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Surface photo-oxidation and Ag deposition on amorphous GeS₂

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Abstract. Bandgap radiation in the presence of gaseous oxygen induces surface and selvedge photo-oxidation of amorphous GeS₂. The phenomenon involves preferential oxidation of the Ge sites and may be understood in terms of the structural and electronic properties of GeS₂. Such photo-oxidized films exhibit very different properties towards the subsequent deposition of Ag, as compared with untreated films. The inverse system (GeS₂ deposition on Ag) exhibits markedly different interfacial properties, not previously recognized; this could have significant implications for the interpretation of bulk photodiffusion experiments.

1. Introduction

Chalcogenide vitreous semiconductors (ChVS) such as GeS₂ demonstrate a number of interesting photoeffects; among these is photodiffusion in which Ag or Zn metal deposited on thin ChVS films is found to dissolve into the ChVS upon illumination with bandgap light [1]. This phenomenon has potential applications in photolithography and device fabrication. Clearly in such a reaction, the nature of the metal–ChVS interface must play an important part in the mechanism [2]. For example, the presence of an induction period before the onset of photodiffusion has been found to be very dependent on the method of ChVS and Ag metal film preparation. This has been variously ascribed [1] to either oxidation of the film, or to formation of a metal–chalcogenide layer at the interface. Surprisingly then, there seems to be little work examining the nature of the metal–ChVS interface. Another very interesting photoeffect is one in which irradiation of ChVS films, in the presence of O₂, was found to lead to massive decreases in the sticking probability of Zn or Cd metal on the surface (factors of $\sim 10^5$) [3, 4]; the sticking probability of Ag is however unaffected. An initial XPS investigation of this effect using As₂S₃ showed that irradiation of the films in air leads to preferential oxidation of the As sites [5]. This implies that the non-chalcogenide site (As or Ge) is crucial in the subsequent nucleation of Zn on the surface. Those experiments, however, were compromised to some extent, since although the XPS measurements took place under UHV conditions, ChVS film preparation took place under much poorer vacuum conditions (10^{-4} to 10^{-6} Torr); the conditions used for photo-oxidation were also relatively poorly controlled.

Here, we report on a much more rigorous Auger spectroscopy study of the photo-oxidation of GeS₂ films. Film deposition was carried out under UHV conditions and

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subsequent photo-oxidation experiments were performed under well-controlled conditions by means of a pressure cell/UHV sample transfer device. We have also examined Ag deposition on both oxidized and unoxidized GeS₂ films to investigate the Ag–GeS₂ interface with a view to shedding light on the sticking probability measurements of Kolobov *et al*: Ag(d¹⁰s¹) does not show the effect whereas Zn (d¹⁰s²) does [4,6]. Additional information was obtained by reversing the order of deposition: i.e. GeS₂ on top of a Ag film. Photodiffusion experiments in which the metal film is deposited first, followed by the ChVS have also been carried out [1], so this provides an opportunity to compare the metal–ChVS interface formed in the two cases. As noted above, the GeS₂ films themselves were grown *in situ* under UHV conditions: they have been previously characterized [7] using XPS and XANES. For present purposes, the major advantage of using GeS₂ is its low vapour pressure [8] under the conditions required for vacuum chamber bakeout. The results are discussed with reference to possible mechanisms of the photo-oxidation and photodiffusion reaction and the anomalous sticking probability of Group IB metals.

2. Experimental details

Experiments were performed in a UHV/high pressure cell system equipped with a retarding field analyser for Auger electron spectroscopy; a quadrupole mass spectrometer; Ag and GeS₂ thermal evaporation sources and a specimen transfer device that permitted sample transport between the high pressure cell and the UHV manipulator. The construction and operating conditions of the GeS₂ source, and the characteristics of the deposited films have been previously described [7]. It was shown by XPS and AES that the source produced films of composition close to GeS₂. All samples were prepared by depositing GeS₂ onto a 0.1 mm thick Ni foil substrate that carried a T1/T2 thermocouple and could be heated resistively. The GeS₂ was deposited at the rate of about 1 monolayer every 5 minutes, or approximately 40 Å per hour, using a source to substrate separation of 2 cm. Exposure of the sample to UV light using a 900 W Xe arc lamp was performed in the high pressure cell by means of a kodial viewport that had a cutoff of 300 nm (4.1 eV). No other filters were used. The high pressure cell was operated at pressures of up to 2 bar of oxygen and was evacuated by means of a sorption pump to $\sim 10^{-3}$ Torr, and subsequently by diffusion pump to 10^{-7} Torr. The sample could then be transferred into the main UHV chamber; typical pump down times to UHV were approximately 15 to 30 minutes, dependent on the pressure used in the high pressure cell. The UHV chamber operated at a typical working pressure of $\approx 2 \times 10^{-10}$ Torr.

