

Raman Spectra of As_2S_3 in Bulk Glass and Amorphous Film Forms

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ABSTRACT

Structural changes induced by light and heat treatment in vacuum deposited amorphous chalcogenide films prepared by thermal evaporation methods with different rates have been investigated using Raman scattering. The changes in the Raman spectra of thermally evaporated amorphous As_2S_3 films after light treatment are interpreted in terms of rearrangement of bonding configurations of molecular species that exist just after deposition. As the evaporation temperature or deposition rate is increased, irradiation with band-gap light and even more annealing of the films induces arsenic-enrichment and the formation of micro crystallites. The reversible photo-induced changes in annealed films involve negligible small change in bonding statistics. Discernable change occurs in the medium-range order.

KEYWORDS:

1. INTRODUCTION

The structural, optical and photo-physical properties of chalcogenide glasses have been permanently the subjects of systematic interest more than 40 years.^{1–4} The interest have been stimulated both by unresolved fundamental scientific problems of non-crystalline materials (e.g., the structure, electronic properties, to say about few) and the need to assess their potential as optical memory elements, for image formation and other useful applications.

The structural and physical properties of amorphous chalcogenides depend on preparation conditions and subsequent sample treatments, although in less sensitive manner as their crystalline counterparts. In many cases the initial structures of amorphous films differs from those of well-annealed films or their bulk-glass counterparts and undergo significant irreversible structural changes in response to band-gap illumination or annealing (so-called photo- and thermo-induced changes). Although the induced effects mentioned above have been reviewed many times, their origin still remains disputable.

In the following communication, we have made an attempt merely to share our experience on examining the influence of preparation conditions (e.rates) and of various treatments (irradiation or annealing) on the structure of fresh (as-deposited) $\text{As}_x\text{S}_{1-x}$ amorphous films. The latter are particularly suitable objects for such a study because

the irreversible changes in the optical properties of these materials, especially in As_2S_3 , are much more pronounced than those in other chalcogenide glasses, e.g., $\text{As}_x\text{Se}_{1-x}$.

2. EXPERIMENTAL TECHNIQUES

Usually the samples used in these studies were amorphous films, typically 5–20 μm thick. The films were prepared in conventional manner, by thermal vacuum evaporation of glassy $\text{As}_x\text{S}_{1-x}$ alloys (high-purity elements were alloyed by melting in evacuated and sealed quartz ampoules) from a molybdenum boat onto glass and quartz substrates. The evaporation was performed under two different conditions: evaporation onto a substrate with deposition rate $\sim 20 \text{ \AA s}^{-1}$ (conventional mode) and evaporation onto a substrate with deposition rate $\sim 1000 \text{ \AA s}^{-1}$ (flash evaporation). The deposition rate was varied by changing the source (evaporation boat) temperature while the substrate temperature was held constant at $T = 300 \text{ K}$. Chemical compositions of the films, e.g., As_2S_3 , were found to be $\text{As}_{39.7}\text{S}_{40.3}$ on the basis of electron microprobe analysis. The lack of crystallinity in the film samples was systematically verified by X-ray diffraction measurements.

Raman spectra were measured by conventional and Fourier Transform IR Raman spectrometry (Bruker, model IFS 55). Laser irradiation of the wavelength of 647.1 and 1064 nm from Kr-ion and Nd:YAG lasers were used for the excitation of the Raman spectra. Such a low energy, especially for the latter case, is well below the values of the optical band gaps for the glassy alloys under study. Thus, no detectable photo structural transformation took place

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under data collection. It is quite naturally that the amplitudes of some Raman lines from $\text{As}_x\text{S}_{1-x}$ films were often low (respectively to that in bulk glass), the spectra usually were “noisy” and not smooth. Back-scattering method was exploited with the resolution of 1 cm^{-1} . Raman spectra of the amorphous films were recorded at sufficiently low incident laser-beam power density (3–5 mW) to avoid possible photo structural changes in a case of 647 nm excitation line. A Kr⁺-ion laser was used as an exposure source and the films were exposed at an intensity of $30\text{ mW} \times \text{cm}^{-2}$. Although structural transformations in $\text{As}_x\text{S}_{1-x}$ films were the subject of numerous articles,^{5–17} some important aspects are still not fully understood.

