Lawrence Berkeley National Laboratory
Recent Work

Title
REACTION AND DIFFUSION IN SILVER-ARSENIC CHALCOGENIDE GLASS SYSTEMS

Permalink
https://escholarship.org/uc/item/73r2t74w

Author
Holmquist, G.A.

Publication Date
1978

REACTION AND DIFFUSION IN SILVER-ARSENIC CHALCOGENIDE GLASS SYSTEMS

Glenn A. Holmquist and Joseph A. Pask

January 1978

LBL-7359 C.2

DISCLAIMER

REACTION AND DIFFUSION

IN SILVER-ARSENIC CHALCOGENIDE GLASS SYSTEMS

Glenn A. Holmquist and Joseph A. Pask

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Mineral
Engineering, University of California
Berkeley, CA 94720

ABSTRACT

The diffusion of Ag from the metal or Ag_2Se in amorphous As_2S_3 and As_2Se_3 at 175°C is accompanied with the reduction of As from a valence of +3 to +2 or +2 to +1 to maintain charge neutrality in the glass. Ag^+ alone diffuses at this temperature, all other ions are essentially immobile. An amorphous reaction product phase is formed in the diffusion zone with a composition range of 28.6 to 44.4 atomic percent Ag. The lower limit corresponds to all As cations of +2 valence (equivalent to amorphous $Ag_2As_2S_3$); the upper limit, the maximum solubility of Ag in these glasses, corresponds to all As cations of +1 valence (equivalent to amorphous $Ag_4As_2S_3$). The diffusivity of Ag in these glasses at 175°C in the concentration range of 10 to 35 atomic percent Ag is

$$\text{Sulfide} - 4 \times 10^{-14} \exp\left[(+0.23 \pm .01)(\text{atomic \% Ag})\right] \text{cm}^2/\text{s}$$
$$\text{Selenide} - 2 \times 10^{-12} \exp\left[(+0.14 \pm .01)(\text{atomic \% Ag})\right] \text{cm}^2/\text{s}$$

I. INTRODUCTION

Diffusion is a manifestation of thermodynamic nonequilibrium in a system. Measurable mass transport in glass at temperatures below the glass transition temperature (T_g) is only by cation movements. The anion structure is relatively immobile. Significant diffusion below T_g then becomes possible only if cation-cation or cation-electrical defect movement maintains electroneutrality.

Amorphous As_2S_3 and As_2Se_3 are "isomorphic" chalcogenide glasses having   identical short range order. Ag diffusion is thus expected to exhibit similar character. Excellent reviews of the electrical properties of amorphous semiconductors have been written by Adler,[1] Mott[2] and Thornburg.[3] The chemistry of these glasses, and of As_2S_3 and As_2Se_3 in particular, has not received the same degree of attention. Matsuda and Kikuchi[4] reported data on the thermal doping (170°C) and photodoping of amorphous As_2S_3 thin films with Ag. Their observation of crystalline As_2S_2 and Ag_2S peaks in the electron microprobe x-ray diffraction data constitutes the first evidence of interfacial redox reactions in the Ag-As chalcogenide system. Reactions have been noted in Ag photodoping work but not specifically identified as redox reactions.[4,5,6,7]

Diffusion studies of Ag in amorphous As_2Se_3 were conducted by Stuptitz and Willert.[8] Radioactive (Ag^{110}) tracer experiments were performed in which a thin film of Ag was vacuum-evaporated on the glass. A diffusivity of $3 \exp(-0.89 \text{ eV}/kT)$ was determined. Neither concentration dependence nor interfacial reactions were reported. In a later work Lebedev, Stuptitz and Willert[9] reported the charge on the diffusing Ag (ion) to be $(1.2 \pm 0.2)e$.

Goldschmidt and Rudman[5] studied the kinetics of the photodissolution of Ag in As_2S_3 glass. A thin film (300Å) of Ag was deposited on a film (5000 to 25000 Å) of As_2S_3. Upon illumination of the interface through the glass film, up to 39 atomic percent of Ag was found to dissolve (photodissolve) into the glass at room temperature; DeNeufville[10] observed 30 atomic percent. No interfacial redox reactions were specifically identified. The kinetics of photodissolution include an illuminated induction time before dissolution commences. It was stressed that "radiation damage" during the initial induction period is essential for subsequent photodissolution. Andreichin's[11,12] work on photopolarization illuminates the nature of Goldschmidt and Rudman's "radiation damage." When As_2S_3 glass was polarized with a constant electrical field and illuminated, a transient current was observed indicating further polarization. Andreichin reported, "Since the conduction is purely electronic, we have neither dipoles, which would be orientated by the field, nor ions, which would move, nor any other similar species." He concluded, "The polarization phenomena in high resistance vitreous semiconductors are of a purely electronic, and not ionic, character."[12]

It is possible to explain photodissolution and photopolarization in terms of redox reactions involving electron transfer between cations. The core of this present work is the recognition of arsenic cation valence changes necessary for redox reactions that occur. However, application of this mechanism to explain other phenomena must be made with caution. Ionic valence change in an amorphous semiconductor induced by illumination has not been documented; the photoreactions of arsenic chalcogenide glasses are not fully understood.[6,7] Ionic valence change

in an amorphous semiconductor induced by an applied electric field was first proposed by Drake, Scanlan and Engel.[13,14] This mechanism was used to explain the conductivity transition characteristic of these semi-conductors. Copper-doped phophate glasses were investigated but the applicability of this model to arsenic chalcogenide glasses was specifically mentioned.[14]

Faure, Mitchell and Bartlett[15] reported dissociative vaporization of As_2S_3 to the AsS and S_2 vapor species. Goldschmidt and Rudman[5] acknowledged this dissociation but only at high vaporization rates. They contended that at their low vaporization rates As_4S_6 is the predominant vapor species. Their films deposited in this manner were reported to be As_2S_3.