3. Results

3.1. Oxidation of germanium sulphide films

Attempts to oxidize GeS₂ films in the absence of UV irradiation using exposures of up to 9×10^{12} litres of O₂ (i.e. 2 bar for 100 minutes) resulted in neither detection of the O KLL Auger signal nor attenuation of the Ge and S Auger signals. Note that the S LM_{2,3}M_{2,3} signal (150 eV, escape depth ≈ 2.7 monolayers [9]) was reproducible to within about 5% in UHV/high pressure cell transfer experiments; a 5% attenuation in the S signal would correspond to about 0.15 of a monolayer of adsorbate. Thus, in the absence of light, even massive exposures to O₂ resulted in negligible perturbation of the surface.

The GeS₂ films were photo-oxidized in the high-pressure cell typically under 0.2 bar pressure O₂. The 300 nm (4.1 eV) cutoff of the kodial window used in the illumination experiments rules out the possibility of gaseous ozone formation in the pressure cell being responsible for any observed reaction; the threshold wavelength for ozone formation is 242 nm [10]. The bandgap of amorphous GeS₂ films is variously quoted as 2.4–3.4 eV [11, 12] so that the window cutoff was sufficiently high to allow bandgap radiation to impinge on the sample. Figure 1 shows the time dependence of the Ge M_{2,3}M_{4,5}M_{4,5} (50 eV), S LM_{2,3}M_{2,3} (150 eV) and O KLL (510 eV) Auger spectra intensities as a function of simultaneous exposure to O₂ and UV irradiation. It is apparent that important changes now take place at the ChVS surface. In all cases, the samples remained clean throughout the photo-oxidation procedure, as evidenced by the absence of any C KLL Auger signal (270 eV). Data were accumulated from the photo-oxidation of three samples; two of these were ≈ 80 Å thick (i.e. 2 hours' deposition), while the third was ≈ 400 Å thick (10 hours' deposition). As can be seen from figure 1, results from the three experiments were quite reproducible, and the extent of photo-oxidation appears to be independent of film thickness. Exposing films to UV radiation for the same period of time but changing the oxygen pressure over the range 0.2 to 2 bar also resulted in no discernible change in O uptake rate. Exposing the films to the UV lamp in the absence of O₂ under 0.2 bar of N₂ did not result in any changes in the relative intensities of the Ge and S Auger signals, within experimental error. Thus we are assured that UV exposure does not in itself affect changes in film composition.

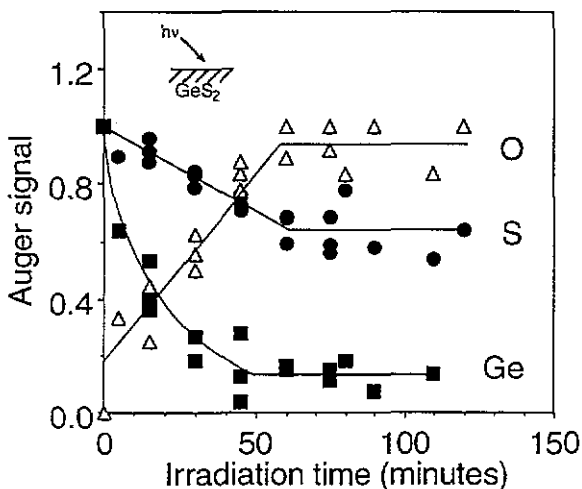


Figure 1. Time dependence of Ge, S and O Auger signal intensities during photo-oxidation of GeS₂ film under 0.2 bar O₂. Signals are reported as a fraction of the maximum observed value.

While exposing the GeS₂ films to UV radiation in the presence of 0.2 bar O₂, the substrate temperature rose to 350 K. Our previous work [7] indicated that such moderate temperatures can lead to eventual slow agglomeration of the films. Over the experimental timescale such effects would be negligible for the much thicker films used here. However, for oxygen pressures below 10⁻³ Torr, the substrate temperature rose to ≈ 400 K during irradiation. At such temperatures agglomeration of the films occurs within the timescale of the light exposure and we therefore did not examine the photo-oxidation under low-pressure conditions. To ensure that the observed high-pressure photo-oxidation was not merely an

artefact of the unavoidable mild heating that took place during UV exposure, GeS₂ films were annealed to 350 K under 0.2 bar O₂ in the absence of light. Over timescales similar to those exemplified in figure 1 no O Auger signal was detected, nor was the evidence for attenuation of the Ge and S intensities. In addition, the (substrate) Ni LVV Auger signal (64 eV) remained undetectable, whereas this signal would be expected to appear should agglomeration of the films occur [7]. Thus, we are assured that the oxidation observed is a true surface photoeffect.

