, a new axis also turned by $\pi/2$ appears. The experiments with anisotropy rewriting were performed at the liquid-nitrogen, room, and elevated temperatures. The possibility of multiple reversible photo-rewriting of anisotropy in ChVS films directly indicates that photo-induced changes in these films proceed as long as irradiation is continued and are not finalized by the stage of shifting of the absorption edge before saturation.

In the case of long-time irradiation, we deal with structural reconstructions, which definitely trace the light polarization. Such a situation is possible only if macrosopically isotropic chalcogenide film consists of nanometer optically anisotropic structural elements, obeying polarization dichroism for absorption. Macroscopical isotropy is fulfilled by equiprobable orientations of absorption axis of different nanoregions. The dichroism of these structural elements is similar to the dichroism of the corresponding crystals. This assumption is based on the qualitative coincidence of the photo-induced dichroism spectra in ChVS films with the dichroism spectra in the corresponding crystals [22]. Absorption of linearly polarized light by an anisotropic structural element substantially depends on the mutual orientation of its dichroic axis and the light polarization plane, which results in spatially inhomogeneous absorption. After photon absorption and heating of the nanoregion to $T_{eff} > T_g$, the nanoregion structure is reconstructed in such a manner that it forgets its initial orientation and the dicroic axis is fixed in an arbitrary (random) direction. As a result of structural changes under the action of linearly polarized light, there appear excess structural elements whose maximum absorption axis is aligned normal to the exciting light polarization plane, which is responsible for macroscopic photo-induced anisotropy. Thus, the light polarization turning, even after long-time irradiation, leads to vector photo-induced effects.

It should be emphasized that photo-induced anisotropy is not a specific feature of the ChVS film state: a similar phenomenon was observed in massive As_2S_3 glasses and in photo-sensitive emulsion layers of As_2S_3 dispersed in gelatin [23]. It is important to emphasize that, although the nanoregion existence in the glassy structure can be evidenced by various experimental techniques, anisotropic features of nanoregions are not revealed. Photo-induced vector effects in chalcogenide glasses provide a unique possibility of probing anisotropic features of the glassy structure at the nanometer scale.

5. Is the light quantum energy sufficient for photo-induced transformation of nanoregions?

Thus, the driving force of photo-induced transformations in ChVS films is the energy of absorbed photons, transformed to vibrations localized on structural nanoregions of glass. At least Q ~ 1 eV is transformed to heat, as discussed above. Is the energy Q ~ 1 eV sufficient to heat the nanoregion to $T > T_g$?

Let us estimate the temperature of heating of the nanoregion of chalcogenide glass during photon absorption. The experimental estimate of the volume heated by one photon is $V_r \sim 10^{-22}$ cm^3. This value is obtained by estimating the necessary number of quanta for photo-induced changes in a known volume of chalcogenide glass.

To find T_{eff}, it is necessary to know the heat capacity of the nanoregion. The greater the heat capacity, the smaller the temperature increase ΔT of nanoregion heated by one photon for a given Q. The heat capacity of condensed media increases with increasing temperature and reaches its limiting value $C_v = 3k_B N_v$, where C_v is the molar heat capacity, k_B is the Boltzmann constant, and N_v is the number of atoms in the heated area (Dulong-Petit law). The molar weight of arsenic sulphide is $\mu = 246$ g/mole. Knowing the arsenic sulphide density ($\rho = 3.4$ g/cm^3), we can find the number of moles in the nanoregion heated by one photon $n = V_r \cdot \rho / \mu = 1.4 \cdot 10^{-24}$. The number of atoms in the nanoregion is found by using the Avogadro number (N_A) and the number of atoms in the substance formulas (5, formula As_2S_3), i.e., $N_v = 5N_A n = 4.2$ (it is seen that the effective estimate yields a smaller number of atoms than the formula has). Thus, the heat capacity of the nanoregion in the high-temperature limit is $C_v^{ex} = 3k_B N_v = 1.8 \cdot 10^{-22} J/K = 1.1 \cdot 10^{-3} eV/K$.

Knowing the photon energy converted to heat (Q ~ 1 eV) and the heat capacity of the nanoregion ($1.1 \cdot 10^{-3}$ eV/K), we obtain the nanoregion overheating temperature ΔT equal to 900 K, T_{eff} is the sum of the initial sample temperature and ΔT. The value of ΔT found is more than enough to convert the nanoregion from the vitreous to the liquid state. Certainly, this estimate is rather rough, but it allows us to feel clearly the characteristic order of these quantities and to verify that the energy in the model considered is sufficient for heating the nanoregion above T_g.

Which factors can be used to correct this estimate? The main source of errors is estimation of the size of the area heated by one photon. If some photons do not participate in photo-transformation of this area for certain reasons, then the transformation area in reality can be somewhat greater, which reduces ΔT. On the other hand, the nanoregion size (~ 1 nm), estimated on the basis of other experiments corresponds to $V_r \approx 10^{-21}\ cm^3$ [14], which qualitatively agrees with the estimate based on the photo-induced effect, but higher by factor 10. Therefore, in this case our estimate ΔT is overestimated by a factor of 10.

There are some factors that lead, vice versa, to higher estimation of ΔT. The heat capacity of arsenic sulphide at room temperature is approximately 2-3 times lower than the Dulong-Petit law, which increases the estimation of ΔT by a factor of 2-3. Another important aspect discussed in [24] is the non-Planck spectrum of phonons under local heating, which may lead to more intense local displacement of atoms, resulting (in terms of temperature) in an increase in ΔT.

