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Photo-amorphization and photo-oxidation of $As_{50}Se_{50}$ thin films deposited onto silicon substrates

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Abstract

The photo-vitrification of $As_{50}Se_{50}$ thin films deposited onto silicon wafer substrates is reported. This process, which was found to be athermal, has been studied using X-ray diffraction measurements, far infrared spectroscopy, EDAX-measurements, and scanning electron microscopy. When the crystallized films were illuminated in order to be amorphized, photo-oxidation of the thin-film samples was also detected. As a consequence, arsenic trioxide microcrystals were formed in the whole matrix of the films. Such behaviour has not been observed with $As_{50}Se_{50}$ films deposited on glass substrates, which clearly demonstrates that the photo-vitrification phenomenon depends strongly on the type of substrate the $As_{50}Se_{50}$ thin film is deposited on. The radiation source is another factor that clearly influences the light-amorphization of a previously crystallized $As_{50}Se_{50}$ thin film. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

It has been observed that amorphous chalcogenides can suffer many light-induced structural changes [1]. These photo-structural changes when reversible, are only observed in well-annealed bulk glasses or amorphous thin films, where they can be removed by annealing near the glass transition temperature [2,3]. On the other hand, except for the metal photo-dissolution phenomenon, irreversible effects generally occur in metastable thin films. It has also been shown that illumination with high-intensity light can lead to photo-crystallization of amorphous $GeSe_2$ [4]. In the present letter, we report on the athermal photo-induced vitrification of $As_{50}Se_{50}$ thin films [5,6]. This process has only been observed when an $As_{50}Se_{50}$ film is crystallized on a silica glass substrate. We present here, for the first time, the photo-vitrification process of $As_{50}Se_{50}$ thin films deposited onto silicon wafer substrates. This photo-structural change will be discussed, not only in terms of far infrared spectroscopy, but also using X-ray diffraction (XRD) measurements.

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2. Materials and methods

Bulk samples were prepared by direct synthesis from high-purity elements (5N), heated together in an evacuated quartz ampoule, at a temperature of ≈ 950°C, for about 24 h. After the synthesis the melt was air-quenched, resulting in a bulk glass of the required chemical composition. The glassy nature of the ingot was checked using X-ray diffraction (Philips, model PW1710). Amorphous thin-film samples were prepared by vacuum evaporation of the $As_{50}Se_{50}$ bulk glass onto silicon substrates. The thermal evaporation process was carried out in a coating system (Edwards, model E306A), at a pressure of $\approx 10^{-6}$ Torr, from a suitable quartz crucible. Electron microprobe analysis of the as-deposited $As_{50}Se_{50}$ thin films indicated that the film stoichiometry is correct within ± 0.5 at.%. The film thicknesses, in the range of approximately 700–1200 nm, were measured with a stylus-based surface profiler (Sloan, model Dektak 3030). The samples were annealed at ≈ 150°C for periods of time of, typically, 72 h in a $\approx 10^{-3}$ Torr vacuum. The $As_{50}Se_{50}$ films were illuminated by use of a 500 W Hg arc lamp (Oriel, model 66032), through an IR-cut filter, and using a light intensity of ≈ 300 mW cm^{-2}. X-ray diffraction, using Cu K_α radiation (1.54 Å), was used to examine the glassy or crystalline nature of the films. The IR transmission spectra were measured, at room temperature, by use of a computer-controlled FTIR spectrometer (Perkin-Elmer, model 2000), in the energy region 720–30 cm^{-1}. The examination of the samples by scanning electron microscopy was carried out in a Jeol JSM-820 electron microscope.

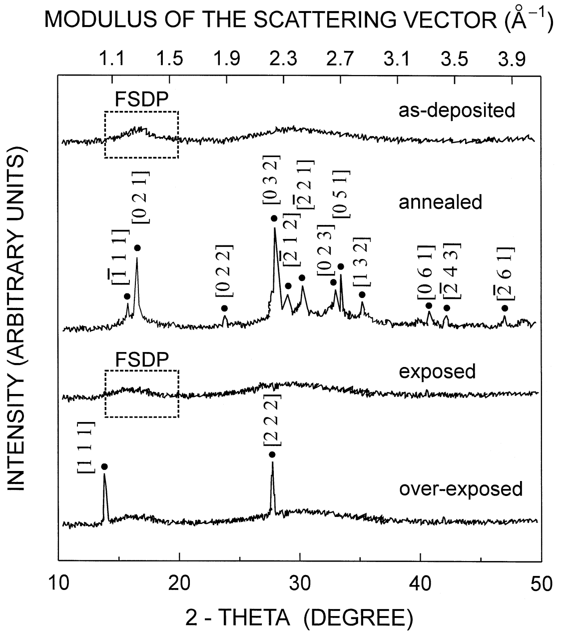

Fig. 1. XRD-patterns (Cu K_α radiation) of the as-evaporated, crystallized, photo-verified and photo-oxidized $As_{50}Se_{50}$ thin films, deposited onto silicon wafer substrates.

