The shift of the absorption edge of thin chalcogenide films with copper

S. R. LUKIĆ, D. M. PETROVIĆ, M. I. AVRAMOV
Institute of Physics, Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 4, 21000 Novi Sad, Serbia

E. MARQUEZ
Departamento de Fisica de la Materia Condensada, Facultad de Ciencias, Universidad de Cadiz, Apdo. 40, 11510 Puerto Real, Cadiz, Spain

Chalcogenide glasses possess interesting electrical and optical properties which make them candidates for various applications requiring, for example, electrical switching, light-induced phenomena, memory and transmission in the infrared spectral range.

These materials have received a great deal of interest as potential candidates for materials transmitting in the visible and close infrared part of the spectra, particularly the wavelengths of the He–Ne and CO_2 lasers [1].

Some amorphous semiconducting materials have recently been studied as potential media for storing optical information. One of the fundamental problems is the reversibility of these processes, and the mode of erasing the optical pulses recorded [2–4].

As part of our systematic investigations of multicomponent glass systems [1, 2, 5–7], the aim of this work is to present some of the results of optical characterization of Cu-containing chalcogenide thin films.

Thin-film samples were prepared by vacuum evaporation of powdered previously synthesized glassy material [6], onto cooled clean glass substrates.

Optical constants, along with some other physical and chemical properties of chalcogenide amorphous semiconductors (ChAS), change under illumination. The shift of the optical absorption edge caused by photostructural transformations is called photodarkening. This reversible effect is observed in chalcogenides such as a-As_xSe [8]. Under optical excitation the position of the absorption edge changes with time, eventually saturating at a value that, for a given wavelength of incident light, depends upon the level of irradiation and on temperature. If the level of irradiation is reduced, photobleaching occurs. If the temperature is raised above a critical value, complete thermal bleaching occurs.

The shift of the absorption edge is one of the indices indicating the quality of the reversibility of photorecording.

The quaternary amorphous Cu–As–Se–I system showed a high degree of transparency in the range 11 500–400 cm^{-1} [9]. The position of the absorption edge of the investigated glasses enabled the use of the He–Ne laser ($\lambda = 638.8$ nm) with a power flux of 40 $mW\,cm^{-2}$ as the effective source of radiation for studying the changes of the amplitude of optical recording on thin films. Films of type $Cu_x[(As_2Se_3)_{0.9}(AsI_3)_{0.1}]_{100-x}$ ($x = 0$, 5, 10 and 15 at %), about 1 μm thick, were analysed. The transparency of the films was also tested at the same wavelength, but using an attenuated laser beam.

In the range 600–1200 nm, the refractive index changes from 2.67 to 3.00 ± 0.07 [7]. At a given wavelength, it shows an increase with an increase in copper content in the sample. The absence of linearity in this dependence in the concentration interval to 15 at % Cu indicates that certain structural changes took place, which has also been confirmed by other methods [9]. Slightly lower values of refractive index of samples in the form of thin film with respect to the glass of the same composition were noticed. This effect occurs often in this type of complex system, since the structure of freshly prepared film does not correspond completely to the structure of initial glasses.

It is known that photo-induced changes in the optical parameters of thin films of some chalcogenide amorphous semiconductors can take place as the result of the irradiation of the sample by some wavelength, characteristic for the material. The initial characteristics of ChAS are restored by their thermal annealing near the softening temperature. Figs 1–4 show the dependence of transparencies of thin films of the system investigated on the wavelength. Fig. 1 represents the spectrum of a freshly-prepared film, Fig. 2 shows the same dependence for the same sample after laser exposure, while Fig. 3 shows the same dependence after annealing.

It was noticed that irradiation produced darkened regions. When as-evaporated film is irradiated by the He–Ne laser light, the absorption edge is shifted toward a longer wavelength (Fig. 2). If the film is annealed at about 150 °C, the absorption edge is shifted toward a shorter wavelength (Fig. 3). If the film is irradiated after this annealing, the absorption edge is shifted toward a longer wavelength again (Fig. 2). The experimental data show the shift of the absorption edge to higher wavelength of between 8 nm (for $x = 0$ at % Cu) to 27 nm (for $x = 15$ at % Cu) after the laser exposure, which corresponds to a change in the refractive index $\Delta n = 0.002–0.009$.

The quantitative characteristics of this effect are presented in Table I.

