LIGHT-INDUCED CHANGES IN AMORPHOUS SELENIUM FILMS CONTAINING Sb ADDITIVES

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The changes in the optical recording properties of amorphous selenium containing antimony additives under laser irradiation have been measured at room temperature.The dependence of the transmissivity on the irradiation energy density shows the existence of certain threshold Eth. In the low-energy region, the transmissivity varies dynamically (reversibly) with exposure. Above an energy density threshold, the persistent changes were attributed to photocrystallization.

Introduction

Chalcogenide glasses whose common feature is the presence of chalcogenide atoms are known to exhibit a variety of photoinduced phenomena [1-4]. Among these phenomena, photocrystallization [5] and reversible photostructural changes [1-4] are of special interest here.

The phase transformation of amorphous selenium (photocrystallization) has been studied by Dresner and Strinfellow [5]. They demonstrate that the crystallization rate of a-Se into trigonal crystals can be essentially enhanced by light illumination. This property makes them attractive for optical data storage. Photocrystallization is also investigated in other materials such as As-Se [6] and GeSe2 [7] using Raman scattering experiments. Thin films of Te-based alloys are the most studied optical recording media because of their excellent laser writing characteristics [8]. However, Te-based thin films tend to degrade rapidly during storage in moist atmosphere. Recently, reversible optical memory with many write-erase cycles (amorphous-crystalline phase transition) was reported in system of Sb-Se [9]. In the present paper, we will examine light-induced change of the optical properties in Sb_xSe_{1-x} amorphous films. We focus our attention mainly on photocrystallization transformation.

Experimental

Sample investigated were amorphous Se and Sb_xSe_{1-x} films, about 1-3 μm thick. These films were prepared by vacuum evaporation of the source material (glassy alloys) onto room-temperature glass plates. A typical coating rate was ~1 μm min^{-1}.The glasses of the Sb_xSe_{1-x} system, where x=0-0.05, were prepared from pure elements by conventional melt quenching (cooling rate ~300 Ks^{-1}). As can be seen from the electron probe microanalysis data, the deposited antimony content is relatively uniform across the film thickness. To allow for the physical properties of the films to equilibrate, they were aged in the dark under normal laboratory conditions.

The experimental basis of this paper involves two types of kinetic experiments: a) a macroscopic probe involving optical changes which occur in the laser-induced photodarkening process; b) a local structural probe by means of Raman spectroscopy and X-ray diffraction.

In the transmission photodarkening (photocrystallization) experiments, The samples were illuminated by He-Ne laser operating at 633 nm. The transmission of the sample was probed using a portion of the He-Ne laser output. The probe light intensity was reduced to 5 mwcm-2 and accordingly no appreciable photoeffect was induced under the monitoring processes.

Results

Figure 1 illustrates the change in transmissivity at room temperature as a function of time with the illumination turned

on and off. Note that illumination intensity was kept constant during on periods. Amorphous films (irrespective of composition) show a decrease in transmissivity with the irradiation time. The development of the photodarkening effect proceed via following stages: there is an initial decrease in optical transmissivity followed by a slower decrease with illumination time up to the saturated value. For such a transitory behavior to be observed, an exposure of 5 J cm^{-2} is required. As seen from the same figure, the degree of change increases with antimony content. When the illumination was turned off, the transmissivity increases. It is necessary to note here that the recovery is not complete. With increasing Sb content the magnitude of bleaching decreases. These transitory changes in transmissivity in cycles on-off illumination can be repeated many times with a good reproducibility. The saturation of the above-mentioned dynamical changes occurs at integrated exposure of 40-60 Jcm^{-2} (exciting light intensity I<1 W cm^{-2}).

When exposure is further increased, significant irreversible changes in transmissivity are observed. Figure 2 shows the dependence of the transmissivity change upon energy density of illumination. The above dependence consists of an initial response (corresponding to the transient change), a slowly varying portion of the darkening curve and a significant decrease in transmision. The latter is finished by a saturation effect. The maximal change in transmission which may be induced by illumination is 80 % of its initial value. Typical response of light intensities diffracted from holographic gratings formed on Sb_xSe_{1-x} films exhibits several stages qualitatively similar to that observed for transmissivity.

