



Photoinduced structural changes in obliquely deposited As- and Ge-based amorphous chalcogenides: correlation between changes in thickness and band gap

Y. Kuzukawa, Ashtosh Ganjoo^{*}, K. Shimakawa

Department of Electronics, Gifu University, Gifu 501-1183, Japan

Abstract

The effect of band gap illumination and annealing below the glass transition temperature on the thickness and the optical band gap of As-based (As_2Se_3 , As_2S_3) and Ge-based (GeSe_2 , GeS_2) obliquely deposited chalcogenide films has been studied. It is observed that in the case of arsenic (As)-based glasses, illumination increases the thickness (expansion) and the band gap decreases (darkening), while as for germanium (Ge)-based glasses, both thickness and band gap show an opposite behavior to that of As-based glasses. By annealing the samples, before and/or after illumination, the trends of the changes in thickness and band gap are reversed. A strong correlation between the changes in thickness and band gap has been established for the first time. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Band gap; Thickness; Chalcogenide films; Illumination

1. Introduction

Various mechanisms [1–7] have been proposed to explain the reversible and irreversible changes in amorphous semiconductors induced by illumination. These studies have been mainly done on thin films prepared at normal incidence, i.e., substrate placed parallel to the evaporation source (flatly deposited) and bulk glasses. These photo-induced changes can be increased by varying the deposition conditions, mainly the angle of deposition, i.e., oblique deposi-

tion of the films, as these films have a columnar structure and a lesser density of atoms [8]. As a result, large changes can be and have been observed with photo-illumination in obliquely deposited chalcogenide films [8–10]. When the substrate is held at an angle to the source of the vapors (boat in the case of evaporation), the deposited atoms create a shadow (or a void) in their vicinity and thus, the density of atoms decreases and atoms are deposited in columns. As the atoms are surrounded by voids, it is relatively easy for them to move and undergo changes once illuminated by photons. In spite of large changes as expected in obliquely deposited chalcogenide films, due to their columnar structure, very little work has been done, mainly on germanium (Ge)-based chalcogenides, to study the effect of photo-illumination on the various properties. It

^{*} Corresponding author. R&D Group, YM Systems Inc., 146 Asahi-cho, Katsura, Nishikyo-ku, Kyoto 615-8027, Japan. Tel: +81-75 392 6611; fax: +81-75 315 1759; e-mail: ashtosh@ym-systems.co.jp.

has been shown by Starbova et al. [11], that As_2S_3 when deposited at an oblique incidence, also has a columnar structure, however, the changes induced by photo-illumination in obliquely deposited As-based chalcogenide films have not been studied until now, to our knowledge. As arsenic and germanium belong to different groups of the periodic table and their configuration with Se(S) atoms and their neighbors is expected to differ, and thus are expected to show different behaviors on photo-illumination. Also, no detailed study has been done on the total volume changes and their correlation with the optical changes, if any exists. The role of annealing and the effects it has on various properties and results of photo-illumination has also not been done in a systematic way.

In this work, the photoinduced effects of the thickness and the optical band gap of obliquely deposited As-based (As_2Se_3 , As_2S_3) and Ge-based (GeSe_2 , GeS_2) chalcogenide films has been studied. We have also observed the effects of pre- and post-illumination annealing on these changes. We are successful in developing a correlation between the changes in thickness and the optical band gap for these materials both for illumination and annealing.

2. Experimental

Films of amorphous As_2Se_3 , As_2S_3 , GeSe_2 and GeS_2 were deposited by conventional evaporation technique at room temperature onto Si and glass (Corning 7059) substrates to study the changes in thickness and band gap, respectively. The samples were deposited by placing the substrate at 80° of incidence to the evaporation source (boat), as the density of atoms is found to be minimum at this incident angle [8]. Se and S containing films were illuminated with a halogen and a mercury lamp (40 mW/cm^2), respectively, in vacuum ($\sim 1 \times 10^{-4}$ Torr) for 2 h through an IR cut filter. The samples were also annealed before and after illumination for 2 h in vacuum ($\sim 1 \times 10^{-6}$ Torr). Thickness and optical band gap were measured for as grown samples, after pre-illumination annealing, after illumination and after post-illumination annealing.

