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Irreversible thermostructural transformations in amorphous As_2S_3 films: A light-scattering study*

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Polarized spectra of evaporated thin films of As_2S_3 glass have been recorded before and after annealing at the glass transition temperature and compared with the corresponding spectrum of the bulk glass. The spectra of virgin films consist of several sharp molecular bands superposed on a networklike continuum which is characteristic of the bulk glass, whereas annealed films yield only the bulk glass spectrum albeit with some indication of residual nonstoichiometry. These results are direct evidence that irreversible thermostructural transformations (or equivalent photostructural transformations) in evaporated As_2S_3 films proceed through polymerization of a metastable molecular glass as suggested by deNeufville, Moss, and Ovshinsky. The polarized Raman spectra of the vapors over As_2S_3 liquid have been obtained and indicate the presence of serveral gaseous molecular species. The molecular constituency of the evaporated amorphous film is also complex but distinct from that of the vapor, an indication that deposition itself introduces some structural alterations.

INTRODUCTION

The topological arrangements of atoms in an amorphous solid can be drastically altered by exposure to heat or to above the band-gap radiation. The configurational changes so induced are characterized, respectively, as thermostructural or photostructural.[1] Photostructural transformations are additionally specified as reversible or irreversible. Naturally those amorphous solids which exhibit reversible photostructural changes have aroused considerable research interest.[1] That interest is a manifestation of the potential technological impact associated with the collateral reversible optical properties they exhibit and their resultant capacity for information storage. But the reversible phenomena exhibited by the best characterized amorphous materials involve extremely subtle structural changes which are therefore difficult to specify.[2] In contrast, the irreversible photostructural changes are generally quite gross and are thus potentially more amenable to careful analysis.

Such an analysis has been initiated by deNeufville, Moss, and Ovshinsky[3] (DMO) who in a recent paper reported on x-ray diffraction and optical index of refraction and absorption studies of photostructural and thermostructural changes in As_2S_3 and As_2Se_3 thin evaporated and sputtered films. By comparing x-ray diffraction profiles of evaporated films which were first illuminated and then annealed with the profiles of films which were first annealed and then illuminated DMO were able to demonstrate that the irreversible thermostructural and photostructural changes involved the same atomic rearrangements. To explain their observations, DMO suggested that a freshly evaporated film was in fact a molecular glass composed of "hard sphere" As_4S_6 molecules which when heated or illuminated polymerize or cross link to form a network structure characteristic of the bulk glass. That interpretation for irreversible structural transformations in As_2S_3 and As_2Se_3 amorphous films is supported by a comparison of x-ray spectra with the predictions of the Finney hard-sphere model from which the film density can be calculated. However, structural analyses based solely on careful x-ray studies such as those of DMO can be refined by the application of long-wavelength optical probes. To quote from a recent review article by deNeufville,[1] "to the extent that irreversible structural changes are associated with polymerization... Raman and infrared spectroscopy constitute obvious tools to improve structural specification. Unfortunately, these standard tools appear never to have been applied directly to the characterization of irreversible or reversible photostructural transformations in chalcogenide systems." Accordingly, the purpose of this paper is to employ Raman spectroscopic techniques to the study of irreversible thermostructural or photostructural transformations in evaporated amorphous As_2S_3 films. In addition, because the film properties depend intimately on the molecular composition of the vapor phase from which they are formed we will also report here the Raman spectra of the gas produced when As_2S_3 bulk glass is melted in vacuum.

APPARATUS AND SAMPLES

The Raman measurements reported here were performed with a spectrometer that consisted of a Jarrel Ash model 25-100 double monochromator equipped with either Jarrel Ash ruled gratings blazed at 1.3 μm and used in second order (film studies) or Jubin Yvon holographic gratings blazed for 5000 Å and used in first order (gas studies). Also employed were an ORTEC modular photon counting detection system, an ITTFW 130 photomultiplier tube cooled to -30 °C and Coherent Radiation Laboratories Model 52 argon and krypton-ion lasers. The apparatus is described in detail elsewhere.[4] To obtain the high-temperature spectra of gaseous arsenic sulfide(s), a nichrome-wire dual-winding water-cooled high-temperature optical furnace was constructed. The furnace was equipped with a chromel alumel thermocouple for monitoring temperature and had an effective collection aperture of f1.0. It too is described in considerable detail elsewhere.[5]

