# SILVER IN PHOTODOPED ARSENIC SULFIDE FILMS : AN EXAFS STUDY

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# SILVER IN PHOTODOPED ARSENIC SULFIDE FILMS : AN EXAFS STUDY

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Résumé
Nous avons mesurés le K-edge EXAFS de l'argent pour un nombre de films du sulfure d'arsenic photodopé et determinés la distance de coordination d'argent à soufre. C'est très semblable à la verre $Ag_{25}As_{25}S_{50}$, comme le XANES. L'on a observé la séparation des phases dans quelques films par l'apparence d'une seconde couche dans la transformation de Fourier.

Abstact
We have measured the silver k-edge EXAFS for a number of photodoped arsenic sulphide films and determined the silver-sulphur coordination distance. This is very similar to the $Ag_{25}As_{25}S_{50}$ glass, as is the near-edge region. Phase separation has been observed in some films by the appearance of a second shell in the Fourier transform.

## INTRODUCTION

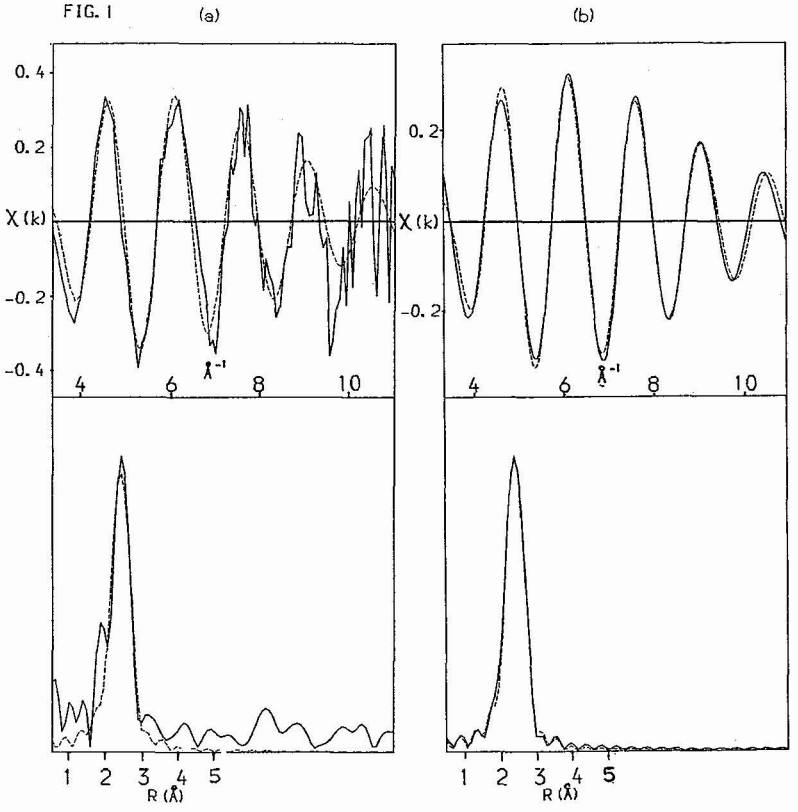
Light-induced dissolution of silver (and copper) into chalcogenide glasses has been studied for some time and has possible applications in sub-micron lithography (1) as a result of the very small amount of lateral diffusion. Raman spectroscopy of photo-doped films based on arsenic sulphide compositions $As_xS_{1-x}$ (x=20, 30, 40) (2, 3) has indicated that when x=30 the structure is very similar to a bulk glass and that the material consists of a homogeneous, uniform phase. In the x=40 arsenic-rich film a phase-separated material containing amorphous arsenic and an amorphous Ag-As-S phase. For x=20 initial formation of a silver sulphide phase is proposed. An understanding of the coordination environment adopted by the silver in the photodoped films may help determine the mechanism of doping and give some indications about phase-separation.

SAMPLE PREPARATION

The films are prepared by evaporating approximately 1000Å of silver onto a mylar sheet followed by 5000-6000Å of arsenic sulphide. This is then exposed (from the chalcogenide side) to a 200W Hg lamp with a filter so that wavelengths in the range 350-500nm reach the sample. The exposure time is approximately 30mins at which time the sample cannot be etched with a dilute alkaline solution. The films derived from using only 4000Å of arsenic sulphide showed a slight milkiness and it is thought that this indicates incomplete doping or phase-separation. The EXAFS of these samples appear to show evidence of Ag--Ag bonding from silver metal. The other films were completely clear.

EXAFS

The EXAFS at the silver k-edge have been recorded on the wiggler beam-line of the SRS at station 9.2. Suitable crystalline model compounds for testing the calculated phase-shifts and comparison with the films, $Ag_2S$ , acanthite, $Ag_3AsS_3$ , proustite, $AgAsS_2$ , smithite, together with a bulk glass of composition $Ag_{25}As_{25}S_{50}$ have been used. Fig. 1 shows the quality of raw data with the least-squares fit, and the fourier-filtered first shell and fit for the film derived from the composition As S and of thickness ratio 5.5:1. All the distances, etc shown in table1 are derived from fourier-filtered data.




