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Characteristics of optical recording on thin films of quaternary glasses Cu–As–Se–I

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The characteristics of optical recording and changes in the hologram parameters of the amorphous quaternary system Cu–As–Se–I are described. The dependence of the relative contrast of recording on the exposure and transparency properties of the film before and after erasure is the basis for discussion of these processes. Investigation into the dependence of diffraction efficiency of the holograms indicates that these quantities are determined by the thin film composition.

1. Introduction

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. Earlier investigations of photoinduced processes in amorphous chalcogenide semiconductors (ChAS) have shown that these materials possess a relatively high resolution, reversibility of recording, and other properties that are of importance for their use in holography and for equipment for optical treatment of information [1, 2] (Table I).

A series of previous experiments has been conducted on a very wide class of multicomponent amorphous systems: As–S, As–Se, M–As–B^{VI}, As–B^{VI}–I, and M–As–Se–I (M = metal, B^{VI} = S or Se) [3–6]. It has been observed that practically all these glasses are, to a smaller or greater extent, photosensitive to a certain wavelength of laser radiation, and the relevant parameters are dependent on the composition of the glass and conditions of its preparation. Four-component systems offer special possibilities because one can substantially influence the properties of the system simply by changing the ratio of their components. This is primarily concerned with the spectral interval of photosensitivity and characteristics of the record-erasure processes. It should be pointed out that a relatively complex technology of obtaining quaternary glasses and of thin films on their bases have been the reason why the processes of optical recording in these systems have received relatively little attention.

We report here the results of our investigations of the optical recording processes and characteristics of holograms in the Cu–As–Se–I system.

2. Experimental procedure

Samples of the system investigated were synthesized and deposited as thin films according to known procedures [7, 8]. A He–Ne laser ($\lambda = 632$ nm) with a power flux of 0.3 W cm^{-2} served as the effective source of radiation for studying the amplitude of optical recording on thin films. The thickness of films was about 2 μm.

Elementary holograms were recorded using the two-beam arrangement. Frequency of the recording was $\nu = 10^3$ lines mm^{-1}. Reading of the holograms was performed at the same wavelength.

Annealing of the films in the study of reversibility properties of the material was carried out in the air atmosphere and at a temperature close to the temperature of the glass softening, T_g. With the aim of determining these characteristics and defining the region of the amorphous phase, a complete derivatographic analysis of the glasses in the range from room temperature to 1000 °C was carried out in the air atmosphere, using a MOM (Budapest) derivatograph. The heating rate was 10 °C min^{-1}, and α-Al_2O_3 was used as the inert standard.

3. Results and discussion

Some previous investigations [9–11] have shown that the introduction of Cu into the As_2Se_3 glass causes an increase in the efficiency (contrast, photosensitivity, reversibility, diffractive efficiency) of optical recording on the thin films of $Cu_x(As_2Se_3)_{1-x}$, $x < 20$ at %. It can be supposed that the Cu atoms interacting with Se atoms produce an additional number of weak As–Se bonds and weak As "dangling" bonds, which are responsible for the process of optical recording. On the other hand, the introduction of I into glasses of the As–Se system also produces an enhancement in the efficiency of optical recording, thus causing (depending on the glass composition) a decrease in the temperature of erasure to $T_c = 40$–80 °C [12]. A consequence of this is also a decrease in mechanical strain which appears in the system film-substrate during the heating. The iodine added is incorporated into the

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TABLE I Parameters of optical sensitivity

Material	Spectral range (μm)	Integral photo sensitivity ($J cm^{-2}$)	Resolution (l in mm^{-1})
ChAS	0.30–0.90	0.1–10	10^4
Organic photochromes	0.30–0.75	0.2–20	4.5×10^3
Inorganic photochromes	0.30–0.52	2–20	4×10^2
Photothermo-plastic materials	0.30–0.64	10–10^2	1.5×10^3
Liquid crystals	Non-selective	10	50
Magnetic films	Non-selective	1–10	10^3

three-dimensional lattice of arsenic selenide, which causes a substantial break of continuity in the glass, and thus creates defect states in the forbidden band of such a semiconductor.