Polarized measurements of $I_{\perp,\perp}(\omega)$ and $I_{\parallel,\perp}(\omega)$ of the amorphous films were performed in the backscattering configuration using the 6471-Å krypton-laser excitation line. Transmission right-angle polarized measurements of $I_{\perp,\perp}(\omega)$ and $I_{\parallel,\perp}(\omega)$ were obtained from the As$_2$S$_3$ vapors. Here $I(\omega)$ is the Raman spectral distribution and the subscripted polarization designations $\perp$ ($\parallel$) correspond to light polarized (or analyzed) orthogonal to (in) the scattering plane. Raman spectra of the amorphous As$_2$S$_3$ films were recorded with sufficiently low incident laser-beam power densities and with sufficiently short exposure times to avoid photostructural changes in the as-deposited films.

The evaporated amorphous As$_2$S$_3$ films used in this work were kindly provided by Energy Conversion Devices, Inc., of Troy, Michigan and were identical to corresponding samples studied by DMO who give complete details of the preparation techniques.[3] The spectra of as-deposited films were recorded and those films were subsequently annealed in a flowing dry nitrogen atmosphere after which spectra were recorded to deduce the effect of thermostructural changes. Once fully annealed for 1 h at $T_g \approx 180$C°: where T_g is the glass transition temperature, subsequent annealing at T_g produced no further detectable changes in the Raman spectra of the film no matter how long annealing was carried out.

To obtain the spectrum of gaseous arsenic sulfide a cylindrical quartz tube of dimension 20-mm o.d. by 6 cm long with a wall thickness of 1 mm was used. Preweighed amounts of bulk As$_2$S$_3$ glass (obtained from Servo Corp. of America, Hicksville, Long Island, N. Y.) were transferred into a dry and degassed cell of known volume. The cell was then sealed under a vacuum of $\approx 10^{-6}$ Torr, attached to a manipulation rod and placed in the optical furnace. The temperature variation over the illuminated region of the gaseous sample was ~5 K.

RESULTS AND DISCUSSION

As noted above, DMO have shown that irreversible thermostructural and photostructural effects in As$_2$S$_3$ films were completely equivalent. We have only examined thermostructural effects; however, we assume the results reported here would be unaltered if the as-deposited films had been illuminated rather than annealed.

The Raman spectra of an as-deposited evaporated As$_3$S$_3$ film, an evaporated and annealed film, and bulk As$_2$S$_3$ glass are compared in Figs. 1(a)–1(c). The contrast exhibited by the spectra of Fig. 1 is quite dramatic. As can be seen from Fig. 1(a), the spectrum of the as-deposited film consists of a

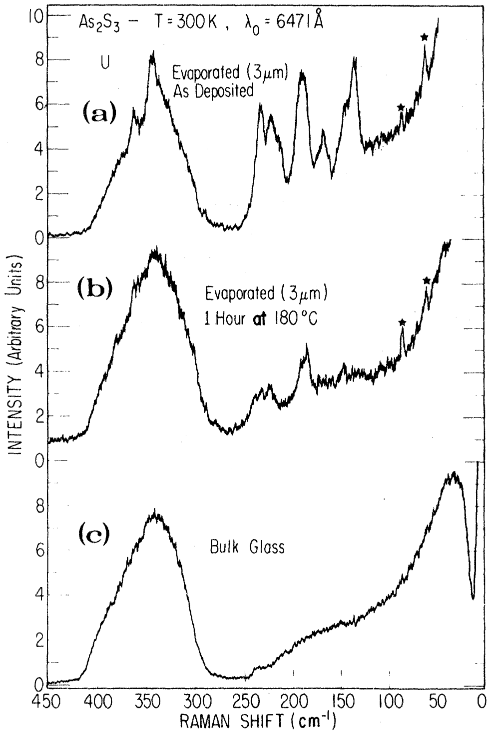

FIG. 1. Polarization unanalyzed (U) Raman spectra of (a) an evaporated as-deposited film, (b) after annealing at 180 °C for 1 h, (c) bulk glass. The spectra were excited with ~30 mW of cylindrically focused 6471-Å Kr radiation and recorded using a spectral slit width of 3.6 cm^{-1}, a time constant of 5 sec and a scan rate of 5 Å/min. The abscissa in this and subsequent spectra is marked in wave numbers but linear in wavelength. The ★'s in this and subsequent figures indicate grating ghosts, an instrumental artifact.