Various valences of arsenic in a selenium anion environment have been reported. Dembrowki[16] conducted an analysis of the As-Se binary system. Thermographic records of the preparation of the alloys from the elements throughout the entire concentration range were obtained. Exothermic maxima indicated the formation of the compounds As_2Se_5, As_2Se_3, AsSe and As_2Se; the arsenic valences are respectively, +5,+3, +2 and +1.

The objectives of the present study were to determine the reactions and diffusion characteristics of Ag in bulk arsenic chalcogenide glass below the transition temperature of the glass. These data also provide solubility information. Glass modifier diffusion in glass is typically concentration dependent. One of the objectives is to determine the concentration dependence of Ag diffusion in these glasses.

II. EXPERIMENTAL PROCEDURES

Materials

Starting materials were powders of amorphous As (99.9999%),[*] Se (99.999%),[**] As_2S_3 (99%),[***] Ag_2S (99%),[**] Ag_2Se (99%).[**] Proper proportions of As and Se to form As_2Se_3 were encapsulated in an evacuated fused silica capsule; As_2S_3 powder was similarly encapsulated. Glasses were formed by heating the capsules to 600°C at 6°C/min while rocking in a furnace (one rock/min), held rocking for 48 hrs to insure homogeneity, and then water quenching.

Ag_2Se powder encapsulated in an evacuated fused silica capsule was melted at 900°C in a stationary furnace and quenched to form a dense polycrystalline solid.

Polycrystalline $AgAsS_2$ (smithite, melting point 417°C, only compound shown in Ag_2S-As_2S_3 phase equilibrium diagram)[17] was formed by heating a mixture of As_2S_3 and Ag_2S in an evacuated fused silica capsule according to the time-temperature schedule indicated in Fig. 1. During the hold at 405°C, since As_2S_3 melts at 300°C, Ag_2S dissolves in As_2S_3. Raising the temperature to 600°C and quenching in air causes the formation of a glass, but including a nucleation period at 280°C and a grain growth period at 375°C the polycrystalline compound is formed.

---

[*] Gallard Schlesinger Chemical Mfg. Corp., Carle Place, NY.

[**] Orion Chemical Co., Glendale, CA.

[***] Pfaltz and Bauer Inc., Flushing, NY.

Diffusion Couples

Ag-As_2S_3 glass and Ag-As_2Se_3 glass couples were fabricated by plating Ag on the polished glass specimens, the Ag often encapsulating the glass as shown in Fig. 2. The surface conduction, which is necessary for plating, varied with the degree of oxygen contamination; surfaces covered with oxide films had the lowest conduction. To reduce the oxide growth, typical polishing techniques were conducted with modification of the final step. The glass specimens were lapped in a slurry of heptane or alcohol with 0.3μm alumina. Thereafter they were immersed in heptane or alcohol until plating. The encapsulated specimens were then exposed to a diffusion heat treatment.
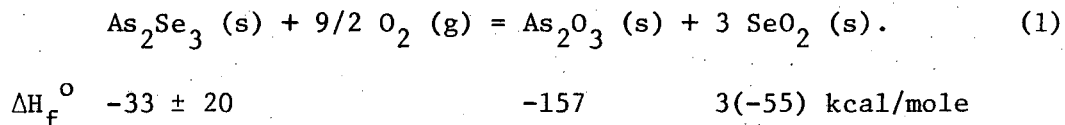
The polycrystalline Ag_2Se-As_2Se_3 glass couples were prepared by holding the polished surfaces of the specimens together with alligator clips during the diffusion heat treatment. These clips allowed proper alignment during potting for subsequent analysis.

All diffusion runs were conducted at 175°C. This temperature is below the glass transition temperatures, Tg, of 205 and 180°C for As_2S_3 and As_2Se_3, respectively.[1,3] The furnace was evacuated to less than 5 x 10^{-6} torr and backfilled with argon to minimize oxygen contamination. Temperature was monitored with a copper-constantan thermocouple to ±2°.

