JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 4, April 2009, p. 391 - 394

Photo-expansion in Ge-As-S amorphous film monitored by digital holographic microscopy and atomic force microscopy

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Using Digital Holographic Microscopy and Atomic Force Microscopy we unambiguously observed considerable photo-expansion at around 3.5 % in virgin as well as in annealed $Ge_{26}As_7S_{67}$ amorphous films having the thickness around 740 nm. This photo-expansion seems to be relatively stable, since after one year ageing its value decreased from 26 nm to19 nm in annealed film, while no relaxation was observed for virgin film.

(Received January 22, 2009; accepted April 24, 2009)

Keywords: Amorphous chalcogenide films, Photo-expansion, Digital Holographic Microscopy, Atomic Force Microscopy

1. Introduction

The first "giant" photo-expansion of the sample thickness d in amorphous chalcogenide (fractional change of the thickness $\Delta d \approx 5\%$) was observed in a flake of As_2S_3 glass illuminated by photons with energy corresponding to Urbach edge [1]. Recently, in some virgin thin films prepared by thermal evaporation from $Ge_{32}As_5S_{63}$ and $Ge_{30.8}As_{5.7}S_{63.5}$ bulks, the "giant" photo-expansion induced by 3h illumination of the films with a high pressure Hg lamp was observed ($\Delta d \approx$ 7-11%) [2,3]. The sample thickness and its changes were determined by the Swanepoel method [4]; films with the thickness varying from 0.6 μm to 1.4 μm were used. More recently Vateva [5] summarized that (i) "giant" photo-expansion of virgin films is observed namely for ternary compositions with mean coordination number (Z) at around 2.7, and (ii) illumination induces also the highest film bleaching – the blue shift of the gap $\Delta E_g \approx$ 17-27%, accompanied by photo-refraction $\Delta n \approx$ -(6-9)%. Here $\Delta x = 100 \times (x_{\text{ill.}} - x_{\text{vir..}})/x_{\text{vir.}}$, where x is the optical gap E_g or refractive index n.

Despite the fact that origin of photo-expansion is not very clear yet, the photo-expansion itself is very interesting and promising phenomena which can be used for various structural and shape modifications of materials [6]. In amorphous chalcogenide films photo-expansion is usually monitored via optical transmission measurements and application of Swanepoel method. In this short note we examined photo-expansion in amorphous Ge-As-S film by Digital Holographic Microscope (DHM) and Atomic Force Microscopy (AFM).

2. Experimental

Films with thicknesses about 700 nm were prepared by vacuum thermal evaporation at $2\text{-}3\times10^{-3}$ Pa with a rate 6-8 nm/sec from the previously synthesized $Ge_{30.8}As_{5.7}S_{63.5}$ glass (Z=2.67) onto Corning 7059 glass substrates. During the evaporation procedure, the sample thickness was controlled using quartz oscillator MIKI-FFV. The chemical composition of the film $Ge_{26}As_7S_{67}$ was checked by electron microprobe X-ray analysis (Joel JSM 35 CF).

The films were exposed in air to a high pressure Hg lamp (500 W) through an IR cut off filter for 45 min. The annealing in Ar atmosphere was performed at the temperature ~350° C for 45 min.

Measurements with digital holographic microscope (DHM) were realized by means of DHMR1000 (Lyncée Tec, Switzerland) operating at 785 nm in reflection configuration using microscopic objectives with 10× and 20× magnification.

AFM measurements were realized using Solver Pro M Atomic Force Microscope (NT-MDT; Russia). The measurements were carried out using high-resolution "Golden" silicon cantilevers type CSG-10 (Au coating, cone angle less than 22°; typical force constant 0.1 $N.m^{-1}$) in contact mode. The images were recorded at scan frequency 0.2 Hz for a resolution 256 × 256 pixel. The details of measurement as well as data processing were described recently [7].

3. Results and discussion

It is known that in some cases photo-expansion is a result of photo-oxidation of the surface and near surface

parts of a sample, see e.g. the case of $As_{50}S_{50}$ amorphous film [8] and $Ge_{10}Ga_{25}S_{65}$ amorphous film [9]. Therefore, in the first step we examined whether in our experiment some indication of photo-oxidation seen in Refs. [8,9] is possible to identified.