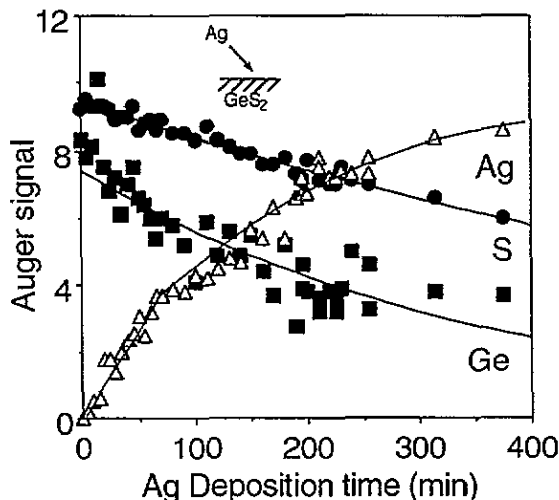


Figure 2. Ag, Ge and S Auger intensities during deposition of Ag on as-deposited GeS₂.

3.2. Silver deposition

Silver was deposited on both an 80 Å as-deposited germanium sulphide film and a similar 80 Å film that had been oxidized to the saturation point (70 minutes in 0.2 bar O₂ + UV light). Figure 2 shows the Ge, S and Ag M₅N_{4.5}N_{4.5} (372 eV) Auger signals observed during silver uptake on the as-deposited germanium sulphide. Similarly, figure 3 shows corresponding data obtained during silver uptake on the oxidized germanium sulphide. Note that in this latter case the O KLL peak showed little or no attenuation during the Ag uptake. Clearly, both the growth mode and the growth rate of Ag change dramatically between the two cases. The data suggest that on the as-deposited GeS₂ film, Ag grows in the monolayer/simultaneous multilayer (MSM) mode. On the photo-oxidized film, Stranski–Krastanov (SK) growth is observed. By comparing the time taken to reach the ‘break’ point in the two cases, we deduce that on the oxidized film, the sticking probability of Ag into the first layer is $\approx \frac{1}{3}$ that on the as-deposited GeS₂ film.

To further examine the Ag–GeS₂ interface, the deposition order was reversed. Figure 4 shows the Ge and S Auger signals for an uptake measurement in which the flux from the GeS₂ source impinged on an ≈ 100 Å thick layer of previously deposited Ag. Figure 5 similarly shows the Ag signals: in this case, the weaker Ag M₄N₃N_{4.5} and M₅N₃N_{4.5} Auger peaks (at 300 eV and 270 eV respectively) are also visible at low coverages. Furthermore, a lineshape change seen in the Ag M₅N_{4.5}N_{4.5} spectrum: after about 10 minutes GeS₂ deposition a shoulder was observed on the positive excursion of the Auger signal at about

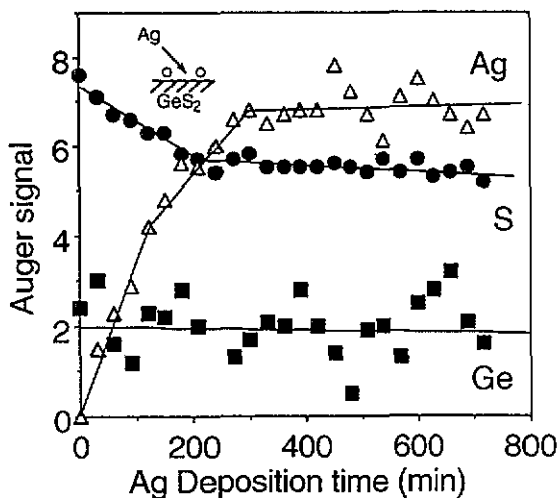


Figure 3. Ag, Ge and S Auger intensities during deposition of Ag on photo-oxidized GeS_2 .

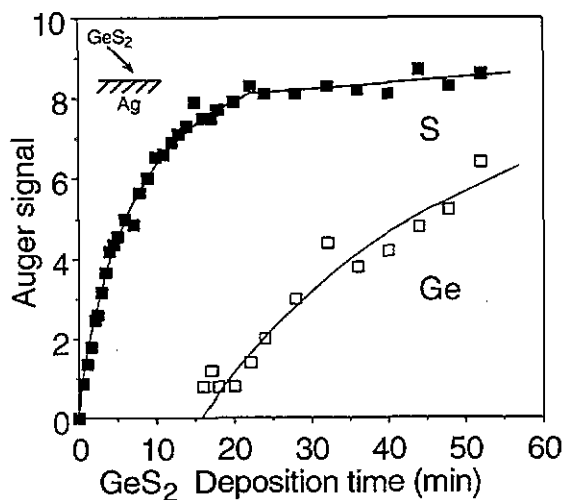


Figure 4. Ge and S Auger intensities during deposition of GeS_2 on a Ag film.

349 eV. This shoulder was not visible in the spectrum of the pure Ag film. The shoulder in the Ag signal was also seen during uptake of Ag on the clean germanium sulphide film and on the oxidized GeS_2 film, although it was less pronounced in the latter case. The origin of this shoulder is unclear, but it presumably cannot arise from plasmon excitations in the substrate, as Auger electrons emitted from the Ag layer do not pass through the substrate in these cases.