Difficulties Due to Oxidation

The time vs. distance diffusion data for selenide couples exhibited anomalous scatter. It is believed, and supported by thermodynamic considerations, that an oxide film (As_2O_3, SeO_2) on the surfaces prevented interface formation until the film was dissipated at the test temperature of

175°C by evaporation and/or solution in the glass. Assuming that ΔH_f^o of As_2Se_3 is within 20 kilocalories of the ΔH_f^o of As_2S_3, the reaction and enthalpy change[18,19] are given by

$$As_2Se_3 \text{ (s)} + 9/2 \ O_2 \text{ (g)} = As_2O_3 \text{ (s)} + 3 \ SeO_2 \text{ (s).} \qquad (1)$$

$$\Delta H_f^o \quad -33 \pm 20 \qquad\qquad -157 \qquad 3(-55) \text{ kcal/mole}$$

ΔH^o for the reaction then is -289 ± 20 kcal. The standard entropy for this reaction is primarily a consequence of condensation of 9/2 moles of oxygen gas, which is approximately 44 entropy units per mole. At 273°K it contributes approximately 54 kcal to the standard free energy of reaction so that the resultant free energy change for this reaction is of the order of -235 kcal/mole.

Electron spectroscopy chemical analysis (ESCA) techniques were used to determine the chemical environment of As and Se in As_2Se_3 glasses with varying amounts of Ag. To form bulk homogeneous specimens, As_2Se_3 and powdered silver metal were crushed and mixed in air with a mortar and pestle. This mixture was pressed into a pellet and heated in argon at 175°C for 48 hours. Crushing the glass in ambient air introduced oxide contamination. Subsequent heat treatment put some of the surface As and Se oxides into solid solution in the selenide glass. ESCA results clearly identified oxygen as a major bulk contaminant. Moreover, these experiments revealed that argon sputter cleaning of the glass surface in the ESCA vacuum chamber created an excellent electrically conductive surface on all samples. Surface charging problems indigeneous to insulators were thereby overcome.

Difficulties due to oxide contamination were encountered in unsuccessful attempts to make dense solid Ag_2S by melting powdered Ag_2S in evacuated fused silica capsules. At about 550°C (mp of Ag_2S = 842°C) the capsules exploded. Apparently oxygen, in the form of Ag_2O was sorbed on the starting sulphide powder allowing the following exothermic reaction to take place:

$$2\ Ag_2O\ (s) + Ag_2S\ (s) = 6\ Ag\ (s) + SO_2\ (g) \tag{2}$$
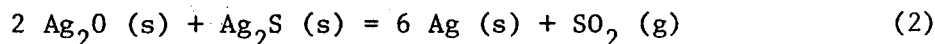
At 700°K, the ΔH^O for this reaction is -59 kilocalories.[18,19] The entropy change is favorable. Oxidation difficulties thus exist both for the sulfides and selenides.

Diffusion Profiles

The silver, arsenic, and chalcogenide profiles of the diffusion couples were determined using an electron microprobe analyzer* wherein an electron beam incident on the sample excites characteristic x-rays which are quantitatively analyzed. The concentration profiles were obtained by traversing the electron beam along a desired path perpendicular to the diffusion couple interface which is perpendicular to the polished surface. The beam traversed the sample in steps, sampling each step for 40 seconds. Excessive heating, which caused evaporation or melting of the glass and/or surface diffusion of the silver, was eliminated by rapidly scanning the electron beam parallel to the interface of the couple during the counting at each point. This procedure reduced the incident energy per square micron per second on the couple. The minimum scan width for damage free operation was 80 microns.

Surface diffusion of silver activated by the incident electron beam was minimized by stepping the scanning beam a minimum step length of two microns and always proceeding from silver-lean to silver-rich areas.

*Model 400, Materials Analysis Co., Palo Alto, CA.

Characteristic x-ray counts during the 40 second counting time were just sufficient to give well-defined statistics for good but not excellent data. All three elements of the diffusion couples were analyzed simultaneously. For qualitative analysis an EDAX[*] analyzer, a modified microprobe analyzer, was used.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Glass-Ag Metal Systems

Diffusion data for the As_2S_3-Ag and As_2Se_3-Ag couples are listed in Table 1. Representative diffusion profiles for each of the systems are shown in Figs. 3 and 4. The number of cations per 100 anions vs. distance are plotted in the figures above each profile on the same distance axis. The As content remains constant at 66 throughout the diffusion zone and into the bulk chalcogenide glass. Thus, the As cations, of any valence, are essentially immobile in the rigid anion structure. The Ag cations alone are mobile at $T < T_g$. The gradient in concentration of As ions is a consequence of a percentage change due to the introduction of Ag ions into the glass and not to As movement. No diffusion into the Ag was detected.

(a) Reactions

The profiles indicate that redox reactions have occurred. A charge balance analysis of ion concentrations at any location in the diffusion zone shows that the As is reduced from a valence of +3 to +2 and then from +2 to +1 in order to maintain charge neutrality in the

---

[*]Model 711, EDAX Inc., Prairieview, IL.

glass with the introduction of Ag which is oxidized to Ag^+. The interpretation of the profile data, augmented with thermodynamic data, is the following.