3. Results and discussion

X-ray diffraction patterns of as-evaporated, annealed and illuminated $As_{50}Se_{50}$ films, deposited onto silicon wafers are shown in Fig. 1. It should be noted the presence of the first sharp diffraction peak (FSDP) in the XRD-patterns of the as-evaporated and illuminated films [5]. However, that feature is not present in the XRD-pattern of the crystallized product. The peak intensities measured in our experiments are different from the reference powder-diffraction data, due to the existence of preferred orientational effects in the crystallized films.

We found in a previous work [7], that the XRD-pattern of $As_{50}Se_{50}$ crystallized films on glass substrates, present the most intense peaks at $2\theta = 27.59°$ and 16.20°. In addition, less intense peaks were observed at $2\theta = 15.31°$, 28.58°, 29.90°, 32.64° and 48.05°. If we compare these data with those obtained for $As_{50}Se_{50}$ crystallized films on silicon substrates, more peaks are resolved in the latter case. Apart from the peaks already found in the former case (except the peak at $2\theta = 48.05°$), peaks at $2\theta =$ 23.36°, 33.06°, 34.85°, 40.45°, 41.75° and 46.60° are clearly present in the XRD-pattern of $As_{50}Se_{50}$ films, deposited onto silicon substrates. Thus, we can certainly assume that the crystallization process, which takes place upon annealing of $As_{50}Se_{50}$ glass films, is different, depending on the type of substrate involved. Furthermore, in both cases, the structure of $As_{50}Se_{50}$ crystallized films is composed of As_4Se_4 quasi-spherical molecules [7].

The crystallized $As_{50}Se_{50}$ films were then exposed, in air, to white light from the mercury arc lamp for a period of time of about 10 h, at room temperature, which caused the *complete* disappearance of the crystalline features in the XRD-pattern (see Fig. 1). This observation obviously implies the photo-amorphization of these $As_{50}Se_{50}$ films. During the illumination process, the temperature increase of the films, as monitored by a thermocouple attached to the surface of the $As_{50}Se_{50}$ films, was never more than ≈ 25°C. This observation gives unambiguous evidence of the athermal character of the photo-induced amorphous-state transformation.

However, one differentiating structural characteristic of the photo-vitrification process which takes place using a glass substrate [7], in relation to that which occurs when a silicon substrate is used, is the total disappearance of FSDP in the former. In the latter, the FSDP does *not* disappear, although it becomes somewhat broader in the light-amorphized state.

On the other hand, Elliott and Kolobov [5], used a quartz tungsten halogen lamp, and observed that both the XRD-patterns of as-evaporated and photo-vitrified $As_{50}Se_{50}$ thin films, deposited onto glass substrates, show the same features, including the FSDP. This observation seems to suggest that the type of radiation source is another factor to be taken into account when an $As_{50}Se_{50}$ crystallized film is to be light-amorphized.

Furthermore, the crystallization–vitrification process was found to be *reversible* with the present $As_{50}Se_{50}$ films, deposited on silicon substrates. That means that the photo-vitrified film could again be crystallized by thermal annealing again at ≈ 150°C, and then, vitrified once more by the corresponding illumination. A similar behaviour was observed, when glass substrates were involved [6,7].

When the time of exposure of an $As_{50}Se_{50}$ crystallized film, deposited onto a silicon substrate, was much longer than that mentioned earlier (in this particular case, we usually carried out the illumination for periods of time of ≈ 20 h), we found that *new* crystalline peaks arise upon irradiation of the film, as shown in Fig. 1. The XRD-pattern corresponding to the *over-exposed* sample could be explained in terms of a photo-oxidation of the film, and the consequent formation of arsenic trioxide crystals. This behaviour has certainly not been observed before during the photo-vitrification process, when glass substrates were used and, apparently, is a characteristic of such photo-induced phenomenon when the thin-film sample is deposited onto silicon wafers. As_2O_3 microcrystals were roughly identified compositionally by EDAX-measurements, and structurally by X-ray diffraction. Scanning electron microscope photomicrograph of the surface of the over-exposed $As_{50}Se_{50}$ thin film, shows an arsenolite microcrystal (see Fig. 2).

On the other hand, the presence of chemical instability in amorphous As_2Se_3 films has already been reported by Trubisky and Neyhart [8]. The decomposition of this glassy material was explained in terms of the following oxidation reaction:

$$As_2Se_3 + 3/2O_2 \rightarrow As_2O_3 + 3Se,$$

taking place at the surface of the film. In fact, the oxidation process represented above is highly favourable, if we consider the calculated heat of that particular chemical reaction, $\Delta H = -124$ kcal/mol. As_2O_3 microcrystals were identified in this case and, consequently, that reaction seemed to describe the source of chemical instability in a-As_2Se_3 films. However, the possible effect of light was not studied in those experiments. The fact that As_2O_3 microcrystals were much more numerous, when a-As_2Se_3 films had been stored under daylight conditions, compared to those that had been kept in complete darkness, clearly indicates that there is an important role played by the light in this oxidation process [1].