3. RESULTS AND DISCUSSION

First of all we consider the results obtained for conventionally prepared amorphous films. Figure 1 shows the Raman spectra for the as-deposited (a), exposed (b), annealed film (c), and bulk-glass (d) forms of As_2S_3 .

Qualitatively similar results for irreversible thermostructural transformation have been firstly reported by Solin and Papatheodorou,⁵ Nemanich et al.,⁶ Frumar^{8,9} and the present authors.^{7–9} The spectrum of the as-deposited film consists of relatively sharp peaks on the background, typical of bulk As_2S_3 glass. These sharp features, characteristic to the as-deposited film, broaden, decrease in the intensity or even disappear irreversibly after annealing or on illumination. Such a behavior indicates that significant (in the sense of amorphous semiconductors) structural modification has take place. Note that in bulk glass and amorphous film with As content exceeding 40 at % all the relatively sharp features mentioned above are also observed. The data analysis^{7–13} indicates that all the sharp spectral features (except of the 490 cm^{-1} band) originate from “wrong” (like-atom or homo-polar) As–As bonds in As_4S_4 molecular units. The presence of As_4S_4 molecules in the as-deposited As_2S_3 films is strongly supported by IR,¹⁴ EXAFS¹⁵ and recent Raman scattering^{7–11} measurements. Taking this into account, as-deposited films

of As_2S_3 possess AsS_3 pyramidal units, which form glassy matrix of As_2S_3 and, in addition, a partially polymerized mixture of As_4S_4 (realgar-type) and S_n molecular species.

After annealing, the spectrum of the as-deposited film becomes very similar to that of bulk glass. However, some broad features, namely maxima at 187 and 230 cm^{-1} , remain. This indicates that some “wrong” bonds of the As–As, S–S-type exist even in well-annealed As_2S_3 films. During this treatment the bond breaking and switching due to an increased mobility of atoms is accompanied (to a considerable extent) by structure polymerization. This is manifested in the S–As–S stretching mode ($120\text{--}170\text{ cm}^{-1}$) frequency spreading and vibration band broadening typical of the bulk glass. Similar behavior in the valence-mode region of As–S and As–As vibration bands takes place if the as-deposited film were initially pre-illuminated by band-gap light. Consequently, one can suggest that the structure of illuminated films remains closer to that of as-deposited films than the structure of annealed ones.

In most studies on arsenic-based chalcogenide films including those examined in the present section the experimentalists deposit amorphous layers at fairly low deposition rates in $10\text{ to }100\text{ \AA s}^{-1}$ range. Illumination of these samples with band-gap light shifts the absorption edge to lower energies (so-called “red” shift or photo darkening). In contrast, setting the evaporator temperature $T_{\text{evap}} = 800\text{--}900\text{ }^\circ\text{C}$ and deposition rate of $\geq 300\text{ \AA s}^{-1}$ leads to a structural modification which in turn results in a decrease in the optical band-gap. The exposed samples behave like “positive” (in contrast to materials with negative image formation) photosensitive layers, i.e., they exhibit a “blue” shift of absorption edge. In Figure 2, typical Raman spectra of un-annealed and annealed films deposited at a higher rate are shown.

In general, it is clear that raising the evaporation temperature and deposition rate leads to significant sharpening of spectral bands. Synchronously, both the

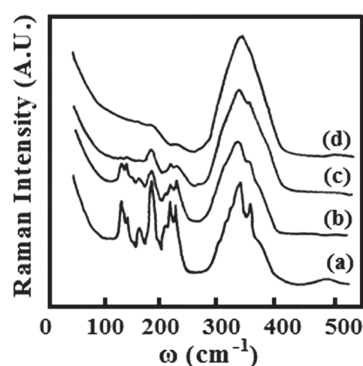


Fig. 1. Raman spectra of (a) as-deposited amorphous As_2S_3 films, (b) photo darkened amorphous As_2S_3 films, (c) annealed amorphous As_2S_3 films and (d) bulk As_2S_3 glass.