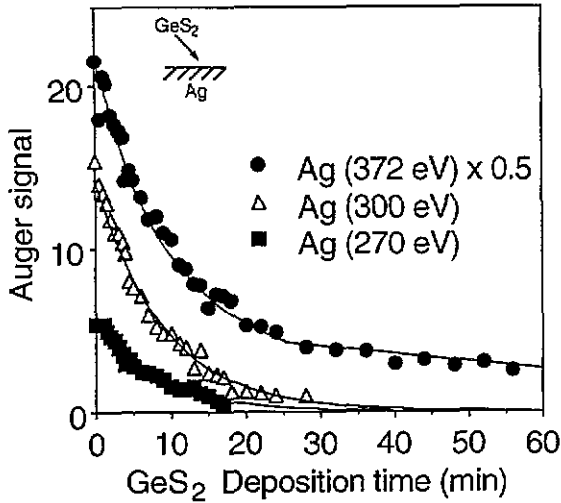


Figure 5. Ag Auger intensities during deposition of GeS₂ on a Ag film.

4. Discussion

4.1. Oxidation of germanium sulphide films

Figure 1 clearly shows a marked attenuation of the Ge Auger signal relative to the S signal upon photo-oxidation. The estimated escape depth for the Ge M_{2,3}M_{4,5}M_{4,5} electrons at 50 eV is ≈ 1.7 monolayers and that for the S LM_{2,3}M_{2,3} electrons (150 eV) is 2.7 monolayers [9]. At 20 minutes exposure, it is apparent that the Ge intensity has attenuated to ≈ 0.4 of its initial value (i.e. corresponding to about one escape depth), whereas the S intensity has attenuated by a factor of ≈ 0.9 . On the basis of equivalent coverage of both Ge and S sites, this would imply an escape depth ratio of 10:1 for S and Ge Auger electrons; this is not physically reasonable. Therefore, we infer that preferential, if not exclusive, photo-oxidation of the Ge sites has occurred, at least in the first layer. The possibility that GeO₂ desorption may have been responsible for the rapid attenuation of Ge intensity can be ruled out, as the relevant heat of vaporization is much too high [13]. At the photo-oxidation saturation point, the Ge signal has decreased to ≈ 0.2 of its initial value which corresponds to about 3 monolayers of the adsorbate-induced attenuation, while the S intensity attenuation of ≈ 0.7 corresponds to ≈ 1 monolayer. This suggests that at the saturation point a significant amount of oxygen has penetrated the surface to form a layer of oxidized GeS₂, the structure of this oxidized selvedge being such that the Ge Auger intensity is preferentially attenuated.

As noted above, the behaviour of the Ge and S intensities during the initial stages of photo-oxidation strongly suggests that oxygen is preferentially adsorbed on Ge sites at the surface. It therefore seems reasonable to assume that the oxygen which enters the selvedge is also bound to Ge atoms. Nothing is yet known about the surface structure of amorphous GeS₂. However, the structure of the bulk glass has been investigated using a variety of techniques [14, 15]. Two general types of structural unit are thought to exist. The first of these is a raft-like structure based on the β (high-temperature) form of crystalline GeS₂. This consists of chains of edge and corner sharing GeS₄ tetrahedra, as is shown in figure 6(a). A particular feature of this structural unit is the so called 'outrigger-raft' of homonuclear S-S bonds terminating at the edge of the structure. The second (less important) structure consists of 'ethane-like' chains of S₃Ge-GeS₃ units, as is shown in figure 6(b).

A possible mechanism for the photo-oxidation reaction might therefore be breakage of the Ge-Ge bond in the second structure, allowing insertion of O to form a bridging Ge-O-Ge structure. However, these sites account for less than one third of the total Ge sites in the glass [14], therefore Ge sites in the raft structures might also be expected to photo-oxidize. Upon irradiation by bandgap light, excitation of electrons can take place from S lone pair states known to lie at the top of the valence band, to S-Ge antibonding states known to lie at the bottom of the conduction band [16]. This would lead to the breaking of Ge-S bonds and the formation of R-Ge+ sites which can then react selectively with O_2 . A particular problem in any such scheme is that of accounting for the fate of the R-S:- sites which are formed simultaneously. A plausible mechanism for this is outlined in figures 7(a-d), where we propose the formation of homonuclear S-S bonds analogous to those in the 'outrigger raft'.