continuum background much like the spectrum of the bulk glass[6] [Fig. 1(c)] but upon which is a superposed series of sharp bands. Most of those bands disappear when the film is fully annealed. With the exception of the features at 180 and 230 cm^{-1}, the bulk glass and annealed film spectra are indistinguishable. The sharp bands in the spectrum of the as-deposited film are signatures of one or more molecular species present in the amorphous film. The continuum background on which they are superposed is characteristic of inelastic light scattering from an As_2S_3 network glass [Fig. 1(c)].[6] On deposition some of the molecular species in the As_2S_3 vapor polymerize to yield the continuum of Fig. 1(a) while some of the molecules affix themselves apparently intact and/or transform to other molecular forms. Upon annealing, the molecular species cross link and polymerize to form a network glass. The features at 180 and 230 cm^{-1} are, we believe, symptomatic of a nonstoichiometric configuration in the As_2S_3 glass and may reflect the presence of some S-S bonds and/or As_xS_y units.[7] As-deposited films annealed not just for 1 h but for several hours at 180 °C yielded spectra identical to that of Fig 1(b). Figure 1 supports, in part, the model of DMO. What remains to be confirmed is their assumption that As_4S_6 is the molecular species which polymerizes when the amorphous As_2S_3 film is annealed or illuminated.

A high-resolution spectrum of an as-deposited evaporated As_2S_3 film is shown in Fig. 2. The Raman shifts of the sharp bands in that spectrum are tabulated in Table I. A total of 14 Raman lines is displayed. The As_4S_6 molecular structure which has point group symmetry T_d is depicted in Fig. 3(a). Using group theoretical techniques[8] it can be shown that the molecular vibrations can be classified according to the irreducible representations of the T_d point group as follows:

$$\Gamma_{\mathrm{vib}} = 2A_1 + 2E + 2T_1 + 4T_2 .$$

Of these the A_1 and E vibrations are Raman active, the T_1 vibration is infrared active, and the T_2 vibrations are simultaneously Raman and infrared active. Thus the free molecule of As_4S_6 should exhibit at most eight Raman lines whereas the spectrum of Fig. 2 shows 14 lines. Moreover of the eight Raman bands produced by an As_4S_6 molecule only the two A_1 bands would be polarized. This prediction is inconsistent with the polarized Raman spectra of the as-deposited amorphous As_2S_3 films shown in Fig. 4. Note from that figure that there are five polarized bands at 215, 223, 234, 344, and 363 cm^{-1}. The additional lines in the spectra of Fig. 2 may in principle result from intermolecular coupling and/or oxide contamination and/or the presence in the film of additional molecular species of sulfur and arsenic.

Intermolecular coupling cannot be definitively ruled out but it is an unlikely source of the additional lines in the spectrum of Fig. 2. Since the As_4S_6 molecule would likely experience a host of environments in a glass the main manifestations of intermolecular coupling would be a broadening of each band.[6] Yet some of the features in Fig. 2 such as the bands at 289 and 107 cm^{-1} are extremely sharp with half widths of ≈ 2 cm^{-1}. Another manifestation of intermolecular coupling is the increased depolarization of the Raman spectrum.[6] As can be seen from Fig. 4, which shows the polarization properties of the Raman spectrum of an as-deposited film, five of the thirteen observed bands are strongly polarized. This result is also inconsistent with band-splitting intermolecular coupling effects.