Initially the Ag is oxidized at the glass interface by reduction of As^{+3} in the glass to As^{+2}:

$$2 \ Ag + As_2S_3 = As_2S_2 + Ag_2S \qquad (3)$$
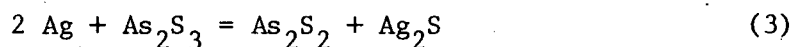
$$\Delta H^o = -6.25 \pm 6.1 \ kcal$$

At intermediate stages every Ag atom oxidized requires a reduction of one As^{+3} to As^{+2}, and the equation can be written as

$$x \ Ag + As_2S_3 = As^{+3}_{2-x}As^{+2}_xAg^{+1}_xS_3 \qquad (4)$$
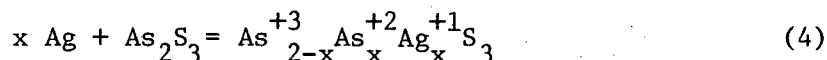
where x varies from 0 to 2. When all of the As^{+3} is reduced to As^{+2}, i.e. x=2, the glass composition becomes $Ag_2As_2S_3$ (28.6 atomic % Ag, 28.6 As, and 42.9 S). Experimental results indicate that further solution of Ag by the glass promotes further reduction of the arsenic to As^+. The equation for the intermediate stages when an As^{+2} is reduced to an As^{+1} by an entering Ag can be written as

$$x \ Ag + As_2Ag_2S_3 = As^{+2}_{2-x}As^{+1}_xAg^{+1}_{2+x}S_3 \qquad (5)$$
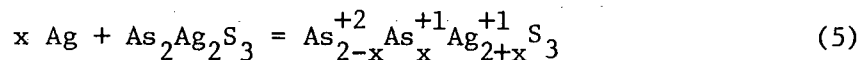
where x varies from 0 to 2. With complete reduction to As^+ (i.e. x=2) the composition becomes $Ag_4As_2S_3$ (44.4 atomic % Ag, 22.2 As, and 33.3 S). Reduction of arsenic to the elemental state, however, is not favored thermodynamically:

$$As_2S_3 + 6 \ Ag = 2 \ As + 3 \ Ag_2S \qquad (6)$$
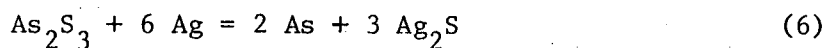
$$\Delta H^o = + 10.35 \pm 3.3 \ kcal$$

Thermodynamic data for the selenides are unavailable. However, the similar chemical nature of sulfur and selenium anions and the observed identical reaction product compositions justify the conclusion of the existence of identical redox reactions for As_2Se_3.

(b) The Reaction Product Phase

In accordance with the redox reactions an amorphous reaction product phase is observed to form when the Ag content is sufficient to reduce all As^{+3} and the product contains As^{+2} and As^+. By definition a phase is any portion of a system which is physically homogeneous within itself and bounded by a surface so that it is mechanically separable from any other portions.[20] Distinct boundaries are observed (Fig. 2) at the cross over points for the As and Ag profiles. Electron microprobe profiles, however, show smooth and continuous Ag gradients across the boundary indicating the existence of complete solid solution of As^{+2} between the two phases. The portion of the profiles containing As^{+3} and As^{+2} correspond to the solution of Ag^+ in the original As_2S_3 glass phase. The transition point between the two phases based on the stoichiometric composition $Ag_2As_2S_3$ corresponds to a composition of 29 atomic percent As and Ag. Within experimental error, the composition at the boundary or crossover point between the As and Ag concentration curves was found to equal this value as seen in Table 1. Also, 44.4 atomic percent is the maximum theoretical solubility limit of Ag in the reaction phase, corresponding to $Ag_4As_2S_3$, and thus in the starting As_2S_3 glass. This value is in good agreement with the experimental data.

(c) Oxidation

Interfacial oxide contamination in these couples, as discussed earlier, is believed to be responsible for the indicated variations in the interfacial Ag concentration and the thickness of the diffusion zones (Table 1) because of the resulting difficulties in forming a true interface.

Sample 46 was polished as described to reduce oxygen contamination. Sample 45 was not, resulting in greater surface oxidation. In support of this suggestion the samples showed different surface conductivities during Ag plating. It is postulated that a large portion of the heat treatment time was utilized by sample 45 to dissolve the oxide layer before a true interface formed and diffusion began. Possible oxide vaporization was prevented as the glass was encapsulated by the silver metal.
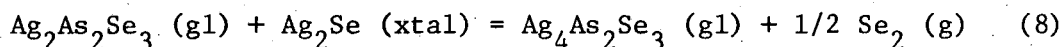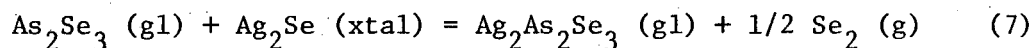
Polycrystalline $Ag_2Se-As_2Se_3$ Glass System

These couples exhibit diffusion profiles similar to the Ag metal-As_2Se_3 glass profiles. Diffusion data for several runs are listed in Table 1 and a representative concentration profile is shown in Fig. 5. The similarity of diffusion profiles with the previous systems indicates that a reduction of As^{+3} also occurs in this system which can be accomplished only by the presence of Ag. Ag becomes available from Ag_2Se by the oxidation of Se^{-2} ions to elemental Se.

(a) Reactions

A reaction product phase is formed, similar to the Ag metal-glass system, by diffusion of Ag^+ into As_2Se_3 as indicated by the constancy of the As/Se ratio in the diffusion zone which extends into As_2Se_3, (Fig. 5).