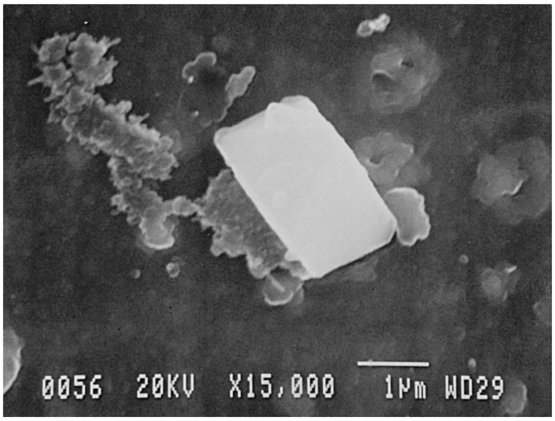

Fig. 2. Scanning electron microscope photograph of an $As_{50}Se_{50}$ photo-oxidized film, where an arsenolite microcrystal can be seen.

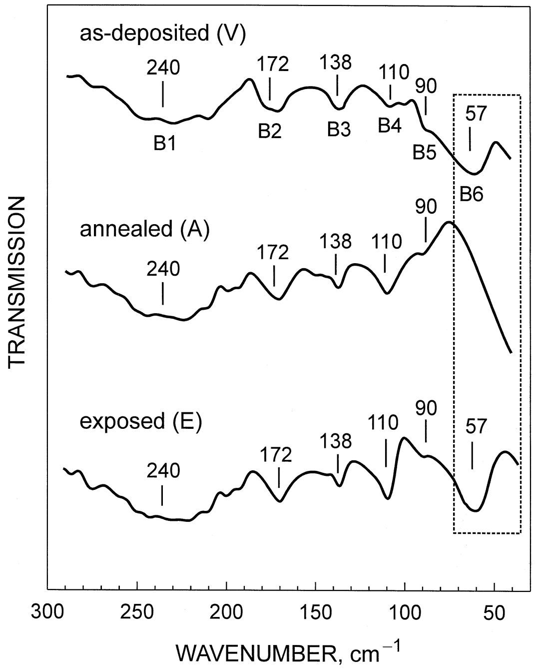

Fig. 3. Far infrared spectra of $As_{50}Se_{50}$ thin films. V, virgin; A, after annealing; E, exposed.

Typical far infrared transmission spectra of as-deposited, annealed and exposed $As_{50}Se_{50}$ films onto silicon substrates are presented in Fig. 3. The main infrared feature around 240 cm^{-1}, in the spectrum of the as-deposited thin-film sample, corresponds to As–Se bond-stretching vibrations [9,10]. The pyramidal molecules $AsSe_3$ and As_2Se_3 are responsible for the absorption band at 110 cm^{-1} [11,12], whereas the band at 172 cm^{-1} is due to deformational vibrations of As–Se bonds [13]. Polymeric Se mode is observed at 138 cm^{-1} (bond-bending mode of the Se chain) and Se_8 rings at 90 cm^{-1} [14,15]. Additionally, there is a strong absorption band at 57 cm^{-1}.

On the other hand, the IR spectrum of the crystallized film shows the existence of absorption bands at wavenumbers very close indeed, to that already found in the IR spectrum of the as-deposited sample. Nevertheless, there is a very significant difference between those transmission spectra: the *complete* disappearance of the band at 57 cm^{-1}, as a consequence of the thermal annealing process.

Finally, illumination with a Hg arc lamp of the annealed sample gives rise, again, to an absorption band at 57 cm^{-1}, in the IR spectrum of the corresponding photo-vitrified thin film. The other absorption bands observed in the IR spectra of the as-deposited and crystallized films are also present in the spectrum of the $As_{50}Se_{50}$ photo-vitrified film.

4. Conclusion

From the above results, we can certainly conclude, that there is a clear change in the absorption band at 57 cm^{-1}, whereas the other IR bands remain practically unchanged. In addition, we have cycled annealing and illumination, and proved that the change observed in the IR absorption band at 57 cm^{-1} is *reversible*. It should be pointed out that, in application of a molecular model to amorphous As_2Se_3, a calculated band at 78 cm^{-1} has been ascribed to the antisymmetric bending vibration in $AsSe_3$ pyramids [10]. A shift to the value of 57 cm^{-1} could perhaps be explained assuming some changes in the angle and/or in the coordination of the As 'central atom'. However, this is not clear since there could also exist some interlayer modes (i.e., van der Waals modes) (L. Tichý, private communication).

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