Thickness measurements were done using spectrometric film thickness measurement system (VM-

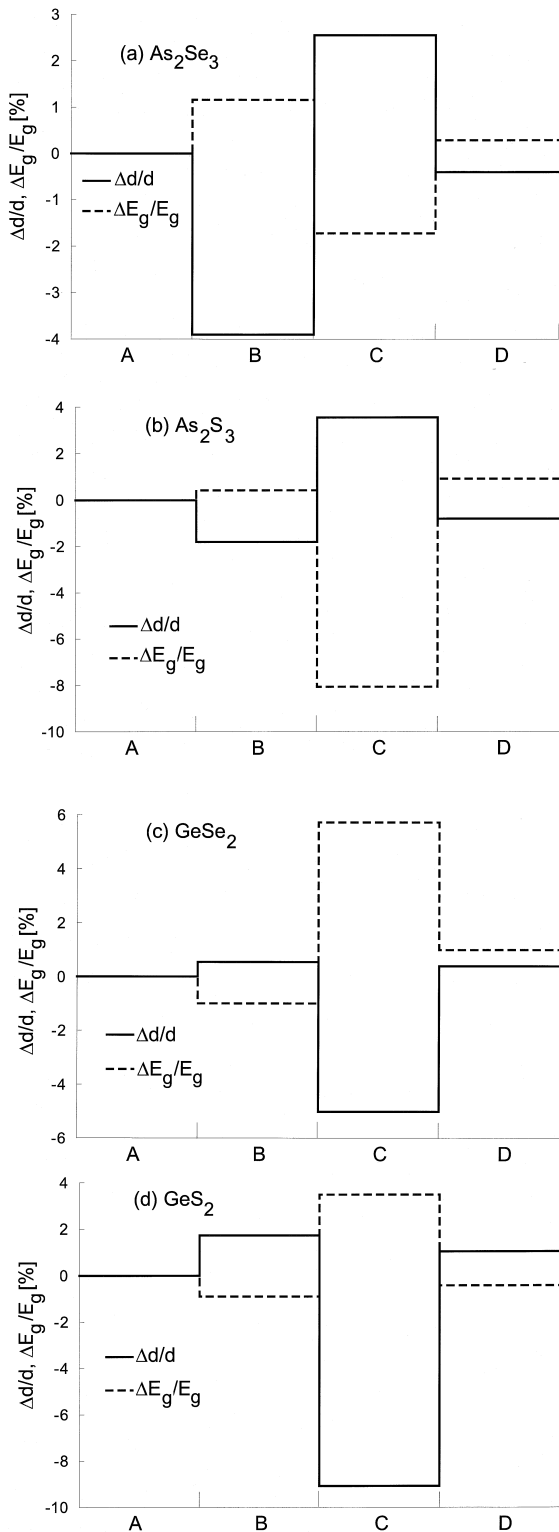
8000J; Dainippon Screen) with a beam spot of 50 μm and an accuracy of ± 1 nm. It is based on the principle of spectral analysis of interference fringes produced by the films. The reflected light beam from the sample, containing the interference information, is fed into a diffraction grating spectroscopy, where it is decomposed into light components of different wavelengths. Different voltages generated at a CCD camera, by these various wavelengths, are fed into a data processor to generate the spectral response curve. Film thickness is determined from the spectral response curve over the wavelength range from 400 to 800 nm and the accuracy is improved by means of curve fitting. Optical band gap was estimated from UV spectroscopic measurements using the Tauc plot.

3. Results

Fig. 1a–d shows the relative changes in thickness ($\Delta d/d$) and optical band gap ($\Delta E_g/E_g$) after various treatments of a- As_2Se_3 , As_2S_3 , GeSe_2 , and GeS_2 samples. The measurement details in the figure are: A, as grown; B, after pre-illumination annealing; C, after illumination; and D, after post-illumination annealing. The solid and the dashed line represents the relative changes in thickness and the optical band gap, respectively.