The following overall equations represent the reactions:

$$As_2Se_3 \text{ (gl)} + Ag_2Se \text{ (xtal)} = Ag_2As_2Se_3 \text{ (gl)} + 1/2 \ Se_2 \text{ (g)} \qquad (7)$$

$$Ag_2As_2Se_3 \text{ (gl)} + Ag_2Se \text{ (xtal)} = Ag_4As_2Se_3 \text{ (gl)} + 1/2 \ Se_2 \text{ (g)} \qquad (8)$$

An accumulation of Se was not observed at the interfaces since it left the couples as a vapor. These endothermic reactions have an entropy contribution due to the vapor species in the reaction product. Therefore, they are thermodynamically favorable at elevated temperatures.

An experiment was devised to verify the existence and analyze the composition of the vapor reaction product. An As_2Se_3- Ag_2Se couple was sealed in a 45 cm. long pyrex tube filled with 0.9 atmosphere of argon. The end of the tube with the couple was held at 175°C for 48 hours. The other end extended out of the furnace allowing it to be at room temperature. A condensate of many small islands of relatively pure selenium, identified by EDAX, formed in the cool end of the tube. Arsenic was also identified in the cool end of the tube due to the fact that some As_2Se_3 could vaporize. The total amount of Se, however, appeared to be far in excess of the amount that may have been transported due to As_2Se_3 vaporization. This supports the reactions represented by Eqs. 7 and 8.

If a selenide analog of smithite existed, it would have been expected that $AgAsSe_2$ would have formed at the interface between Ag_2Se and As_2Se_3 by interdiffusion of As^{+3} and $3Ag^+$. Since Ag entered As_2Se_3 by the indicated redox reactions, it can be concluded that the redox reaction was energetically more favorable under the conditions of the experiment. If a smithite analog exists, it may have formed in the presence of a sufficiently high ambient pressure of Se.

(b) Diffusion Runs

Couple #27 (Table 1) was reaction rate limited since the maximum solubility of Ag in the glass was not realized after 30.8 hours at 175°C. Moreover, the formation of the reaction product did not occur as indicated by a Ag content that did not exceed 30 at %. Couple #31 (Table 1) as well as #25 (Fig. 5) showed the formation of the reaction product and the presence of a diffusion limited process even though they were held at 175° for shorter times. It thus appears that the Se was able to escape more readily in the latter cases and did not retard the arsenic reduction process.

Consideration of the geometry of the couples after the diffusion anneal justifies the conclusion that the observed kinetics are dependent on the escape of the vapor reaction product. Planar diffusion couples always opened like a "clam shell" pivoting about a small volume of material where the interface was formed. The extent of clam shell opening, hence the ability of the vapor to escape, varied randomly among couples. Accordingly, the extent of the rate at which Ag was supplied to the glass phase varied randomly. Oxygen contamination undoubtedly also contributed to the variability of the results as discussed.

Polycrystalline $AgAsS_2$-As_2S_3 Glass System

Since a solid piece of Ag_2S was not available, a diffusion couple of $AgAsS_2$-As_2S_3 was prepared. In accordance with the phase diagram indication that these compounds are at equilibrium,[17] no diffusion was detected after 400 hrs at 175°C. This result also indicates that mutual solubility is very low or that the chemical interdiffusion is extremely low at this temperature.

The couple was formed by holding the polished surfaces with an
alligator clip as before. Furthermore, in the absence of a redox reaction
the couple did not open up like a "clam shell" during diffusion as in the
previous system.

Diffusivities

Glass modifier diffusion in glasses is typically concentration
dependent. A Boltzmann-Matano analysis based on an approach given by
Boltzmann[21] can then be applied which is valid if the following require-
ments are fulfilled: (1) the diffusion is isothermal, isotropic and one-
dimensional, (2) the diffusion is not reaction rate limited, (3) there
is no volume change with introduction of the diffusing species, and (4)
the driving force for diffusion is a gradient in the chemical potential
of the diffusing species (negligible electrical potential field). Re-
quirements (1) and (2) are essentially fulfilled experimentally by coup-
les #42, #46-1, #46-2 and #31 listed in Table 1. For calculations, the
assumption is made that there is no volume change with diffusion. Also,
since holes are identified[22] as the mobile species for electronic con-
duction in these sulfide and selenide glasses, it is assumed that their
mobility is high enough to eliminate the potential field. The
drift mobility[1] of holes at fields of 10^5 volt/cm is approximately 3 x
10^{-5} cm^2/volt sec.

The reaction process is diffusion controlled if the Ag concentration
at the Ag rich interface for these couples is found experimentally to be
~44 atomic percent. The Boltzmann-Matano analysis requires the location
of the interface across which there are equal and opposite diffusion
fluxes. However, in these systems since only

one component is diffusing, i.e., Ag going into solution, the original interface is invariant. Therefore, they are the Ag-glass and the Ag_2Se-glass interfaces as revealed by the diffusion profiles.

