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LIGHT AND ION INDUCED INTERDIFFUSION IN AMORPHOUS CHALCOGENIDE NANOMULTILAYERS

I. Ivan*, D. L. Beke[a], S. Kokenyesi, I. A. Szabo[a], A. Csik[a,b]

Department of Experimental Physics, University of Debrecen, Bem ter 18/a, 4026 Debrecen, Hungary
[a]Department of Solid State Physics, University of Debrecen, 4010 Debrecen P. O. Box 2, Hungary
[b]On leave from the Institute of Nuclear Research, Hungarian Academy of Sciences (ATOMKI), H-4001 Debrecen, P. O. Box 51, Hungary

Comparative investigations of light and ion irradiation induced intermixing have been performed in amorphous Se/As_2S_3 and $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ multilayer films with composition modulation period 6-6.5 nm. It was established that both light and ion irradiation induced interdiffusion is accompanied by optical bleaching and volume expansion of the film. Good correlation between the kinetics of intermixing, measured by low angle X-ray diffraction, and the kinetics of optical transmission changes was observed, which in turn allows an *in situ* tracking of the diffusion processes by optical measurements. The results and the possible mechanism of light and ion irradiation enhanced interdiffusion are discussed within the framework of thermal spike model.

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1. Introduction

Amorphous chalcogenide semiconductors are known to exhibit changes of their optical, mechanical and physico-chemical properties under exposure to light with photon energy equal or larger than the optical band gap of the material [1]. These phenomena are connected with some structural changes of the amorphous network induced by the excitation with light. Similar phenomena have been observed under the action of γ, electron or ion irradiation [2-5]. It is particularly interesting, that structural transformations caused by light and H^+ and D^+ ion irradiation are almost entirely the same, as it was shown recently by Raman scattering measurements [5].

Basic effects of light interaction with amorphous chalcogenide thin films and nanomultilayers made of amorphous chalcogenides are very similar, since the well known photo-stimulated effects occur in the appropriate components of the multilayer. What makes them different is the interdiffusion between the adjacent layers occurring due to the light absorption [6]. Such light induced intermixing has been observed experimentally in nanomultilayers of several composition, such as Se/As_2S_3 [7], $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ [6], Se_xTe_{1-x}/As_2S_3 [8]. As a result of interdiffusion optical bleaching and giant volume expansion occur in multilayers, which can be used for optical recording and fabrication of surface relief patterns [2,6,9]. Although the peculiarities of photobleaching and volume expansion accompanying the intermixing have been studied in several types of multilayers, the mechanism of the basic effect, the light enhanced interdiffusion itself is not well understood. Only recently the first attempt towards the theoretical description of this phenomenon has been made

* Corresponding author: ivani@delfin.unideb.hu

in which the enhancement of diffusion was connected to local heating involving a few atoms for a very short time in the photon absorption region [10]. Similar concepts are frequently used for description of the ion beam mixing and radiation damage in solids. In this paper we report the results of detailed investigation of the light and ion beam enhanced interdiffusion in Se/As_2S_3 and $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ multilayers with the aim of testing the model mentioned above.

2. Experimental

High quality amorphous multilayers (ML) were prepared by cyclic thermal vacuum evaporation onto corning 7059 glass and polished silicon substrates. The bilayer thickness was 6-6,5 nm for both types of multilayers, while the thickness of the narrow band gap layer (Se or $As_{0.2}Se_{0.8}$) was 4 nm and 2.5 nm in the case of as Se/As_2S_3 and $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ ML respectively. Samples with two different total thicknesses of 0.9 μm and were prepared. Photodiffusion and optical bleaching induced by He-Ne laser light were measured on 2.7 μm thick samples to provide efficient absorption at the wavelength of the He-Ne laser (λ=633 nm). All other measurements were carried out on the 0.9 μm samples.

To study the light or ion beam induced intermixing the samples were irradiated with 5 mW He-Ne and 17 mW green dioede (λ=532 nm) lasers or with 180 keV D^+ ions in the 3.6×10^{14}-1.6×10^{16} ion/cm^2 fluence range.At this energy the D^+ ions pass completely through the ML with a nearly uniform energy loss throghout the thickness. The ion current density was about 2.4×10^{-7} A/cm^2. The beam to sample angle was either 45° (for the *in situ* measurement of optical bleching) or 90° (for the X-ray and volume expansion measurements). The weakened by neutral filters beams of the same lasers were used for in situ measurements of the transmission changes of the samples during the interdiffusion.