It is obvious that a more complex glass structure (i.e. the deviation from the stoichiometric composition) leads to an increase of disorderliness in the system and to an increase in the population of defects and lability of the structure. As a consequence, a decrease in the irreversibility changes, i.e. an increase in the reversibility of the optical recording, should be observed. These are the reasons for scientific and practical interest in studying the Cu–As–Se–I system.

The existence of a wide region of glass formation in the Cu–As–Se–I system [4] enables one to obtain materials of desired properties which will vary in a relatively large interval. Table II presents some characteristic parameters which are of importance for recording on thin films based on this system. As can be seen from Table II, an increase in the concentration of copper at an approximately unchanged ratio of other components leads to an increase in microhardness (H) and temperature of softening (T_g).

In Fig. 1, some characteristic diagrams of the thermal analysis of glasses of the Cu–As–Se–I system are presented. From these, it is possible to obtain the softening temperature (maximum 1), which represents the limiting temperature to which the thin film can be heated with the aim of erasing the recording. In addition, these investigations provide the basis for deducing the mechanism of thermal decomposition of the glass. It has been established that in the interval of 300–600 °C, the structural units $CuAsSe_2$, Cu_3AsSe_4, As_2Se_3 and AsSeI are decomposed (exothermic maxima 2, 3 and 4) and the process is completed by the formation of copper oxide ($\Delta m_{exp} = 12\%$, $\Delta m_{cal} = 12.52\%$).

Typical curves illustrating the interdependence between the relative contrast of the recording and the exposure in the first recording and the recording after the annealing (recording–erasing cycle) are presented in Fig. 2. The ordinate axis represents the relative contrast (K) which is defined as the ratio of transparence coefficients for the exposed and unexposed part of the film, while the abscissa is the exposure.

It can be seen after the thermal erasure of the recorded information that the repeated recording is less efficient (Fig. 2, curve 2). The maximum value for the relative contrast in the first recording was $K_1 = 5.2$, and after annealing this was lower, $K_2 = 3.4$, with a tendency to remain approximately constant in the subsequent recording–erasure cycles.

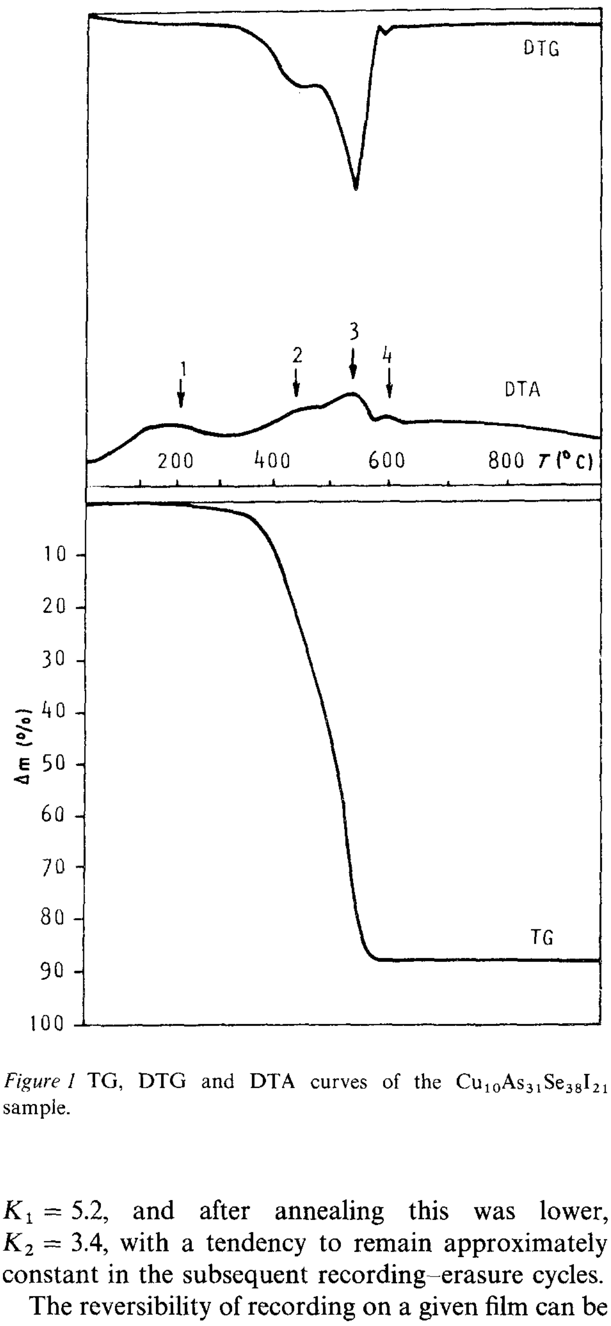

Figure 1 TG, DTG and DTA curves of the $Cu_{10}As_{31}Se_{38}I_{21}$ sample.