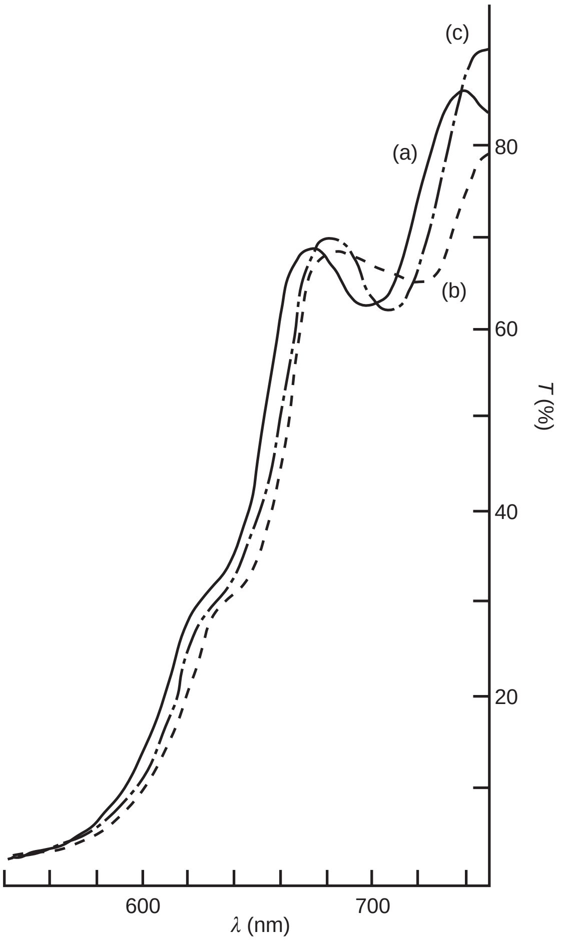

Figure 1 Shift of edge in optical transmission on illumination of the $(As_2Se_3)_{0.9}(AsI_3)_{0.1}$ film: (a) as-evaporated film, (b) He–Ne laser irradiated film and (c) thermally annealed film.

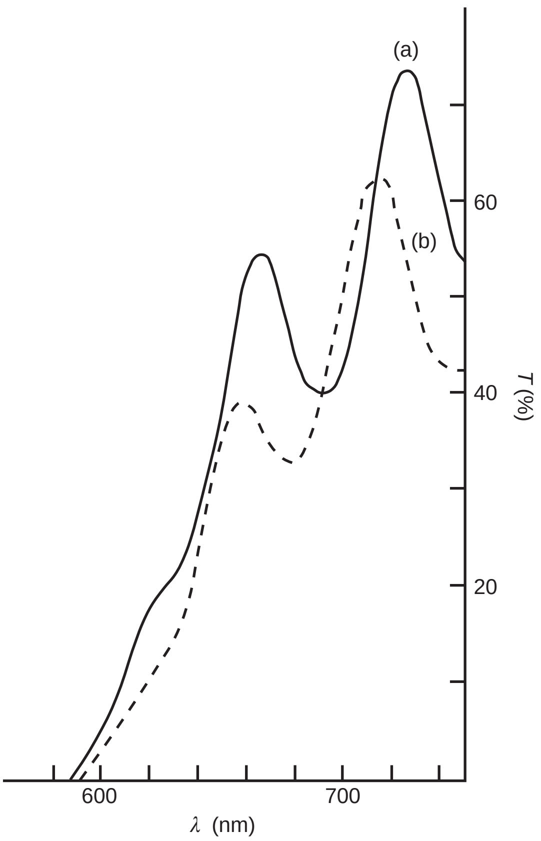

Figure 2 Shift of edge in optical transmission on illumination of the $Cu_5[(As_2Se_3)_{0.9}(AsI_3)_{0.1}]_{95}$ film: (a) as-evaporated film and (b) He–Ne laser irradiated film.

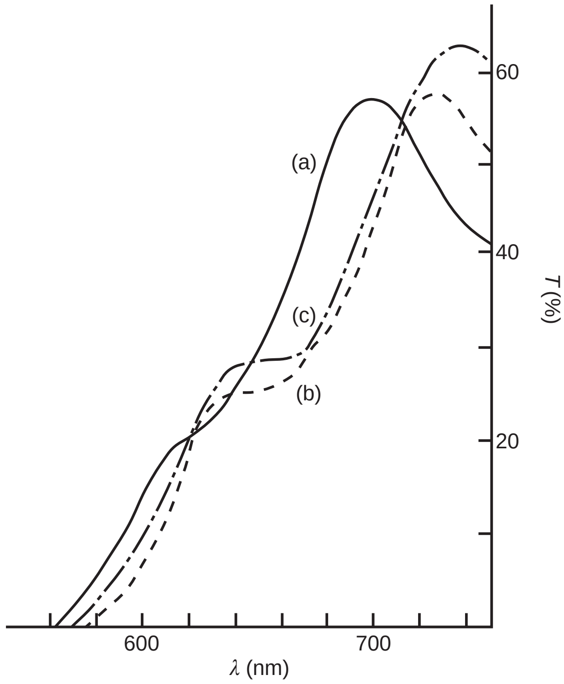

Figure 3 Shift of edge in optical transmission on illumination of the $Cu_{10}[(As_2Se_3)_{0.9}(AsI_3)_{0.1}]_{90}$ film: (a) as-evaporated film, (b) He–Ne laser irradiated film and (c) thermally annealed film.