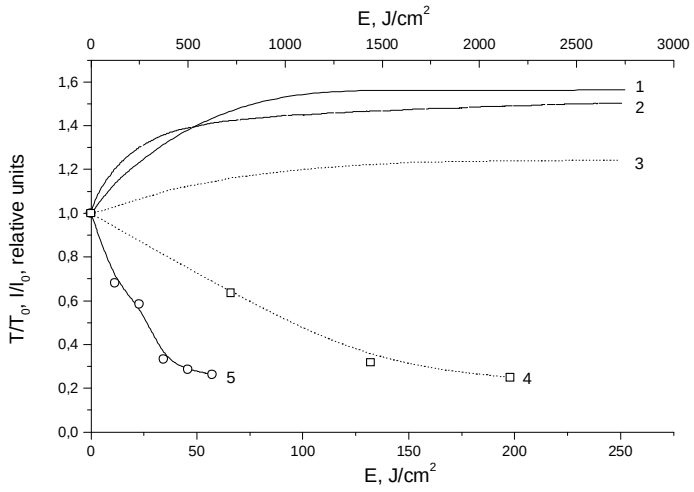
Low angle X-ray diffraction (LAXD) measurements in θ-2θ geometry were used for the measurement of the bilayer thickness and the degradation of the ML samples after different irradiations.

For the measurement of volume expansion a standard transmission electron microscopy grid with 62 μm period was put on the sample, which was then irradiated and the step height between irradiated and non-irradiated regions was measured by atomic force microscope.

3. Results and discussion

It was observed, that both laser and ion irradiation causes efficient intermixing in both investigated ML. Similarly to the photoinduced interdiffusion, the ion beam induced mixing also was accompanied with optical bleaching and volume expansion of the samples. In order to compare the kinetics of the two phenomena, the changes of the magnitudes, relative to the initial, of the intensity of the first order LAXD peak, transmission at the wavelength of the measuring laser and the volume were plotted against of the total energy deposited in the sample by ion and laser beams (see Fig. 1,2). For this reason the stopping powers of D^+ ions in films with the average composition and density of the multilayers were computed using the SRIM program [11].

The first thing which is apparent in Fig. 1 is that there is a good correlation between the decay of the first order LAXD peak intensity and of the corresponding kinetics of optical bleaching measuerd at fixed wavelength for light and ion irradiation induced interdiffusion as well in both of the studied samples. It agrees with our earlier indirect observation that the normalized rate of photobleaching is linearly proportional to the effective coefficient of interdiffusion in such multilayers [12]. It is of great importance, since it enables the tracking of the diffusion process through in situ measurement of the optical transmission.



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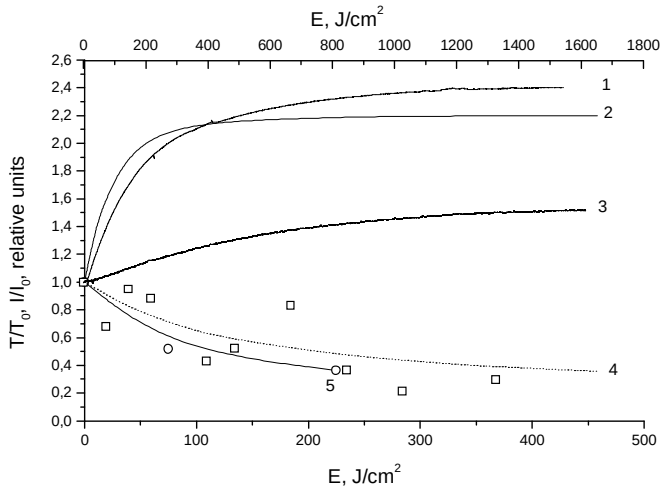

b

Fig. 1. Relative change of the optical transmission measured at λ=532 nm (1,2) and at λ= 633 nm (3) and of the first LAXD peak intensity (4,5) plotted against the energy deposited (a) in Se/As_2S_3 ML during ion (1,5) and laser irradiation at λ= 532 nm (2) and λ= 633 nm (3,4); (b) in $As_{0.2}Se_{0.8}/ As_{0.2}S_{0.8}$ ML during ion (2) and laser irradiation at λ= 532 nm (1,5) and λ= 633 nm (3,4). The dotted curves belong to the upper scale. All measurements were done at T= 293 K.

The other result one can see in Fig. 1. that in both investigated ML in the case of ion beam mixing the transmission change saturates approximately at 100-150 J/cm^2 (curves 1 and 2 in Fig. 1. (a) and (b) respectively). Nearly the same exposition is needed for saturation of the optical bleaching in the case of intermixing induced by light with λ= 532 nm wavelength (curves 2 and 1 in Fig. 1. (a) and (b) respectively), while if the sample is illuminated with λ=633 nm light the process saturates at considerably higher expositions (curves 3 in Fig. 1. (a) and (b); note, these curves belong to the upper scale). This difference most probably is related to different light absorption properties of the components at the two wavelengths. At 633 nm the absorbance of the wide band gap component and even of the interface layer, where the mixing occurs, is very low, therefore very little part of absorbed energy is effective to cause intermixing. The light with 532 nm wavelength is absorbed much more effectively in the interface layer and thus more effectively initiates the mixing process,