The reversibility of recording on a given film can be assessed from the ratio of the contrast in the first recording and of that in the subsequent recordings. The values of the contrast (K) and reversibility coefficients of optical recording (R) for the films based on the system under investigation are presented in Table II.

Fig. 3 illustrates a typical example of how the diffraction efficiency (η) depends on the exposure. This

TABLE II Some characteristic parameters for recording on thin films

Composition	Microhardness H (kg mm^{-2})	Softening temperature, T_g (°C)	Shift of the absorption edge, $\Delta\lambda$ (nm)	Contrast of the recording $k = T_o/T$	Reversibility $R = K_1/K_2$	Diffraction efficiency η (%)
$Cu_{10}As_{32}Se_{36}I_{22}$	75.5	127	8	1.7	3.5	0.5
$Cu_{10}As_{33}Se_{42}I_{15}$	110.0	150	11	2	2.8	1.0
$Cu_{20}As_{29}Se_{36}I_{15}$	114.5	165	14	2.9	2.5	1.2
$Cu_{20}As_{31}Se_{42}I_{7}$	189.0	187	20	4.0	1.4	2.0
$Cu_{20}Se_{30}Se_{36}I_{14}$	189.0	180	13	2.5	1.1	1.0
$Cu_{30}As_{25}Se_{30}I_{15}$	128.0	144	11	2.2	1.2	1.0
$Cu_{10}As_{30}Se_{30}I_{30}$	89.4	95	3	1.2	4	0.2
$Cu_{14}As_{45}Se_{37}I_{4}$	195.0	180	30	6	1.1	2.5
$Cu_{30}As_{26}Se_{40}I_{4}$	190.0	175	12	2.5	1.1	1

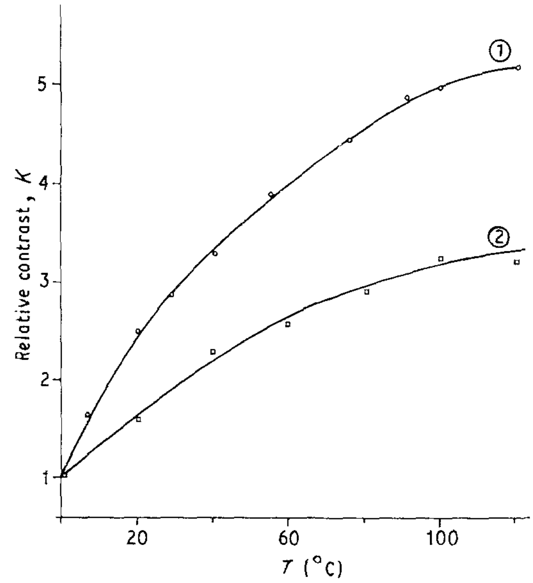

Figure 2 Dependence of relative contrast of the recording on exposure for thin film of $Cu_{14}As_{45}Se_{37}I_4$. Curve 1, first recording; curve 2, first recording after annealing.

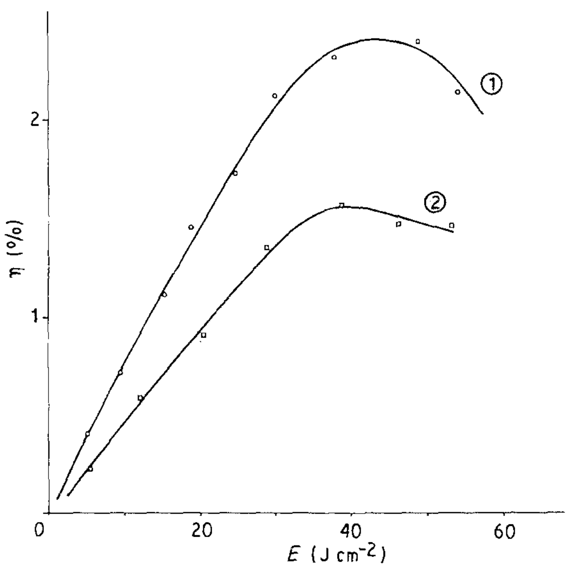

Figure 3 Dependence of diffraction efficiency of the hologram recorded on the $Cu_{14}As_{45}Se_{37}I_4$ film. Curve 1, first recording; curve 2, second recording.