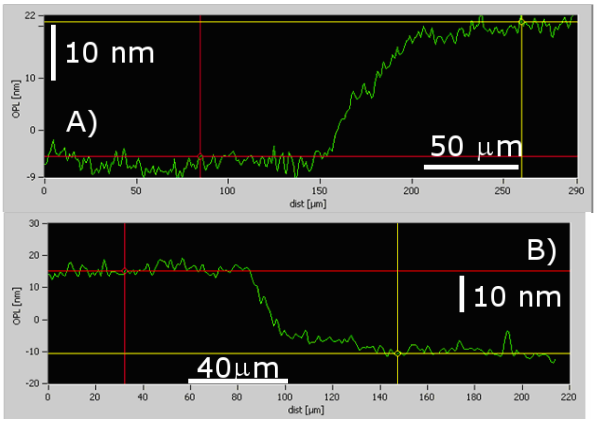

Fig 1. Digital holographic microscopic (DHM) measurements of photo-expansion in $Ge_{26}As_7S_{67}$ thin films; line-scans across the surface of boundary of the virgin → illuminated sample: (A) virgin film; illuminated part of the film is on the right side (Δd = 26 nm). (B) annealed film; illuminated part of the film is on the left side (Δd = 26 nm).

In Fig.1 typical line scan is shown across the surface of boundary of the virgin → illuminated sample (*v-i*), panel A, and across the surface of boundary of annealed → illuminated sample (*a-i*), panel B. The scans were performed on the area around 420 × 420 μm^2. The jump like change in the thickness Δ*d* = 26 nm reflects photo-expansion, the scatter in the scan line indicates the roughness of the sample surface. It is obvious that the roughness after illumination and before illumination (in virgin and annealed samples) remains to be comparable. One can hardly expect similar roughness for photo-oxidized, fresh and annealed samples and hence, we suppose that observed photo-expansion is not associated mainly with photo-oxidation of the sample surface. Moreover, as can be seen in Fig. 2, panel A, the 3D DHM image of the surface boundary of annealed → illuminated sample clearly indicates similar surface topology with some accidental spikes which locally increase surface roughness. These spikes most probably correspond to the surface contamination by some dust particles. In Fig.2, panel B, series of line scans corresponding to panel A in Fig. 2, taken from different places of the sample, indicate (i) good reproducibility in Δ*d* = 18.5 nm and (ii) comparable roughness on various places of annealed and illuminated sample. It should be noted that the measurements summarized in Fig. 2 were taken one year after sample illumination, hence, in comparison with the results shown in Fig.1, panel B, some relaxation in photo-expansion is observed at around 28.8 % (= 100 × (26-18.5)/26).

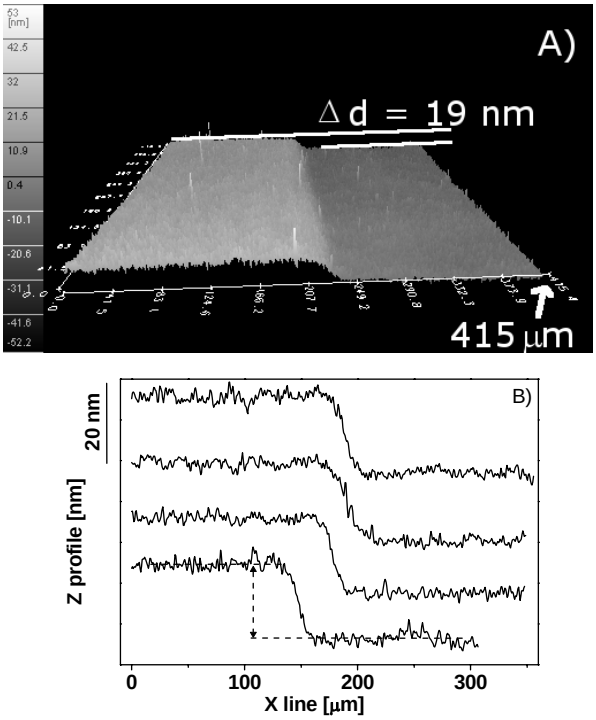

Fig 2. 3D DHM image of photo-expansion of annealed $Ge_{26}As_7S_{67}$ film after one-year relaxation (illuminated part on left-hand side; Δd = 18.5 nm). A) 3D image (exported directly from DHM software) supplied with axes description; B) corresponding line-scans.