even though the light absorption asymmetry in the bilayer still remains high for the favor of the narrow band gap layer. This is in good accordance with the recently developed thermal spike model of photo-stimulated diffusion [10], which predicts the asymmetry of the diffusion process (i.e. that the diffusion coefficient is concentration and site dependent and is much larger in the narrow band gap layer than in the wide band gap one, and that the apparent coefficient of the interdiffusion governing the mixing process will be somewhere in between of the diffusion coefficients in the wide and narrow band gap layers). It also enables the tuning of the light sensitivity of the MLs varying the thickness and the composition of the narrow and wide band gap layers [6,12,13]. The ion energy loss is distributed approximately homogeneously within the bilayer thickness and effectively enhances the atomic migration in the narrow and wide band gap layer as well. So, in this way it is clear why the intermixing induced by the ion beam is more effective than mixing induced by He-Ne laser light.

Ion beam mixing is a complex phenomenon with several contributing effects such as ballistic and thermal spike mixing and different regimes of radiation-enhanced diffusion (RED) [14]. They can be separated on the basis of their different temperature and flux dependences. Our preliminary experiments indicate that the ion beam mixing (actually the optical bleaching have been measured) in our case depends very little on temperature in the range from 100 K to 293 K. In principle it can be characteristic for both the ballistic and thermal spike mixing, but the first possibility can be ruled out since it is expected to cause effect lower for two orders of magnitude than those have been observed in our experiments [15]. The photo-induced diffusion also have been observed to possess little temperature dependence at low temperatures, which indicates that the concept of the thermal spike mixing can be used for the photo-induced interdiffusion as well.

We believe that the electronic stopping, which has 99 % contribution to the energy loss of ions in our case, is mainly responsible for the ion irradiation induced intermixing in our samples. The ion energy is first transferred to the electronic subsystem and then to the lattice via electron-phonon coupling. The latter is also considered to be the key feature to explain the similarity of the light and ion irradiation induced structural and optical changes in homogeneous chalcogenide thin films [4,5]. Our observations are consistent with the more and more accepted opinion [16] that contrarily to metals (where effects connected with electronic excitation and inelastic energy loss are absent), in semiconductors and insulators electronic excitation by radiation plays at least as important role in radiation induced phenomena as elastic collision processes do. The same is true for polymers and molecular solids [17].

In Fig. 2 the evolution of the volume expansion during the light and ion irradiation induced intermixing is shown. One can see that the saturation of the volume expansion is observed at higher expositions than of the photobleaching (curves 2 and 1 in Fig. 1. (a) and (b) respectively). It suggests that the optical transmission is more sensitive to the initial part of interdiffusion process, while the maximum volume change is achieved only after more thorough mixing. The same can be observed in the case of ion irradiation induced interdiffusion. Unfortunately, for technical reasons the volume change induced by ion irradiation could not be measured up to saturation, therefore its magnitude cannot be compared with the photo-induced one. It should be noted, that the magnitude of the observed photo-induced volume expansion in Se/As_2S_3 ML was approximately twice as large as it was previously obtained in hologram recording experiments [9,18]. Probably it is due to the higher contrast between the irradiated and unirradiated areas obtained by this measurement method than by holographic one, however the role of strains present in such MLs [19] also cannot be ruled out. The volume expansion observed in the $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ ML is in good accordance with the previously measured one with the same method [6].

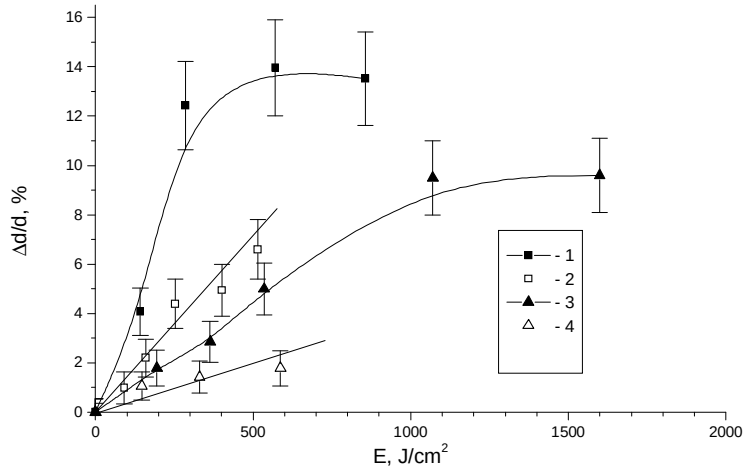

Fig. 2. Volume expansion plotted against the energy deposited in Se/As_2S_3 (1,2) and $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ (3,4) ML during D^+ ion (2,4) and laser (1,3) irradiation at λ= 532 nm.

4. Conclusions

The optical bleaching and volume expansion due to laser and ion irradiation induced intermixing in amorphous Se/As_2S_3 and $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ nanomultilayers have been compared and correlated with direct low angle X-ray diffraction measurements of the interdiffusion. The experimental results show good agreement with the thermal spike model of intermixing.

Acknowledgements

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