As is seen from Fig. 1a, for As_2Se_3 , the thickness decreases with annealing (thermal-contraction), while the band gap increases (thermal-bleaching). After illumination, the thickness increases (photo-expansion) while the band gap decreases (photo-darkening). Annealing the samples after illumination again decreases the thickness and increases the band gap. Now looking at Fig. 1b for As_2S_3 , we observe a similar behavior with illumination and annealing. This indicates that, for As-based glasses, photo-illumination always increases the thickness and decreases the band gap while as annealing before or after illumination decreases the thickness and increases the band gap.

Next, we look at the results for Ge-based glasses. As can be seen from Fig. 1c, for a- GeSe_2 , annealing the samples increases the thickness (thermal-expansion) and the band gap decreases (thermal-darkening). After illumination, the thickness decreases considerably (photo-contraction) and the band gap in-



creases (photo-bleaching). Annealing the samples after illumination results in an increase of thickness and decrease of the band gap. Again from Fig. 1d, for a- GeS_2 , a similar behavior is observed in the changes induced by illumination and annealing, however, the magnitude of changes are different for different compositions. Thus, it can be concluded that in Ge-based glasses, illumination always decreases the thickness (photo-contraction) and increases the band gap (photo-bleaching), while annealing before or after illumination always shows an opposite behavior.

4. Discussion

As can be seen from the results discussed above, for both As- and Ge-based films, increase of the thickness and decrease of the band gap and decrease of the thickness and the increase of the band gap occur simultaneously, both for annealing and illumination. The contraction and bleaching of Ge-based chalcogenides with illumination, in the present work, seems to correlate with the results of other workers [8–10]. Spence and Elliott [9] in their study on the effect of illumination on obliquely deposited Ge-based chalcogenides, have proposed that oxygen assisted bond reconstruction and light induced surface oxidation results in the increase in the band gap. However, they were able to reach this conclusion for samples illuminated in air. Singh et al. [10] in their work on the changes in thickness of obliquely deposited Ge-based chalcogenide thin films, attribute the decrease of thickness to rearrangement of the bonds on exposure to light followed by the collapse of the columnar structure of the films while Rajgopalan et al. [8] conclude that the changes in band gap are due to the photo-induced volume changes. However, no exact relationship between the changes in thickness and the band gap has been established till now.

Fig. 1. Relative changes in the thickness and the optical band gap for obliquely deposited thin films of (a) a- As_2Se_3 , (b) a- As_2S_3 , (c) a- $GeSe_2$ and (d) a- GeS_2 . The solid and the dashed line represent the changes in thickness and the optical band gap, respectively. A, B, C and D are defined in the text.

As already mentioned above, both for As- and Ge-based samples, increase in thickness and decrease of the band gap and decrease in the thickness and increase of the band gap occur simultaneously. This simultaneity is true for illumination and for annealing. We propose a correlation between the changes in thickness and band gap.

It is clear from the results that, the observed changes in thickness and the optical band gap, with illumination, are up to 11% and 8% in thickness and optical band gap, respectively, for these obliquely deposited samples. These changes are quite large as compared to those observed in normal incidence deposition samples, where fractional changes in volume and the band gap are smaller. However, it should be noted here that the changes in the band gap with illumination for obliquely deposited As- and Ge-based glasses show a behavior similar to that of normal deposition samples (photo darkening in As-based glasses and photo bleaching in Ge-based glasses), however for pre-illumination annealing, the results are not similar but opposite to those observed in the case of normal deposition samples. The results of photo-illumination and annealing effects observed in Ge-based glasses are observed to be opposite to those observed in As-based glasses.

5. Conclusions

It is observed that, by annealing, thickness decreases and band gap increases in As-based samples while illumination increases the thickness and decreases the band gap. For Ge-based glasses, the

effect of annealing and illumination is found to be opposite to that of As-based glasses. Also, annealing the samples before or after illumination always shows an effect which is opposite to that of illumination both for As- and Ge-based films. It has been observed that the changes in thickness and band gap are larger for obliquely deposited chalcogenide films. We find a correlation between the changes in thickness and optical band gap.

Acknowledgements

One of the authors (A.G.) would like to thank Mr. Y. Ikeda of YM Systems Inc., Japan for continued encouragement and fruitful discussions during this work.

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