With respect to film contamination with arsenic oxide, Berkes *et al.* have shown that in the presence of oxygen, illuminated As_2S_3 films undergo photoinduced oxidation to form As_2O_3 crystals.[9] Berkes *et al.* did not specify the specific crystalline form of As_2O_3 produced but that form was most likely claudetite I which is a monoclinic crystal with space-group symmetry $C_{2h}^5(p2_1/n)$.[10] The vibrational excitations of arsenic oxide in the gaseous, liquid, and glassy state as well as the crystalline forms arsenolite and claudetite I have recently been studied by Papatheodorou and Solin[11] and by Flynn, Solin, and Papatheodorou.[12] The Raman spectrum of claudetite I is dominated by an extremely intense band at 480 cm^{-1} which is ≈ 20 times more intense than the next strongest band at 72 cm^{-1}. There is no evidence whatsoever in the spectrum of the as-deposited As_2S_3 film (Fig. 2) for a band at either 480 or 72 cm^{-1}. We conclude that the bands in the spectra of Fig. 2 do not result from As_2O_3 contamination. While Berkes *et al.* did not

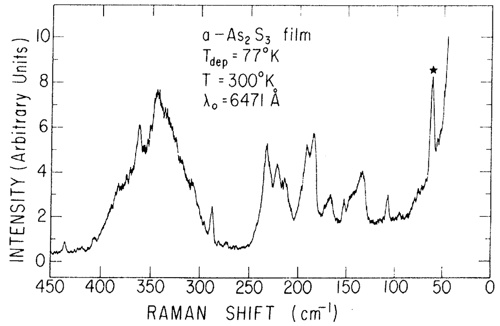

FIG. 2. Polarization unanalyzed Raman spectrum of an evaporated as-deposited As_2S_3 film excited with ≈ 60 mW of cylindrically focused 6471-Å Kr radiation and recorded with a spectral slit width of 2.5 cm^{-1}, a time constant of 5 sec and a scan rate 5 Å/min.

identify the molecular crystal As$_4$O$_6$, arsenolite, as a by-product of photo-oxidation of amorphous As$_2$S$_3$ films, that crystalline form of arsenic oxide might conceivably have contaminated our films. The Raman spectrum of arsenolite is dominated by two strong bands at 371 and 86 cm^{-1} neither of which appears in the spectrum of Fig. 2. Clearly, the spectral features exhibited by As$_2$S$_3$ amorphous films are intrinsic and not a manifestation of arsenic-oxide crystal formation.

On the basis of the above discussion we cannot ascribe the thermostructural or photostructural transformations of evaporated As$_2$S$_3$ films solely to the polymerization of the As$_4$S$_6$ molecular species since other molecular entities must be present in the amorphous film to account for the observed Raman spectra. The as-deposited As$_2$S$_3$ films were described by DMO as a "dense random packing of As$_4$S$_6$ molecules" because they believed[3] that the vapor in equilibrium with liquid As$_2$S$_3$ derived by

TABLE I. Vibrational modes of the As-S system.[a]

Evaporated film[b]	As$_2$S$_3$ (orpiment crystal)[c]	As$_4$S$_4$ (realgar crystal)[e]	As$_2$S$_3$ vapor[b]
	26		
	37		
	63		
	67		
	70		
107(?)	106		
135(dp)	136		
148(dp)	144	143	140(dp)
153(dp)	154		
	157		
169(dp)	167		
	173		
185(dp)	179	184	180(p+dp)[f]
192(dp)		194	193(p)
	203		
215(p)			
223(p)		221	220(p)
234(p)			235(p)
			249(dp)
			269(p)
289(?)	290		
	294		
309(?)	309[d]		303(dp)
	312		
	324	329	322(p?)
344(p)		345	345(p?)
	354[d]	355	354(dp)
	356		
363(p)	360		366(p)
	368	370	371(?)
		376	
383(?)[h]	383		
			416(p)
435(?)[h]			
			497(dp)
536(?)[h]			
			555(dp)
567(?)[h]			
608(?)[h]			
			715(p)
			747(p)

[a] Raman shifts are accurate to ± 2 cm^{-1}.

[b] p, polarized; dp, depolarized.

[c] From Ref. 6.

[d] Doublet.

[e] From Ref. 19.