Factors decreasing ΔT can be comparatively fast departure of some part of phonons from the heated area (rapid decomposition into long-wave phonons) and reduction of the photon energy fraction spent on nanoregion heating. Thus, there are many poorly formalized factors that do not allow an accurate estimate of ΔT to be made. Nevertheless, the large margin of the rough estimate (900 K) allows us to assume that heating to one or two hundred degrees is fairly realistic, which is obviously sufficient to convert the nanoregion into the liquid state.

In the local heating model, ΔT sufficient for converting the nanoregion to the liquid state is different for different temperatures of chalcogenide glass. In the range close to T_g, the photon energy transformed to heat may turn out to be sufficient not only for heating one nanoregion above T_g, but also a certain area outside this region. At low temperatures, the photon energy is sufficient to heat only one nanoregion to a temperature higher than T_g, and the sample volume transformed by the photon is independent of temperature. Therefore, we can expect that V_r is weakly dependent on temperature for low temperatures and increases near T_g. This expectation is in the agreement with experimental data of [17].

6. Conclusions

A simple approach for photo-induced changes in chalcogenide glasses is reviewed. This approach takes into account the inhomogeneity of the glassy structure at the nanometer scale, which consists of nanoregions. Existence of nanoregions is evidenced by various experimental techniques. In the framework of the model, photo-induced effects in chalcogenide glasses are caused by heating of the nanoregion during light quantum absorption above the glass transition temperature. Subsequent quenching of nanoregions from the liquid state fixes the photo-induced transformation. It is shown that in the case of chalcogenide glasses the reasonable estimations indeed lead to such heating.

It seems that the nanometer structure of chalcogenide glasses is reminiscence of its crystalline analog, implying the polarization dichroism for nanoregions. In the framework of the model, photo-induced vector changes occur because of selective absorption predominantly in those nanoregions whose maximum absorption axis coincides with the direction of polarization in the light wave. The model explains the existence of photo-induced vector effects even after long-time irradiation of the chalcogenide sample.

References

[1] M. A. Kastner, D. Adler, H. Fritzsche, Phys. Rev. Lett. **37,** 1504 (1976).
[2] S. R. Elliot, E. D. Davis, J. Non-Cryst.Sol. **35-36,** 849 (1980).
[3] H. Fritzsche, Phys.Status Solidi B. **246** 1768 (2009).
[4] V. G. Zhdanov, B. T. Kolomietz, V. M. Lyubin, V. K. Malinovsky, Phys. Stat. Solidi (A) **52,** 621 (1979).
[5] A. A. Lebedev, presented in: Vitreous State, Proc. III All-Union Workshop, Leningrad: Acad, of Sci. of the USSR p. 7 (1960).
[6] W. H. Zachariasen, J. Chem. Phys. **3**, 162 (1935).
[7] V. K. Malinovsky, N. V. Surovtsev, Glass Physics and Chemistry **26**, 217 (2000).
[8] J. C. Phillips, J. Non-Cryst.Sol. **43**, 37(1981).
[9] B. Hüttner, W. Pompe, Phys. Stat. Sol. (B) **114**, 503 (1982).
[10] G. J. Morgan, D. J. Smith, J. Phys. C **7**, 649 (1974) 649.
[11] V. G. Karpov, D. A. Parshin, Zh. Eksp. Teor. Fiz. **88**, 2212 (1985).
[12] J. Jäckle, "Low-frequency Raman scattering in glasses", presented in *"Amorphous Solids: Low-Temperature Properties"*, edited by W.A. Phillips p.135 (Springer, Berlin, 1981).
[13] V. K. Malinovsky, A. P. Sokolov, Sol. St. Commun. **57**, 757 (1986).
[14] V. K. Malinovsky, V. N. Novikov, A. P. Sokolov, Usp. Fiz. Nauk 1**63**, 119 (1993).
[15] A. P. Sokolov, A. Kisliuk, M. Soltwisch, D. Quitmann, Phys. Rev. Lett. **69**, 1540 (1992).
[16] S. Sugai, A. Onodera, Phys. Rev. Lett. **77**, 4210 (1996).
[17] V. K. Malinovsky, V. G. Zhdanov, J. Non-Crystalline Solids. **51**, 31 (1982).
[18] W. A. Weinstein, T. E. Orlowskii, W. H. Knox, T. M. Nordlung, G. Monrou, Phys. Rev. B **26**, 4777 (1982).
[19] R. Baumgartner, M. Engelhardt, K. F. Renk, Phys. Lett. A **94**, 55 (1983).
[20] S. V. Nemilov, Fiz. Khim. Stekla **4**, 129 (1978).
[21] S. B. Mamedov, M. D. Mikhailov, P. M. Pecheritsyn, Fiz. Khim. Stekla **7**, 503 (1981).
[22] V.P. Zakharov, V. S. Gerasimenko, Structural Features of Semiconductors in the Amorphous State, Kiev, Naukova Dumka (1976).
[23] V. G. Zhdanov, V. K. Malinovsky, L. P. Nikolova, T. A. Todorov, Optics Commun. **34**, 329 (1979).
[24] V. K. Malinovsky, Yu. E. Nesterikhin, V. N. Novikov, A. P. Sokolov, Avtometriya **2**, 3 (1986).