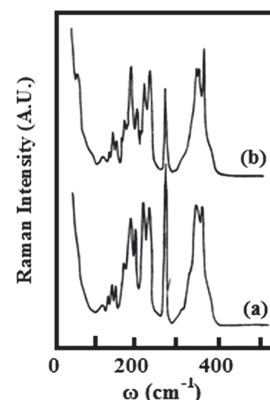


Fig. 2. The Raman spectrum of As_2S_3 film prepared with high deposition rate (see the text for details). (a) un-annealed sample and (b) annealed sample.

smooth background and the high-frequency component at 490 cm^{-1} , which represent S–S bonds polymerized in the glass network, disappear. At the same time, additional spectral features at 120, 150, 200, 233 and 273 cm^{-1} appeared. Note that the peak at 273 cm^{-1} which dominates the Raman spectrum of the film deposited at high deposition rate is not resolved in As_2S_3 crystals and $\alpha, \beta\text{-As}_4\text{S}_4$ polymorphs. This feature was observed in the Raman spectrum of crystalline As_4S_3 sample obtained by vacuum sublimation of As_4S_3 melt.¹⁶

As the deposition rate increased, the films were found to become sulfur-deficient. This is the case even for sulfur-rich compositions (see Fig. 3). One of the reasons for such As-enriching of the samples may be the partial fragmentation of As_2S_3 into As_2S_2 and sulfur species during the deposition. Note that an increase in temperature from which the melt was quenched has a similar effect on the structure of melt-quenched As_2S_3 , as was demonstrated by Yang et al.,¹⁵ Mikla et al.⁷ and Zitkovsky and Bolchand.¹⁷

Only a slight change in the Raman spectrum was observed after irradiation of such films. In contrast, annealing leads to further narrowing of the bands, splitting, and intensity redistribution. A distinct shoulder at 60 cm^{-1} appeared in the low-frequency region of annealed films. Probably, this shoulder corresponds to the lattice (intermolecular) vibrations of the $\alpha, \beta\text{-As}_4\text{S}_4$ crystals.¹³

It is important to point out here that the transformation of the Raman spectrum with As content increasing above stoichiometric $\text{As}_{0.4}\text{S}_{0.6}$ composition is similar to that observed with an increase in deposition rate for As_2S_3 as-deposited films (see Figs. 2 and 4 for comparison). Results suggest that high deposition rate induce microcrystallites formation. Annealing further enhances the crystallization processes and the films become polycrystalline. The above structural transformations, observed for the films deposited at high rates, are irreversible in the sense that the initial structure (and structure-related properties) cannot be eliminated by annealing at the temperatures close to the glass transition temperature, T_g . Moreover, the films deposited at higher rates always appeared smooth,

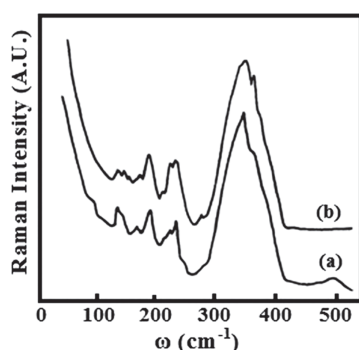


Fig. 3. Typical Raman spectra observed for $\text{As}_{0.30}\text{S}_{0.70}$ films. Curve (a) is the spectrum of the film prepared in conventional manner (slow-deposited), curve (b) corresponds to the fast-deposited film.

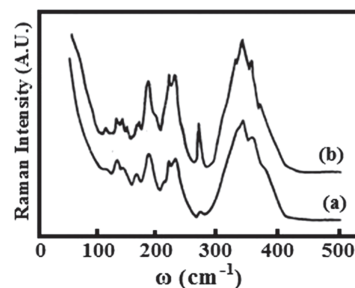


Fig. 4. Raman spectra of $\text{As}_{0.44}\text{S}_{0.56}$ films prepared by (a) slow evaporation and (b) fast evaporation.

but took on a “dusty” appearance after light- and, especially, heat-treatment.

Regarding the films prepared in conventional mode (slow-deposited films), we have examined how photo darkening of well-annealed films and bulk samples (i.e., reversible photo induced changes) influences their structure. Undoubtedly, the magnitude of reversible photo induced changes is small compared to irreversible ones. Structural changes detected by means of direct structural probes (e.g., X-ray diffraction¹⁸) were subtle. Indirect probes of local structure by means FT Raman spectroscopy (which is believed more sensitive than conventional Raman spectroscopy) indicate only negligibly small changes. At the same time, it should be noted that low-frequency light scattering which is sensitive to mediate-range order can provide some structural information in terms of correlation length. In Ref. [8] authors observed an increase in the intensity of the 231 cm^{-1} Raman band characteristic of As–As vibrations in a- As_2S_3 with photo darkening. In contrast, the present authors cannot detect even slight changes in Raman spectrum in the frequency range $100\text{--}500\text{ cm}^{-1}$. Only low-frequency Raman spectra show discernible changes caused by band-gap illumination.