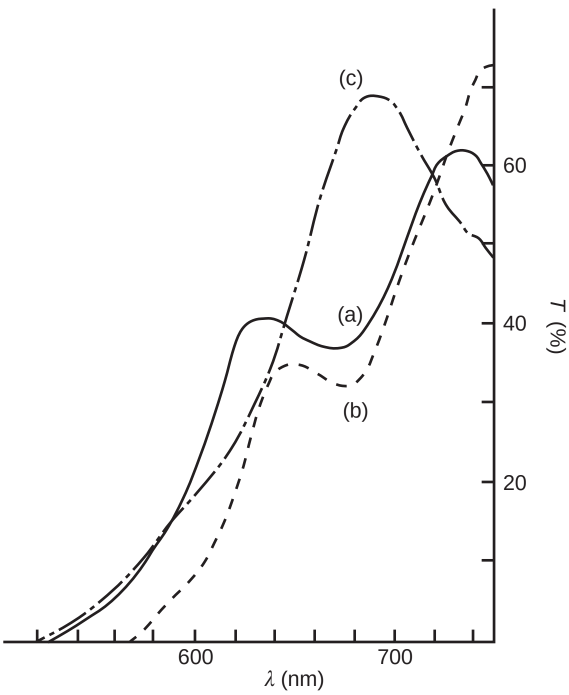

Figure 4 Shift of edge in optical transmission on illumination of the $Cu_{15}[(As_2Se_3)_{0.9}(AsI_3)_{0.1}]_{85}$ film: (a) as-evaporated film, (b) He–Ne laser irradiated film and (c) thermally annealed film.

These phenomena of subsequent recording and erasing can be observed cyclically with good reproducibility.

It should be pointed out that the reversibility of parameters in the cycles subsequent to the erasure by annealing is enhanced.

The photodarkening effect is observed only in disordered materials which contain the chalcogen elements S, Se and Te. With respect to the fact that the investigated films contain Se, these results are to

TABLE I The shift of the absorption edge on $Cu_x[(As_2Se_3)(AsI_3)]_{100-x}$ thin films

Composition	Shift of the absorption edge, $\Delta\lambda$ (nm)	Corresponding change of energy ΔE (eV)
$(As_2Se_3)_{0.9}(AsI_3)_{0.1}$	8	0.026
$Cu_5[(As_2Se_3)_{0.9}(AsI_3)_{0.1}]_{95}$	12	0.032
$Cu_{10}[(As_2Se_3)_{0.9}(AsI_3)_{0.1}]_{90}$	15	0.052
$Cu_{15}[(As_2Se_3)_{0.9}(AsI_3)_{0.1}]_{85}$	27	0.093

be expected. However, the shift of the absorption edge could be expected as the consequence of photocrystallization, but since the experimental curves are not smeared, most probably the effect is not present in this case.

References

1. D. M. PETROVIĆ, S. R. LUKIĆ, M. I. AVRAMOV and V. V. KHIMINETS, *J. Mater. Sci. Lett.* **5** (1986) 290.
2. S. R. LUKIĆ, D. M. PETROVIĆ, I. I. TURYANITSA and O. V. KHIMINETS, *J. Mater. Sci.* **26** (1991) 5517.
3. S. R. OVSHINSKY and H. FRITZSCHE, *IEEE Trans. Electron. Dev.* **20** (1973) 91.
4. V. V. KHIMINETS, *Kvantovaya elektronika* **25** (1983) 63.
5. D. M. PETROVIĆ, V. V. KHIMINETS and M. I. AVRAMOV, *Phys. Status Solidi A* **90** (1985) 151.
6. S. R. LUKIĆ, D. M. PETROVIĆ, M. I. AVRAMOV and A. F. PETROVIĆ, in Proceedings of ETAN ’92, Yugoslavia, edited by D. Uskoković (Society for Electronics, Telecommunications, Automation and Nuclear Engineering, Belgrade, Yugoslavia 1992) p. 35.
7. S. R. LUKIĆ, D. M. PETROVIĆ, A. F. PETROVIĆ and I. I. ROSOLA, *J. Mater. Sci. Lett.* **13** (1994) 1769.
8. J. P. DE NEUFVILLE, in Proceedings of the 5th International Conference on Amorphous and Liquid Semiconductors, edited by J. Stuke and W. Brenig (Taylor & Francis, London, 1974) p. 1351.
9. S. R. LUKIĆ, D. M. PETROVIĆ and S. J. SKUBAN, in EMRS 1993. Fall Meeting, 4th European East–West Conference and Exhibition, St Petersburg edited by I. V. Gorynin (EMRS-f.e.m.s.-Mat. Tech. “Prometey”, St. Petersburg, Russia 1993) p. F-38.

Received 15 November 1996
and accepted 25 July 1997