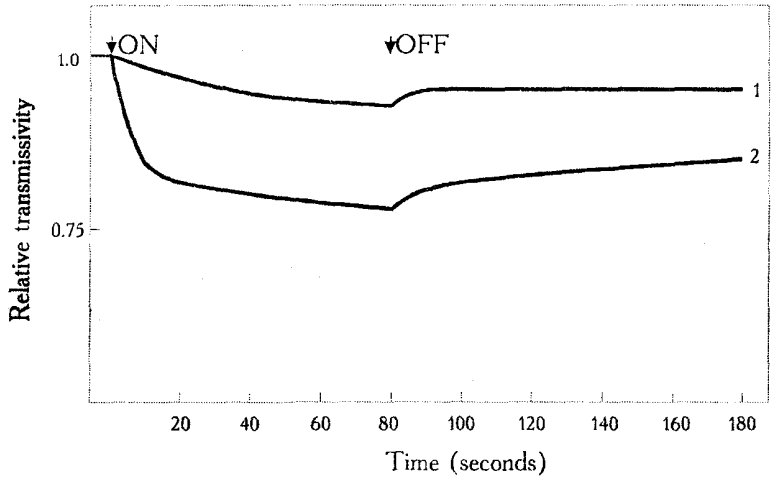

Fig. 1. Time dependence of the transitory changes in transmissivity in Sb_xSe_{1-x} films. x=0.01, 0.05 in curves 1-2, respectively. Thickness 1.5 μm and intensity 0.5 Wcm^{-2}.

Discussion

We may divide the transmissivity and diffraction efficiency versus energy density data into two different regions with a separation at the threshold energy Eth. For E<Eth, the observed photoeffects are transient (dynamical) and characteristic of amorphous phase. In other words, one can exclude radical structural reorganization at this stage and the system remains in the amorphous phase.

On the contrary, above Eth, the observed behavior may be explained by photoinduced crystallization. The data presented make it possible to resolve successive stages of photocrystallization: first – microcrystallite

formation (exposure range 100<E<200 Jcm-2); second – microcrystallite enlargement: third and final – further increase in the size and the concentration of microcrystallites.

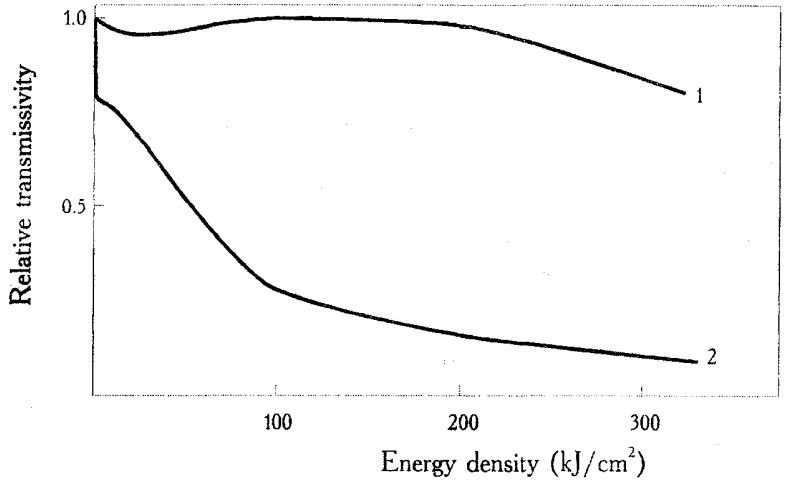

Figure 2. Exposure dependence of the photoinduced effect in transmissivity for Sb_xSe_{1-x} films. x=0.01 (1) and 0.05 (2).

On the basis of the Raman and X-ray diffraction data, we cocnclude that the main features of the photocrystallization effect in Sb_xSe_{1-x} alloys are the same (at least in qualitative sense) as in pure amorphous selenium. It should be noticed that a-Se undergoes a transformation to the most stable (at room temperature) crystalline modification – hexagonal form [10]. X-ray diffraction and Raman scattering investigations suggest that photoinduced crystallization is caused by alignment of Se chain molecules.

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ФОТОІНДУКОВАНІ ЕФЕКТИ В ПЛІВКАХ АМОРФНОГО СЕЛЕНУ З ДОДАТКАМИ Sb

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Приводяться результати досліджень характеристик оптичного запису в аморфних шарах Sb_xSe_{1-x} при лазерному опроміннні. Розглянуто величину оптичного пропускання від величини експозиції та встановлено пороговий характер змін. Чітко розмжовані нестаціонарні (динамічні) зміни та фотокристалізаційні процеси.