We have made the series of line scan measurements in order to examine reproducibility of our measurements. In Fig. 3 the relevant results are summarized indicating that the difference in Δ*d* [nm] = 26-18.5 = 7.5 exceeds significantly our error, hence, we conclude that some photo-expansion relaxation proceeds in the sample studied.

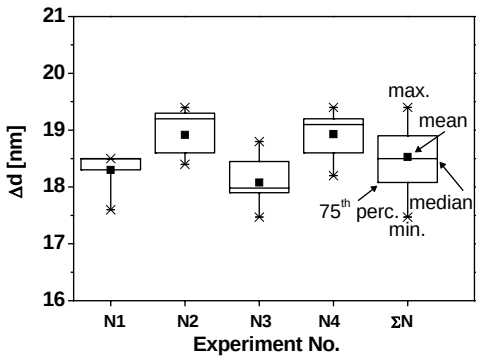

Fig 3. The box-plot of Δd determination for annealed $Ge_{26}As_7S_{67}$ film after one-year relaxation determined by DHM in four days (N1-N4) and as a sum of all experiments (ΣN). The box-plot is formed from minimal and maximal value (whiskers), values of 25th, 50th and 75th percentile and arithmetic mean (square in box).

For verification of photo-expansion values obtained by DHM we used Atomic Force Microscopy. Using "scratch" method recently applied in the study of photo-expansion in another Ge-As-S film [7] we determined photo-expansion for the sample (*v-i*) and sample (*a-i*), both for one year after illumination, i.e. for relaxed samples. In Fig. 4, panel A, topological image of the scratch on the sample is shown and in panel B four typical line scans across the scratch for the thickness measurements are shown. The bottom line scan is realized across the glass substrate scratch indicating that possible scratch of the substrate is negligible and can not influence measured values of the thickness and Δd values. In Fig. 5 the results of the thickness measurements of annealed - illuminated (*a-i*), and virgin - illuminated (*v-i*) samples are summarized. It is evident that measured photo-expansion mean values Δd(*v-i*) = 24 nm and Δd(*a-i*) = 19 nm agree with Δd values determined using DHM. The samples were relaxed one year in darkened desiccator at room temperature.

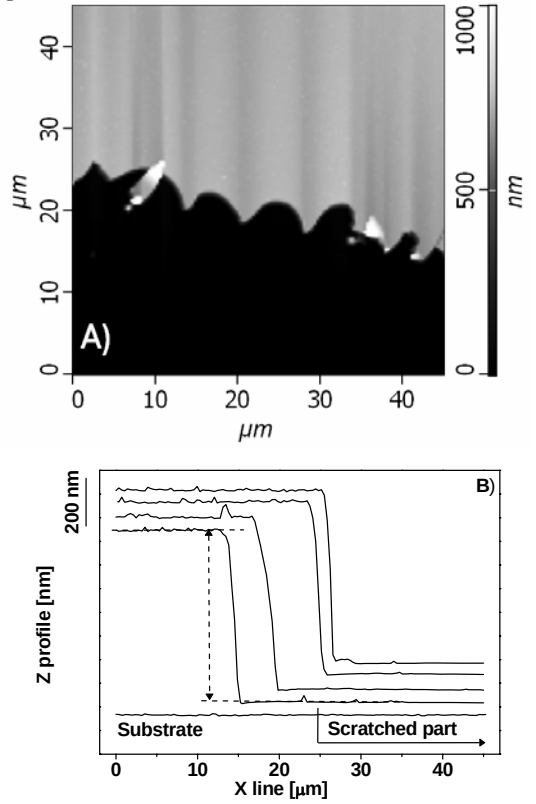

Fig 4. A) Topological AFM image of the scratch used for determination of the thin film thickness (virgin $Ge_{26}As_7S_{67}$ film) and B) corresponding line-scans perpendicular to scratch. The line-scan of scratched pure substrate glass is added..