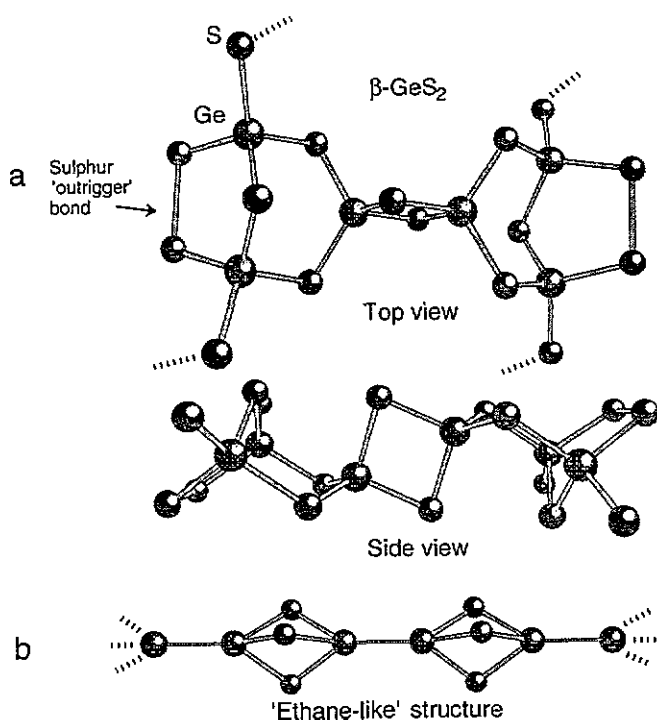


Figure 6. (a) The 'outrigger raft' structure of amorphous GeS_2 based on the high-temperature β form of crystalline GeS_2 . The top view lies approximately down the c axis, the side view approximately down the a axis of β - GeS_2 . (b) The 'ethane-like' structure of amorphous GeS_2 .

The geometry of these two types of GeS_2 structural unit can also provide an (admittedly speculative) explanation for the preferential attenuation of Ge intensity in the saturated photo-oxidized film. What is striking about the structure in figure 6(a) is its open nature and, as is seen in the side view, the protrusion of S atoms above the plane of the surface. The raft structure is layered, and it could be imagined that such units lie on the surface, with S atoms protruding upwards. Upon oxidation then, these atoms would not be obscured by the O atoms on the surface Ge sites, while S on a raft lying below the surface would similarly not be obscured by O within the same layer and would also be less attenuated by reason of the open nature of the structure.

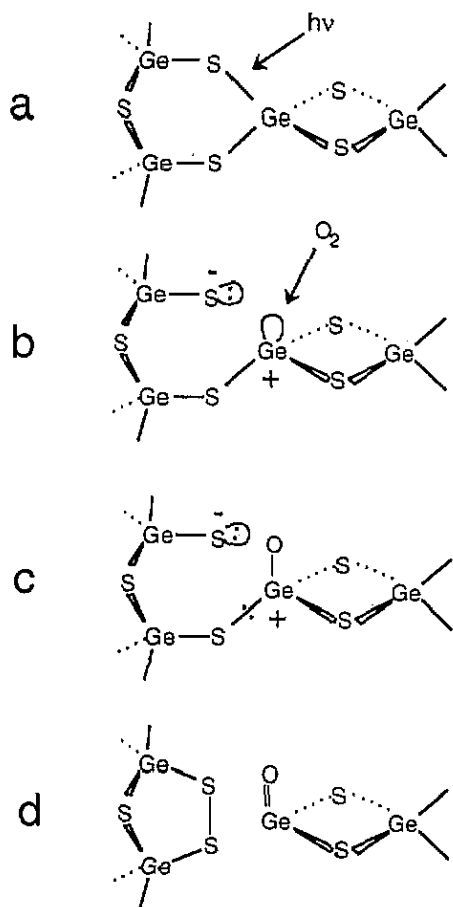


Figure 7. (a)–(d) Proposed mechanism for the photo-oxidation of GeS₂.

The present results are in good agreement with previous studies of the photo-oxidation effect. An XPS study of As₂S₃ films photo-oxidized in air showed preferential As (non-chalcogen) oxidation, as well as evidence for the presence of oxygen atoms in the bulk [5]. It was suggested that the role of UV light in the photo-oxidation is to break As–S bonds at the surface, forming dangling bond species R–As⁺ and R–S[–]. The R–S[–] dangling bond has a noble gas configuration so is relatively inert, while the R–As⁺ has an empty lone pair orbital, so can react rapidly with O₂, in analogy to our proposed mechanism for GeS₂ photo-oxidation.

Related work on GeS₂ oxidation using bulk analytical techniques has concentrated on an irreversible photobleaching effect (shift of the bandgap to higher energies) [12, 17] which is observed when GeS₂ films are illuminated in air. In such cases Tichy *et al* [17] have observed IR bands corresponding to the dominant feature in GeO₂ glass, as well as transitions assigned to vibration of the S_{3–x}O_x–Ge–O–Ge–O_xS_{3–x} structural unit. This photobleaching effect does not occur in GeS₂ films illuminated in vacuum (~10^{–4} Torr), suggesting that it is a direct consequence of film oxidation, as is indeed strongly indicated by the present results. Note also that the type of structural units proposed by Tichy *et al* are consistent with our model for photo-oxidation of the surface and selvedge. They also found that the IR band

intensity and degree of photobleaching saturate at similar illumination times as observed in our experiments (2 to 3 hours as compared with about 1 hour in our case). Spence and Elliott [12] have also observed photobleaching and associated Ge–O IR bands. However, they found that for films similar to our own, photobleaching was observed without the appearance of Ge–O IR bands. This was attributed to formation of a surface oxide which could not be observed using IR spectroscopy, although it could still clearly visibly perturb the bandgap.