Figure 5 is the summary of the low-frequency Raman data measured at room temperature. As_2S_3 glassy samples were illuminated for different times ranged from 1 to 240 min. One can observe gradual shift of the above peak to higher frequencies with the illumination time. In addition, the intensity of the low-frequency peak also changes.

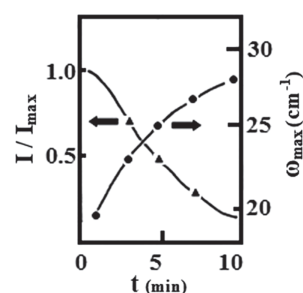


Fig. 5. Changes in the low-frequency peak position and relative intensity with exposure time. I_{max} is the peak intensity for virgin sample.

The intensity of so-called Boson peak seemed to decrease at reversible photo darkening.

Irreversible structural changes that occur in thin films prepared in conventional regime upon optical illumination can be understood in terms of the mechanism described in Refs. [5–14, 19]. These changes are associated with a photo polymerization of As₄S₄ and S_n molecular species. The resultant structure is layer-like two-dimensional with restored chemical ordering.

Flash evaporation enhances significantly compositional as well as structural disorder in amorphous samples compared to stoichiometric composition. An increase in As concentration leads to a condensation of As₄S₃ and some other As-rich molecular species; chemically disordered molecular solid is obtained. These compositions are unstable; phase separation occurs upon thermal annealing and light irradiation. Irreversible photo induced changes observed in fast-deposited films differs from irreversible changes in conventionally prepared amorphous films from a phenomenological point of view and also with respect to their origin.

On the basis of present Raman results we can suggest that, in contrast to the irreversible structural changes, changes in local structure do not accompany the reversible photo-induced changes observed in well-annealed amorphous films. This means that covalent (intra-molecular) bond breaking is unlikely to be the dominant mechanism responsible for reversible light-induced effects in amorphous chalcogenides.

The most significant changes are observed in the low-frequency region ($\omega_{\max} \approx 25 \text{ cm}^{-1}$ for As₂S₃) of light scattering spectra. The presence of the Boson peak signifies certain medium-range order in the amorphous structure.^{20–22} The position and the intensity of the peak can be used to estimate the structural correlation length $R_c \sim (\omega_{\max}/V)^{-1}$, where ω is the frequency of the peak maximum and V is a sound velocity, and to characterize the degree of structural ordering. The structural correlation length is generally associated with the dimensions of some cluster-like structure. For a-As₂S₃, the R_c value is $\sim 7.6 \text{ \AA}$. The clusters may exist in the form of linked pyramids. Although the origin of low-energy excitations in disordered solids is still disputable, differences in the parameters of Boson peak observed for annealed and photo darkened states are presently attributed to changes in medium-range order. A decrease in the peak height and a shift to higher ω values may be related to an increase in structural randomness. This is consistent with an increase in structural disorder under illumination detected by EXAFS spectra.^{15,23} In spite of experimental results presented on Raman scattering, photo darkening is accompanied by certain structural change on the scale of medium-range order: weakly linked AsS₃ pyramids move with respect to each other, as proposed in Ref. [24]. The advantage of this mechanism is that it does not require

covalent bonds breaking. There exists another possible explanation—modification of short-range order (see e.g., Refs. [24–28]). It seemed that unconventional (diffraction-like) experiments are the only that can give unambiguous evidences on the origin of structural changes at reversible photo darkening.

4. CONCLUSIONS

In this section the influence of thermal evaporation conditions and subsequent light and heat treatments on the atomic structure was studied. The major experimental findings of these studies may be summarized as follows.

The pronounced irreversible change observed in the Raman spectra of slowly deposited films with illumination is direct evidence for gross structural changes caused by optical irradiation occur. Such behavior has been interpreted in terms of a photo polymerization mechanism. The films were found to become sulfur-deficient as the deposition (evaporation) rate increased, because of partial fragmentation of As₂S₃ into As₃S₂ and sulfur during the deposition. Fast-deposited films are unstable and phase separation occurs upon light irradiation. The reversible photo induced effects in well-annealed amorphous films involve structural modifications in the medium-range order.

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