The origin of observed photo-expansion remains to be unclear. Of interest is the fact that for virgin and for well annealed films, illuminated for one and the same time, the photo-expansion remains to be nearly the same, although the accompanying photo-induced band gap changes are different in sign and magnitude. Our optical measurements have shown that the irreversible photo-bleaching is very high, while the reversible photo-darkening is relatively low [2, 5]. This indicates that (i) not only some general one-to-one correspondence between photo-darkening and photo-expansion is lacking [6, 11], but (ii) most probably one-to-one correspondence does not also exist between photo-bleaching and photo-expansion. Stability of photo-expansion seems to be interesting since even after one year of ageing Δd(*a-i*) decreased to 19 nm while, even more, Δd(*v-i*) = 24 nm which is the value practically identical with the value Δd(*v-i*) = 26 nm measured for unrelaxed sample. The network of our composition ($Ge_{26}As_7S_{67}$, $Z \approx 2.6$) can be classified as a stressed-rigid network ($2.4 < Z < 2.8$) [10] and the excitation in such networks may be stable due to reasonable network rigidity. In our case ($Z \approx 2.6$) rather weakly stressed-rigid network and sufficient free volume in the network of the Ge-As-S system allows excitation propagation but, at the same time, the network rigidity assists to conservation of excitation. This can be the reason why ageing of photo-expansion in our sample is rather low.

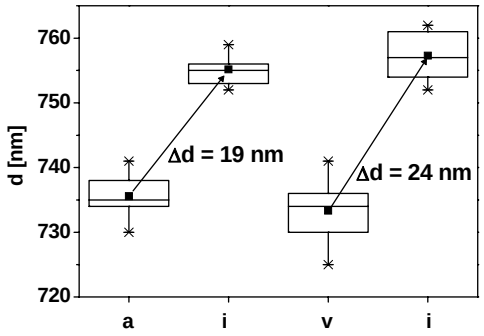

Fig. 5. The film thickness measured by AFM using "scratch" method for annealed, virgin and corresponding illuminated parts of $Ge_{26}As_7S_{67}$ films after one-year relaxation. The box-plot description is similar to Fig. 3.

4. Conclusions

Using Digital Holographic Microscopy and Atomic Force Microscopy we unambiguously identified existence of high photo-expansion in $Ge_{26}As_7S_{67}$ amorphous thin film. The magnitude of photo-expansion was found at around 26 nm (≈ 3.5 %) for illumination of virgin as well as annealed films. The magnitude of photo-expansion of annealed films decreases slightly to 19 nm after one year of ageing. No ageing in photoexpansion was observed in case of illuminated virgin film (*v-i*). We suppose that both, the high photo-expansion and its stability are associated with convenient rigidity of the film network.

Acknowledgement

P.K. acknowledges support from the project VZ 0021627501, L.T. acknowledges support from the project

AV0Z 40500505. The investigation is carried out in the frame of the bilateral project between Bulgarian and Czech Academies of Sciences.

References

[1] H. Hisakuni, K. Tanaka, Appl. Phys. Lett. **65,** 2925 (1994).
[2] F. Yakuphanoglu, D. Arsova, E. Vateva, J. Optoelectron. Adv. Mater. **9**, 334 (2007).
[3] D. Arsova, K. Beeva, E. Vateva, V. Pamukchieva, K. Beev, S. Sainov , J. Optoelectron. Adv. Mater. **9**, 3115 (2007).
[4] J. Swanepoel, J. Phys. E **16**, 1214 (1983).
[5] E. Vateva J. Optoelectron. Adv. Mater. **9**, 3108 (2007).
[6] K. Tanaka, A. Saitoh, N. Terakado, J. Optoelectron. Adv. Mater. **8**, 2058 (2006).
[7] P. Knotek, L. Tichý, Thin Solid Films **517**, 1837 (2008).
[8] J.T. Bloking, S. Krishnaswami, H. Jain, M. Vlcek, R.P. Vinci, Opt. Mat. **17**, 453 (2001).
[9] S. H. Messaddeq, M. Siu Li, S. Inoue, S. J. L. Ribeiro, Y. Messaddeq, Appl. Surf. Sci. **252**, 8738 (2006).
[10] S. Mamedov, D.G. Georgiev, T. Qu, P. Boolchand, J. Phys. Condens. Matter **15**, S2397 (2003).
[11] K. Shimakawa, Y. Ikeda, J. Optoelectron. Adv. Mat. **8**, 2097 (2006).

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