parameter of the holographic process characterizes the radiation power (luminosity) of the resulting image, and is a function of a number of parameters. In a general case, the expression for diffraction efficiency can be written as [13]

$$\eta = f(E, I_s/I_r, \theta, d, c, \lambda)$$

where I_s and I_r are the respective intensities of the indicator beam (the beam coming from the object) and reference beam; θ = the angle between the two beams of laser radiation; λ = wavelength of the recording and reading of the hologram; d = film thickness; E = exposure; and c = a factor depending on the composition and technology of the film.

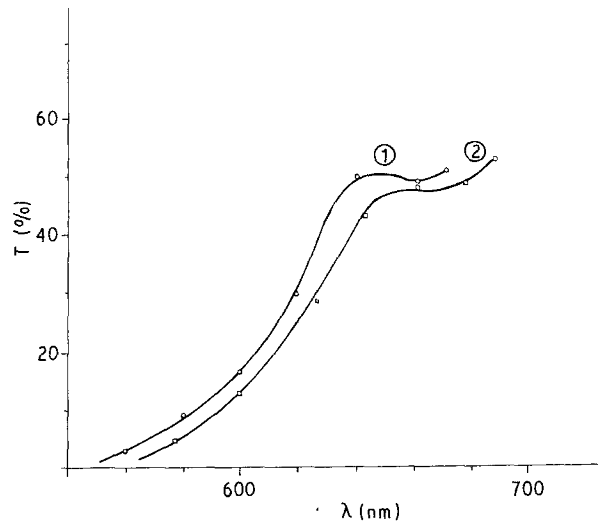

Figure 4 Transparence dispersion of the $Cu_{14}As_{45}Se_{37}I_4$ film. Curve 1, freshly-prepared film; curve 2, film after annealing.

In the present study, by an appropriate choice of parameters of the recording medium (effective thickness, composition, technology) [14], the optimization of the holographic recording is reduced to the problem of the recording condition (E, I_s/I_r, θ, λ).

Fig. 3 illustrates the dependence of diffraction efficiency on the exposure for $I_s/I_r = 1$, $\theta = 14°$, and $\lambda = 632$ nm. Curve 1 represents the efficiency of the first recording. It can be concluded that a maximum value for η is obtained at an exposure of $E = 42\,\mathrm{J\,cm^{-2}}$, and this quantity diminishes as a consequence of the overexposure of the film (i.e. the contrast between the lines and background of the diffraction grating is decreased). Curve 2 represents the diffraction activity of the same film after erasing the recorded hologram by heating the film to a temperature close to its softening temperature and the repeated recording. As can be noticed, the η value has decreased from 1.5 to 2 times.

Fig. 4 shows the dependence of transparencies of thin films of the system investigated on the wavelength of the initial radiation. Curve 1 represents the spectrum of a freshly-prepared film, while curve 2 shows the same dependence for the same sample after annealing. It can be noticed that the average shift of the absorption edge is about 30 nm, which corresponds to a change in the refractive index $\Delta n = 0.03$–0.06 [15]. This shift is approximately 2–3 times smaller than in the case of films of the binary As–Se system. In accord with the changes in η and n, and depending on the glass composition, the fundamental characteristics of the amplitude-phase recording (relative contrast and diffraction efficiency) are changed, as can be seen from Table II. Also, an increase in the efficiency of recording is observed with an increase of the copper content to a limit of 12% at an I content of 5–7 at % and the approximately equal concentrations of Se and As. At an increased content of Se with respect to As in the four-component system, a decrease in the efficiency of recording is observed in the binary As–Se system [16].

The results presented here show that the efficiency of the first cycle of optical recording becomes worse when going from the binary As–Se, through the ternary As–Se–I to the quaternary Cu–As–Se–I system. However, it should be pointed out that the reversibility of parameters in the cycles subsequent to the erasure by annealing is enhanced.

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