GeS₂ films left in air in the absence of light also exhibit the photobleaching/oxidation phenomenon. In this case, the oxidation is attributed to a hydrolysis reaction [17]



Such a reaction would lead to S loss by desorption of H₂S, with concomitant disappearance of the S Auger signal. This behaviour could explain the rather different results observed in the only other surface study of photo-oxidized GeS₂ films [18, 19]. In that case, GeS₂ films were deposited *ex situ*, photo-irradiated in air, then transferred to the spectrometer for XPS analysis. Films were deposited at oblique angles (> 80°), under which conditions numerous voids are expected to occur in the film [12], increasing the surface area. The XP spectra clearly demonstrated Ge oxidation occurred, but in contrast to our results showed complete removal of S from the surface region, as evidenced by total quenching of the S 2p signal. This was attributed to desorption of S from the surface as sulphur oxides. However our results, obtained under much more controlled conditions and in the complete absence of water vapour, clearly show that S remains on the surface during the photo-oxidation. It therefore seems highly likely that the disappearance of S signal intensity observed by Harshavardhan and Hegde was due to hydrolysis which took place during film preparation and subsequent sample transfer.

Finally, we note that the complete lack of oxidation we found in the absence of light, even under very high O₂ exposure, indicates that the surface must have a very low concentration of the types of defects which might be expected in a ChVS. In particular, paramagnetic defects in which an unpaired electron is associated with Ge are known to exist in the bulk GeS₂ glass [20]. Were such defects to exist at the surface in any concentration, they might well be expected to react with O₂. Thus, it is likely that the surface terminates in a layer which consists of fully co-ordinated GeS₄ tetrahedra, as well as the possibility of Ge–Ge and S–S bonding, in analogy with the most important structures which exist in the bulk glass [14, 15]. The surface thus remains chemically inert towards oxygen until photoinduced cleavage of Ge–S bonds triggers preferential oxidation of the Ge sites, as discussed above.

4.2. Silver deposition

Figure 2 shows the Ag, S and Ge signals for Ag uptake on clean GeS₂ (i.e. without photo-oxidation). Several points are immediately apparent. First, the Ag intensity data show a distinct break at 75 minutes deposition. This is followed by a smooth curve which by extrapolation to infinity saturates at a signal intensity of 10.05 ± 0.25 units. The first breakpoint occurs at an Auger intensity of 3.9 units, approximately $\frac{1}{3}$ of the saturated value. Given that the escape depth of the Ag Auger electrons is ≈ 3.5 monolayers, a Ag signal $\frac{1}{3}$ of the maximum limiting value is consistent with one monolayer coverage of Ag on GeS₂. These observations illustrated in figure 2 are good evidence of a MSM growth mode. The limiting Ag signal (obtained by extrapolating the curve in figure 2) is considerably lower than the corresponding signal for a pure Ag film deposited on the Ni substrate ($43.2 \pm$

0.2 units). At the same time, the best fit to an exponential decay curve gives a limiting value of 2.75 ± 0.25 units for the S and Ge signals respectively at long deposition times. These observations, as well as the fact that a change in Ag peak shape is seen when Ag is deposited on GeS₂, is good evidence that the surface layer does not consist of pure Ag, but is instead some type of mixed Ag–S–Ge compound.

Some idea of the nature of this compound can be inferred from previous investigations of Ge chalcogenide films photodoped in the bulk with Ag. EDAX measurements of GeS₂ photodoped with Ag show a final bulk composition of Ag_{0.23}Ge_{0.23}S_{0.54} [21] while EXAFS measurements [22] on the chemically similar GeSe₂ show that in the photodoped film, Ag is incorporated into the structure by forming Ag–Se bonds exclusively. In analogy to this latter result, we might assume that as it is deposited, Ag reacts with the GeS₂ film to form Ag–S bonds. The relative atomic densities of Ag in the layer reacted with GeS₂ and in the pure Ag film may be estimated by taking the ratio of the saturated Ag signal in the reacted overlayer to the Ag signal from a thick Ag film. The relative atomic densities of S and Ge can be estimated in the same fashion, using the GeS₂ film as a standard. In this way, the relative atomic densities of S and Ge in the reacted layer are calculated as 0.19 ± 0.02 and 0.08 ± 0.02 respectively. This strongly suggests that the overlayer is Ag rich, because these values are approximately half those characteristic of the bulk photodoped material above. The calculated relative atomic density of Ag in the reacted layer is 0.23 ± 0.01 , which initially seems inconsistent with the above. However, the changes observed in the Ag lineshape when reacted with GeS₂ leads to a broadening of the peak, and hence an underestimation of the true Ag signal from the measured peak-to-peak amplitude. Thus, the Ag–S–Ge overlayer does indeed have a composition that is Ag rich, as compared with the bulk photodoped film. This is to be expected as here we are adding Ag to the small volume of the ChVS in the vicinity of the selvedge, whereas in the photodoped film, the Ag has been distributed uniformly throughout the bulk.