[f] Overlapping bands.

[g] Weak but reproducibly observed.

[h] Not displayed in Figs. 1 or 2.

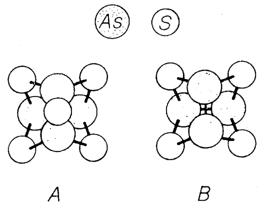

FIG. 3. Molecular structure of (a) As_4S_6 and (b) As_4S_4.

melting the bulk glass was composed solely of As_4S_6 molecules as inferred from electron diffraction studies.[14] However, the existence of the As_4S_6 molecules is questionable since it is based on the early electron diffraction investigation alone. More recent mass spectrometric studies[7] and density measurements[15] of vapors over crystalline or liquid As_2S_3 show that the As_4S_6 if present is a minor vapor constituent and that other species such as AsS, As_4S_4, As_4, and S_2 are the predominant species.

To clarify the character of the vapor phase, we have obtained polarized Raman spectra of the gas produced when bulk As_2S_3 glass is melted and evaporated. Those spectra are shown in Fig. 5. The band positions and polarization characteristics are tabulated in Table I. The spectrum of vaporized bulk As_2S_3 glass exhibits many intrinsically interesting excitation-wavelength-dependent phenomena such as preresonance Raman scattering,[16] and resonance fluorescence[16] which will be reported elsewhere.[17] The spectrum of Fig. 5 is preresonance and as such is quite reflective of the nonresonant spectrum except for enhancement.[16] It is important to point out that the minimum temperature at which reliable vapor phase Raman spectra such as those of Fig. 5 could be obtained was ≈ 600 °C whereas the film preparations were carried out at a much lower source temperature ≈ 350 °C. Nevertheless, absorption spectra of the vapor recorded at several temperatures in the range 350–825 °C are not only complex but indistinguishable when the temperature-dependent eigenstate populations are accounted for.[17] Thus the gas from which the amorphous films of Figs. 1, 2, and 4 were prepared can be assumed to contain the same molecular species as the vapor from which the spectra of Fig. 5 were obtained.

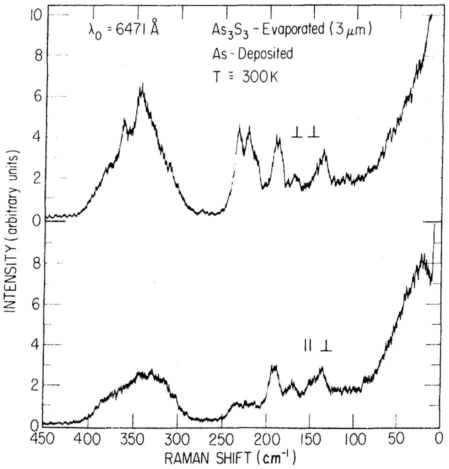

FIG. 4. Polarized Raman spectra of an evaporated as-deposited amorphous As_2S_3 film excited with ≈50 mW of cylindrically focused 6471-Å Kr radiation and recorded with a spectral slit width of 3.6 cm^{-1}, a time constant of 5 sec and a scan rate of 5 Å/min.

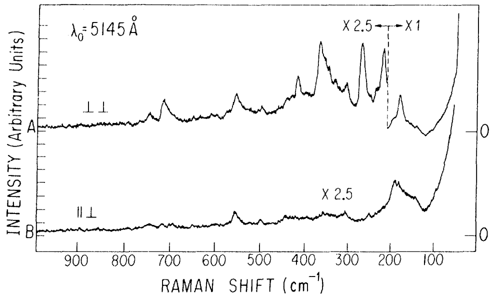

FIG. 5. Polarized Raman spectrum of As_2S_3 vapors at 600 °C excited with 1.1 W of 5145-Å Ar radiation and recorded with a spectral slit width of 8.6 cm^{-1}, a time constant of 2 sec and a scan rate of 12.5 Å/min.