The diffusion profiles of #42 (Fig. 3), #46-1, #46-2 (Fig. 4), and #31 were analyzed to determine Ag diffusivities. These profiles were judged to best fulfill the analysis requirements and to exhibit the least oxide contamination. The calculated diffusivities are shown in Fig. 6. Inherent in the graphical analysis is an increasing inaccuracy as the extremities of the curves are approached. Therefore, diffusivity values below 8% and above 42% Ag were not plotted.

The concentration dependence of Ag diffusion into the As chalcogenides at 175°C can be approximated as being exponential between 10 and 35% Ag:

$$\text{Sulfide} - 4 \times 10^{-14} \exp \left[(+0.23 \pm .01)(\text{atomic \% Ag}) \right] \text{cm}^2/\text{s}$$

$$\text{Selenide} - 2 \times 10^{-11} \exp \left[(+0.14 \pm .01)(\text{atomic \% Ag}) \right] \text{cm}^2/\text{s}$$

The concentration dependence of Ag diffusion increases rapidly from 35 to 44% Ag. It should also be observed that the diffusivity varies smoothly across the reaction product phase composition limit of ~29% Ag in either glass.

CONCLUSIONS

Silver diffusion in As_2S_3 and As_2Se_3 glasses (below T_g) is accompanied by the reduction of the As to maintain charge neutrality. Reduction to the elemental state does not occur. An amorphous phase is formed when all As^{+3} is reduced to the +2 valence state with the introduction of 28.6 at % Ag. The maximum solubility of Ag in As_2S_3 or As_2Se_3 is 44.4 atomic percent which occurs when all As is reduced to the +1

valence state.

Ag can be used for making an electrical contact to As chalcogenide containing amorphous semiconductors. It follows from results of this study that the optimum contact would be formed by consecutive deposition of the amorphous semiconductor film and the Ag contact film without breaking vacuum. Oxide film formation would thus be eliminated. Pristine glass surfaces were found to have excellent surface conduction whereas oxide covered surfaces did not.

Stuptitz and Willert[8] reported a concentration independent diffusivity of Ag in As_2Se_3 of 3×10^{-11} cm^2/sec at 175°C for Ag concentrations ≤ 0.01 atomic percent. Assuming that their diffusion activation energy is concentration independent and combining it with the concentration dependence determined in this work, the diffusivity of Ag in As_2Se_3, in the concentration range of 10 to 35 atomic percent, at temperatures below T_g is

$$0.02 \exp \left[-0.89 \text{ eV}/kT + (0.14 \pm .01)(\text{atomic \% Ag})\right] cm^2/s.$$

ACKNOWLEDGMENT

REFERENCES

1. D. Adler, "Amorphous Semiconductors," CRC Crit. Rev. S.S. Sci. 2, [3], (1971).

2. N. F. Mott, "Electrons in Disordered Structures," Adv. Phys. 16, 49-144 (1969).

3. D. D. Thornburg, "Physical Properties of the $As_2(Se, Te)_3$ Glasses," J. Elect. Mat. 2 [4], 495-532 (1973).

4. A. Matsuda and M. Kikuchi, "Observations of Fundamental Processes in Ag Photodoping of Amorphous As_2S_3 Films," Suppl. J. Japan Soc. Appl. Phys. 42, 239-248 (1973).

5. D. Goldschmidt and P. S. Rudman, "The Kinetics of Photodissolution of Ag in Amorphous As_2S_3 Films," J. Non-Xtal. Sol. 22, 229-243 (1976).

6. I. Shimizu, H. Sakuma, H. Kokado and E. Inoue, "The Photodoping of Metals into Solids for New-type Imaging Systems," Bull. Chem. Soc. Japan 44, 1173-1173 (1971).

7. H. Kokado, I. Shimizu, T. Tatsuno and E. Inoue, "A Photoelectric Study of the Interface Between Metallic Silver and Vitreous As_2S_3," J. Non-Xtal, Sol. 21, 225-232 (1976).

8. P. Stuptitz and I. Willert, "Diffusion of Ag and Au in As_2Se_3," Phys. Stat. Sol. (a) 28, 223-226 (1975).

9. E. A. Lebedev, P. Stuptitz and I. Willert, "Transport of Ag Under the Influence of an Electric Field in Glassy As_2Se_3," Phys. Stat. Sol. (a) 28, 461-466 (1975).

10. J. P. DeNeufville in, "Amorphous and Liquid Semiconductors," ed. J. Stuke and W. Brenig, Taylor and Francis, London, p. 1351 (1974).

11. R. Andreichin, "Conductivity and Photopolarization Properties of Vitreous As_2S_3," J. Non-Xtal. Sol. $\underline{4}$, 73-77 (1970).

12. R. Andreichin, "High Field Polarization, Photopolarization and Photoelectret Properties of High Resistance Amorphous Semiconductors," J. Electrostat. $\underline{1}$, 217-230 (1975).

13. C. F. Drake, I. F. Scanlan and A. Engel, "Electrical Switching Phenomena in Transition Metal Glasses Under the INfluence of High Electric Fields," Phys. Stat. Sol. $\underline{32}$, 193-208 (1969).