The behaviour of the photo-oxidized film towards Ag uptake is very different. The uptake curves in figure 3 indicates that in this case Ag grows in a SK mode (i.e. monolayer followed by islanding) in marked contrast to the MSM mode exhibited on the clean film. The attenuation factor for the S signal at the break point is 0.75 which is consistent with formation of a single contact layer. Significantly, the Ge signal is clearly not attenuated during Ag uptake, while the O KLL signal (not shown) shows little or no attenuation. These observations suggest that (i) the initial sticking of Ag is *only* at the S sites and not on the oxidized Ge sites and (ii) that O is mainly associated with Ge sites, not S sites. The second point is however less certain, since the O signal was weak, and characterized by a relatively large escape depth (≈ 5 ML). The Ag signal at the breakpoint is almost twice that in the case of the clean GeS₂ film. This, as well as the observation that the shoulder observed in the Ag Auger spectrum was significantly less pronounced in the present case, suggests that the Ag–S interaction is not as strong, and that the overlying islands are essentially pure Ag. The onset of island growth on the (photo-oxidized) surfaces is consistent with the findings of Oldale and Elliott [21] at much higher metal coverages: they noted the island morphology of Ag films < 100 Å on GeS₂. Given the nucleation of Ag islands at S sites, why do the Ge and O signals remain essentially invariant up to a metal loading equivalent to ≈ 4 ML Ag (figure 3)? The equivalent of a 4 ML deposit on top of the initial Ag–S sites corresponds to the formation of an Ag cluster with radius ≈ 2.6 Å. Given the open structure of GeS₂ (figure 6(a), the Ge–S bond length being 2.22 Å) one can appreciate that such clusters would not significantly screen nearby Ge and S atoms at this very early stage of the nucleation process. The time taken for completion of one monolayer (≈ 225 minutes),

was three times longer than on the clean films: thus, the ratio of sticking probabilities in the first layer is 3:1 for the clean and photo-oxidized films.

These changes in growth mode and relative sticking probability of Ag on GeS_2 upon photo-oxidation were not observed by Kolobov *et al* [4] under their relatively poorly controlled conditions. Their measurement techniques were not sensitive to the growth mode, nor to sub-monolayer quantities of metal deposition. Deposition rates were also far higher, and changes occurring in the first layer were therefore undetectable. In the case of the work on Zn deposition under similar conditions, the sticking probability changed by orders of magnitude under photo-oxidation [4] which made these effects much easier to observe. The present work suggests that changes in the nucleation and growth behaviour during the very earliest stages of metal deposition are likely to be of critical importance to an understanding of these phenomena. Most recently, we have shown that with Zn/ GeS_2 photo-oxidation does indeed induce profound changes in mechanism and growth behaviour [6].

While it is more usual to perform photodiffusion experiments by depositing first the ChVS then the metal, experiments can also be carried out by preparing systems where the deposition order is reversed (i.e. ChVS on metal). The 'inverse mode' uptake curves shown in figures 4 and 5 for which the flux from the GeS_2 source was deposited onto a Ag film, show some characteristics rather different from the 'normal' mode. Previous work [7, 23] has shown that the flux from the GeS_2 source consists of a 2:1 ratio of GeS and S_2 molecules (which generate a deposited film of composition GeS_2). What is clear from figure 4 is that in the inverse mode Ge does not appear on the surface until 15 minutes deposition. Thus, it appears that GeS has a very low sticking probability on the Ag film as compared with S_2 . Previous work on the sticking of S_2 on Ag (111) [24] demonstrated rapid formation of an initial overlayer of S, followed by epitaxial growth of $\gamma\text{-Ag}_2\text{S}$. Therefore in the present case it seems likely that within the first 15 minutes of the deposition growth of a Ag_2S overlayer also occurs due to reaction of the S_2 component of the flux with the Ag film. From the attenuation of the Ag-372 peak we estimate that <5 monolayers overlayer of Ag_2S grow before uptake of Ge due to GeS sticking. After the Ge signal starts to appear, both the S and Ag-372 signals (which previously followed approximately exponential curves) begin to level off, as shown in figures 4 and 5. This suggests that as GeS begins to nucleate on the surface, GeS_2 begins to grow as islands on top of the Ag_2S overlayer.