Recall that As_4S_6 molecules in the vapor phase should produce eight Raman bands of which two are polarized. In contrast the spectrum of Fig. 5 exhibits at least 18 bands of which at least nine are strongly polarized. Moreover, the Raman spectrum of pure As_4S_6 vapor can be approximately deduced from the quite simple and very well characterized spectrum of its isomorph As_4O_6. The two A_1 polarized modes dominate the spectrum of As_4O_6 and occur at 556 and 381 cm^{-1}.[12,13,17] The monoclinic crystalline forms of As_2O_3 (claudetite I) and As_2S_3 (orpiment) are isomorphous and exhibit a remarkable intercrystalline frequency scaling relationship.[12] The vibrational frequencies of claudetite I scale consistently to those of orpiment by the scale factor 0.82.[12] If we apply that scale factor to the tetrahedral isomorphic molecular species As_4O_6 and As_4S_6 we expect the Raman spectrum of the latter to yield two strong polarized bands at 456 and 312 cm^{-1}. That expectation is not compatible with the spectra of Fig. 5.

It is apparent that the vapor produced by melting bulk As_2S_3 glass in vacuum is not composed solely of As_4S_6 molecules. The large number of strongly polarized Raman bands is suggestive of the presence of additional species in the vapor. Of the likely candidates S_2 and As_4 each produce only one polarized Raman band so their presence in the vapor along with As_4S_6 still would leave several polarized bands in the spectrum of the vapor unaccounted for. Consider, also the spectral contribution that might accrue from As_4S_4. The As_4S_4 molecule [14] which is depicted in Fig. 3(b) has point-group symmetry D_{2d}. Its molecular vibrations can be group theoretically classified as follows

$$\Gamma_{\text{vib}} = 3A_1 + 2A_2 + 2B_1 + 3B_2 + 4E .$$

Of these all but the A_2 modes are Raman active so the As_4S_4 molecule could contribute 12 Raman bands of which three would be polarized. Thus a vapor containing not only As_4, S_2, and As_4S_6 molecules but also As_4S_4 molecules could not produce the number of polarized bands observed in the spectrum of Fig. 5. Other as yet unidentified species must be present in the vapor. Nevertheless it is noteworthy that realgar, a molecular crystal formed from As_4S_4 molecules, exhibits many Raman bands which are coincident with the bands produced by evaporated amorphous films. This can be seen from Table I in which the Raman shifts for realgar reported by Ward[19] are tabulated. Unfortunately polarization data are not available for realgar.

A comparison of the Raman spectrum of the vapor produced when bulk As_2S_3 glass is melted in vacuum (Fig. 5) with the line spectrum of an as-deposited evaporated As_2S_3 film (Fig. 2) is revealing since the two spectra are quite distinct. Whatever the molecular constituency of the vapor produced by melting As_2S_3 bulk glass in vacuum, that constituency is apparently not preserved in the deposition process.

SUMMARY AND CONCLUSIONS

Our results provide a direct confirmation of that part of the DMO model which ascribes irreversible thermostructural and photostructural transformation in evaporated As_2S_3 films to polymerization of a partially cross linked molecular glass. The polymerization process, however, appears to involve several distinct molecular species one of which may be As_4S_6. The molecular composition of the vapor produced by melting bulk As_2S_3 glass in vacuum is quite complex, is not merely As_4S_6, and is not preserved in the deposition process used to produce As_2S_3 amorphous films. Raman spectroscopic techniques alone are markedly inadequate for a proper identification of those molecular species present in As_2S_3 vapor.

Among those amorphous solids which may exhibit photostructural or thermostructural transformations As_2Se_3 and As_2S_3 have been themost extensively studied while there has to our knowledge been no investigation of reversible or irreversible structural transformations in amorphous As_2O_3. Yet As_2O_3 which should exhibit effects similar to those produced by As_2Se_3 and As_2S_3 if illuminated with higher energy photons is an ideal candidate for such an investigation. Unlike As_2S_3 and As_2Se_3 its vapor phase is well characterized and indeed consists simply of As_4O_6 molecules.[13,17] Moreover, bulk As_2O_3 glass is ideally prepared not by melt quenching but by vapor deposition.[10] Thus it may be possible to produce with As_2O_3 a bulk glass that exhibits irreversible thermostructural and photostructural transformations.

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