14. C. F. Drake and I. F. Scanlan, "Bond Type, Polarization and Electron Conduction in Some Oxide and Chalcogenide Glasses," J. Non-Xtal. Sol. $\underline{4}$, 234-237 (1970).

15. F. M. Faure, M. J. Mitchell and R. W. Bartlett, "Vapor Pressure Study of Arsenic Trisulfide," High Temp. Sci. $\underline{5}$, 128-137 (1973).

16. S. A. Dembroki, "The As-Se System," Rus. J. Inorg. Chem. $\underline{7}$, [12], 1454-1456 (1962).

17. F. M. Jaeger and H. S. vanKlooster, Z. Anorg. Chem. $\underline{78}$, 266 (1912).

18. R. D. Freeman, Dept. of Chem. Oklahoma State Univ. Research Report #60, "Thermodynamic Properties of Binary Sulfides," (1962) Stillwater, Oklahoma.

19. J. P. Coughlin, Bulletin 542, Bureau of Mines, "Contributions to the Data on Theoretical Metallurgy XII, Heats and Free Energies of Formation of Inorganic Oxides," U.S. Printing Office, Washington, DC (1954).

20. E. M. Levin, C. R. Robbins and H. F. McMurdie, "Phase Diagrams for Ceramists," The American Ceramic Society, Columbus, OH (1964).

21. L. Boltzmann, "Integration of Diffusion Equations by Variable
Diffusion Coefficients," Ann. Physik, 53, 959 (1894).

22. C. H. Seager and R. K. Quinn, "DC Electronic Transport in Binary
Arsenic Chalcogenide Glasses," J. Non-Xtal. Sol. 17, 386-400 (1975).

Table 1. Diffusion Data at 175°C

Couples	Atomic %[*]			Thickness, μm	
	Ag	As	S or Se	Diffusion Zone	Reaction Product
As_2S_3-Ag					
#42 - 120 hrs (Fig. 3)				87	75
Boundary	29	29	42		
Ag-Interface	42	23	36		
As_2Se_3-Ag					
#46-1 - 5 hrs				125	113
Boundary	28	28	41		
Ag-Interface	44	22	33		
#46-2 - 5 hrs (Fig. 4)				142	135
Boundary	30	30	40		
Ag-Interface	44	22	34		
#45 - 5 hrs				40	35
Boundary	29	29	41		
Ag-Interface	42	23	35		
$As_2Se_3-Ag_2Se$					
#25 - 21.6 hrs (Fig. 5)				212	196
Boundary	28	28	43		
Interface	40	24	35		
#27 - 30.8 hrs				188	0
Boundary	30	30	40		
Interface	30	30	40		
#31 - 25 hrs				230	204
Boundary	28	28	43		
Interface	46	22	31		

[*]Experimental error in compositions is ± 2 at %.