The 'inverse mode' deposition (GeS_2 on Ag) experiments clearly demonstrate the formation of a silver sulphide layer several monolayers thick at the metal-ChVS interface. This is quite a different result from that observed in the normal mode (Ag on GeS_2) experiments, and should be considered and taken account of in planning and interpreting photodiffusion experiments. The demonstrate affinity of Ag for S as opposed to Ge at the interface allows us to infer that in the case of Zn deposition on GeS_2 , the nucleation sites must be quite different from those with Ag uptake, and that these Zn-nucleating sites must be somehow closely associated with Ge.

5. Conclusions

(i) In the presence of bandgap radiation and gaseous oxygen, the surface and immediate subsurface regions of GeS_2 films undergo a photo-oxidation reaction. This is a true surface process which does not involve gas-phase photochemistry. The films are inert to O_2 in the absence of UV light.

(ii) Such treatment leads to preferential oxidation of the Ge sites. It is possible to rationalize this behaviour in terms of the electronic and structural properties of GeS_2 .

(iii) Photo-oxidized films show very different properties towards the subsequent sticking of Ag, as compared with untreated films. Specifically, a reacted Ag-S-Ge layer is observed to grow on the untreated films in the MSM mode. On the photo-oxidized films, Ag grows in an SK mode with a decreased sticking probability and without compound formation; it fails to interact at all with the oxidized Ge sites. These changes in Ag growth mode and sticking probability have not been previously recognized. The lack of interaction between the Ag and oxidized Ge sites suggest that the previous Zn and Cd results [3, 4] are related to the failure of Zn or Cd to nucleate at oxidized non-chalcogen sites.

(iv) Inverting the system, i.e. depositing GeS₂ on Ag, produces an interface with very different properties. An interfacial silver sulphide layer, several monolayers thick, is formed between the Ag substrate and the growing GeS₂ film. This has not been recognized previously and could have significant implications for work on photodissolution of Ag in GeS₂.

Acknowledgments

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References

- [1] Kolobov A V and Elliott S R 1991 *Adv. Phys.* **40** 625
- [2] Elliott S R 1991 *J. Non-Cryst. Solids* **130** 85
- [3] Kolobov A V and Lyubin V M 1986 *Pis. Zh. Tehk. Fiz.* **12** 374
- [4] Bedel'baeva G B, Kolobov A V and Lyubin V M 1989 *Phil. Mag.* **B 60** 689
- [5] Kolobov A V, Badyal J P S and Lambert R M 1989 *Surf. Sci.* **222** L819
- [6] Horton J H and Lambert R M 1993 in preparation
- [7] Horton J H, Moggridge G D, Ormerod R M, Kolobov A V and Lambert R M 1993 *Thin Solid Films* at press
- [8] Kubachewski J, Evans E L and Alcock C B 1967 *Metallurgical Thermochemistry* 4th edn (London: Pergamon)
- [9] Briggs D and Seah M P (ed) 1990 *Practical Surface Analysis Volume 1: Auger and X-ray Photoelectron Spectroscopy* 2nd edn (Chichester: Wiley)
- [10] Calvert J G and Pitts J N 1966 *Photochemistry* (New York: Wiley)
- [11] Elliott S R 1990 *Physics of Amorphous Materials* 2nd edn (Harlow: Longman Scientific & Technical)
- [12] Spence C A and Elliott S R 1989 *Phys. Rev. B* **39** 5452
- [13] Surnev L 1981 *Surf. Sci.* **110** 439
- [14] Boolchard P, Grothaus J, Tenhover M, Hazle M A and Grasselli R K 1986 *Phys. Rev. B* **33** 5421
- [15] Armand P, Ibanez A, Dexpert H and Philipott E 1992 *J. Non-Cryst. Solids* **139** 137
- [16] Louie S G 1982 *Phys. Rev. B* **26** 5993
- [17] Tichy L, Triska A, Ticha H and Frumar M 1986 *Phil. Mag.* **B 54** 219
- [18] Harshavardhan K S and Hegde M S 1987 *Phys. Rev. Lett.* **58** 567
- [19] Harshavardhan K S and Hegde M S 1989 *Solid State Commun.* **69** 117
- [20] Zhilinskaya E A, Lazukin V N, Valeev N K and Oblasov A K 1989 *J. Non-Cryst. Solids* **124** 48
- [21] Oldale J M and Elliott S R 1991 *J. Non-Cryst. Solids* **128** 255
- [22] Oldale J M, Rennie J H S and Elliott S R 1988 *Thin Solid Films* **164** 467
- [23] Karbanov S G, Belousov V I, Zlomanov V P and Novosiolova A V 1968 *Vestnik. Mos. Gos. Univ.* **5** 93
- [24] Schwaha K, Spencer N D and Lambert R M 1979 *Surf. Sci.* **81** 273