FIGURES

1. Time-temperature schedule for $AgAsS_2$ formation.

2. Photomicrograph of polished cross-section of specimen #46-2.

3. Specimen #42 diffusion profile: $Ag-As_2S_3$ couple, 120 hrs.

4. Specimen #46-2 diffusion profile: $Ag-As_2Se_3$ couple, 5 hrs.

5. Specimen #25 diffusion profile: $Ag_2Se-As_2Se_3$ couple, 21.6 hrs.

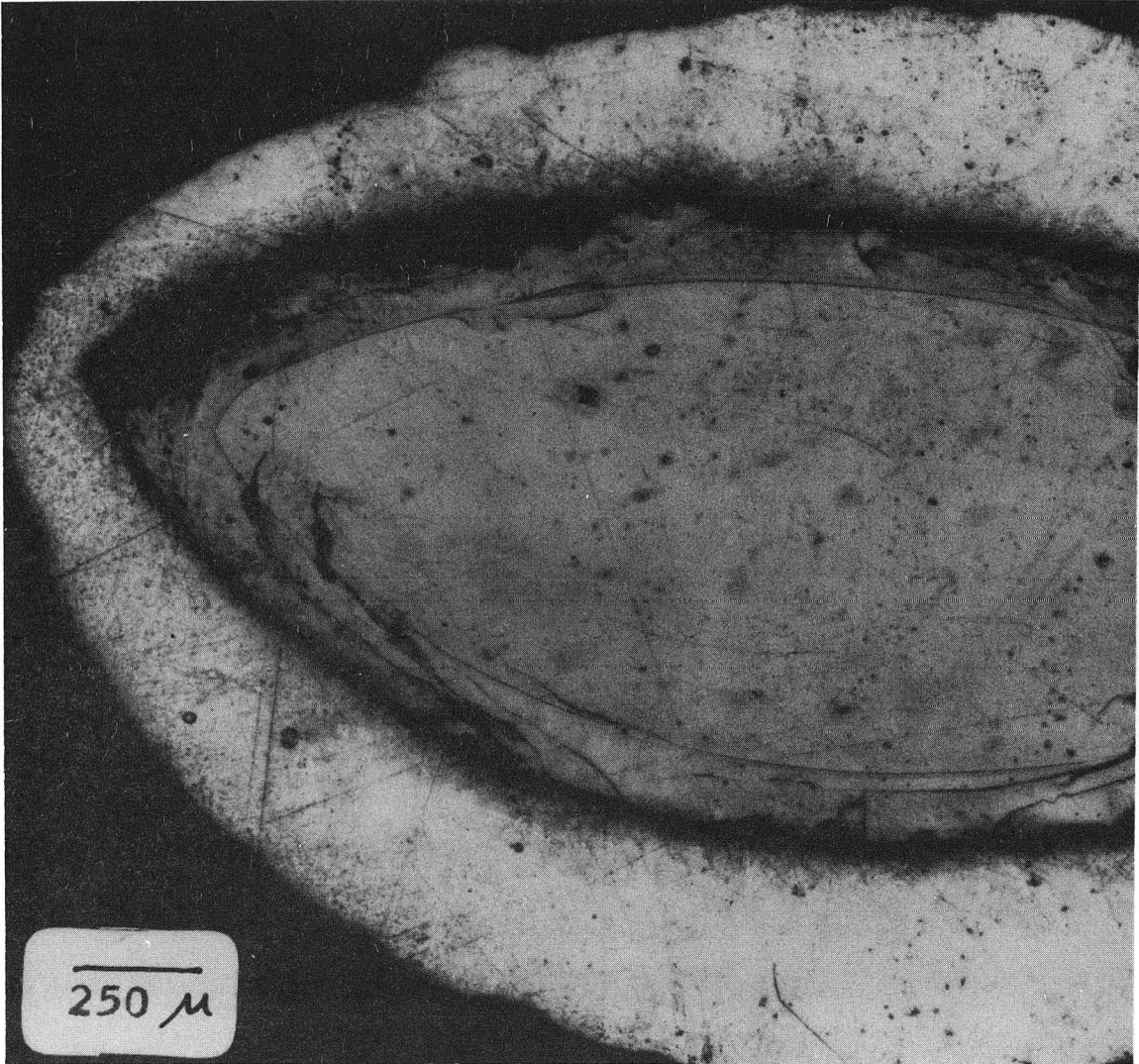6. Ag diffusivity vs. Ag concentration data for As chalcogenide glasses.

—23—

TIME TEMPERATURE SCHEDULE FOR

$As_5Ag_6S_2$ [SMITHITE] FORMATION
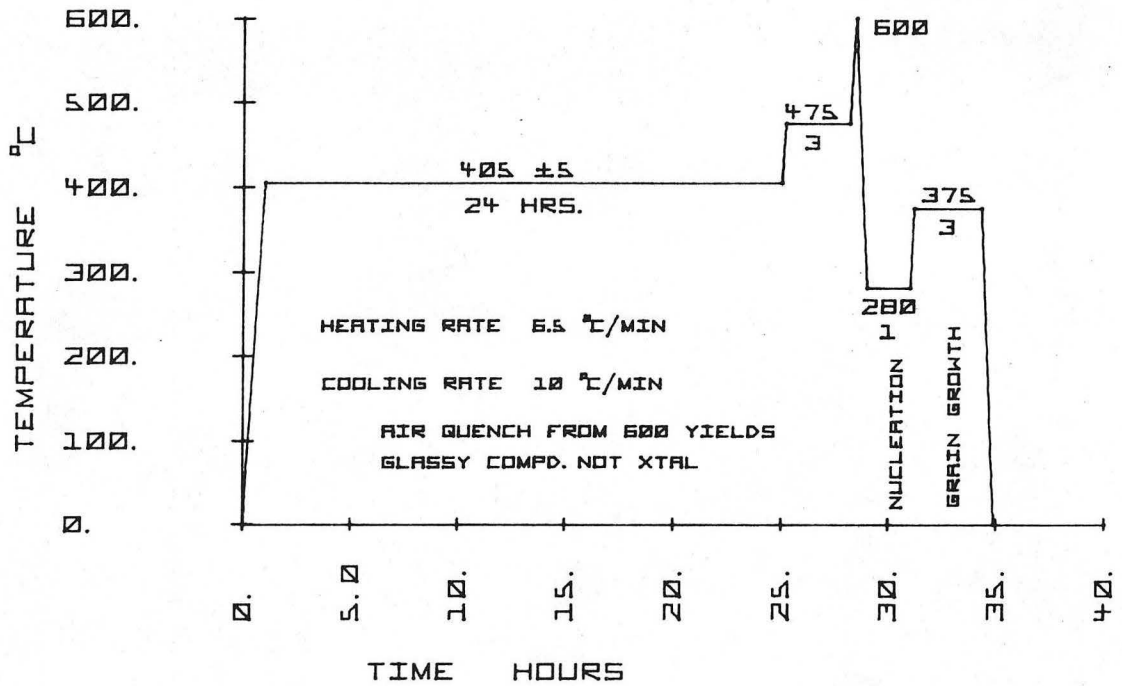
USING As_2S POWDER PRESSED INTO CYLINDRICAL
PELLETS 1 CM. HIGH AND 1 CM. DIAMETER

XBL 778 9882

Fig. 1

250 μ

XBB777-6958

Fig. 2

Fig. 3

XBL 778-9884

Fig. 4

XBL 778-9888

Fig. 5

XBL 778-9886

Fig. 6

XBL 778-9891