$k^3$-weighted EXAFS above the silver K-edge and FT for the $As_{30}S_{70}$ (5.5:1) film. (a) Raw data (b) first-shell fourier-filtered data. ——Expt. ---Theory

FIG. 2

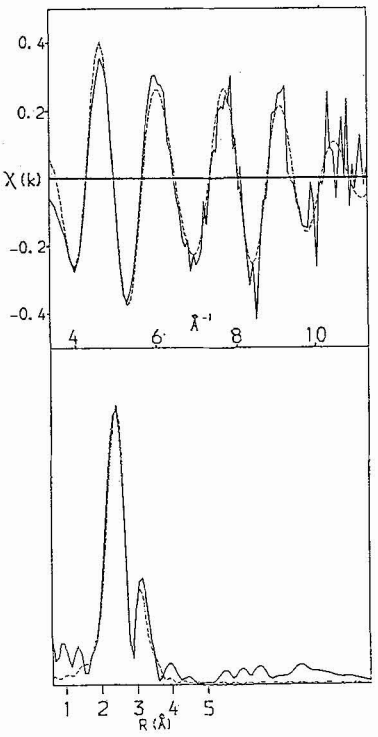
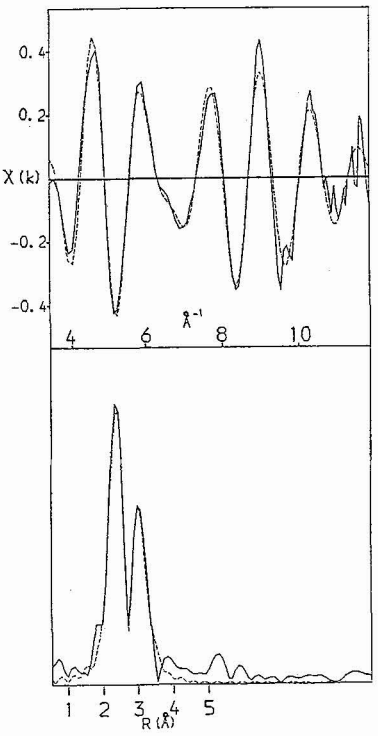



FIG. 3




2. k-weighted EXAFS above the silver K-edge and FT for the $As_{30}S_{70}$ 4.0:1 film. ——Expt. ---Theory
3. k-weighted EXAFS above the silver K-edge and FT for a very thick inhomogeneous film. ——Expt. ---Theory

All the films had basically the same EXAFS i.e. a single frequency from a first-shell of sulphur atoms. In two cases, however, a second-shell is observed. When a very thick film (approx. 1 micron silver) was prepared the second shell (fig. 3) arises from Ag--Ag of phase-separated silver metal. In the $As_{30}S_{70}$ film (4:1 thickness) (fig. 2) the second shell is smaller and its interpretation is less clear. There is a similar peak in $Ag_2S$ arising from Ag--Ag non-bonding interactions at approx. 3.0Å, but the distance is incorrect. The former explanation is favoured but more work with purposely-induced inhomogeneity is required.

The silver-sulphur coordination which is likely to be quite disordered, in line with the model compound, has been fitted in k-space using one shell of sulphur atoms, and allowing the coordination number and Debye-Waller factor to vary. The models have been treated similarly for comparison purposes. For example it is possible to use all five coordinating distances in $Ag_2S$ but the fit is little improved. Any conclusions, therefore, based on the numbers and Debye-Waller factors at this stage would be rather speculative and discussion is confined to the bond distance and more general aspects.

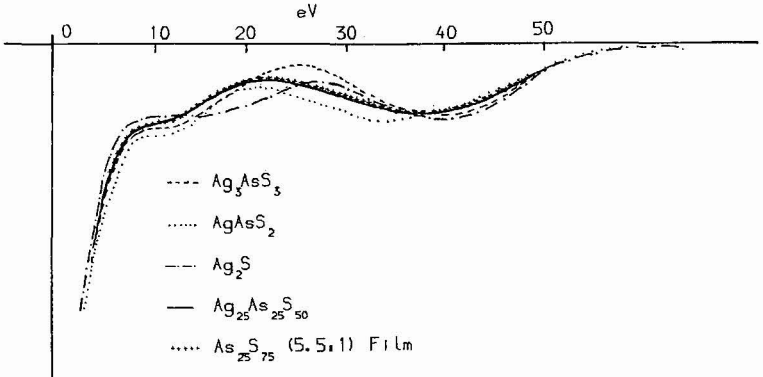
TABLE1

| Comp. of starting As-S material | Thickness ratio of As-S/Ag | $R_{EXAFS}(R_{XTAL})$ Ag-S | N | A ($2\sigma^2$) |
|---|---|---|---|---|
| $Ag_2S$ | - | 2.48 (2.51) | 2.2 | 0.020 |
| $Ag_3AsS_3$ | - | 2.42 (2.44) | 2.0 | 0.014 |
| $AgAsS_2$ | - | 2.51 (2.53) | 2.9 | 0.023 |
| $Ag_{25}As_{25}S_{50}$ (glass) | - | 2.47 | 2.6 | 0.024 |
| $As_{25}S_{75}$ | 5.5:1 | 2.45 | 2.8 | 0.020 |
| $As_{25}S_{75}$ | 4.0:1 | 2.46 | 2.6 | 0.020 |
| $As_{30}S_{70}$ | 5.5:1 | 2.47 | 2.3 | 0.017 |
| $As_{30}S_{70}$ | 4.0:1 | 2.45 | 2.3 | 0.017 |
| $As_{40}S_{60}$ | 4.5:1 | 2.46 | 2.4 | 0.018 |

The main silver-sulphur in the films is at 2.46Å which is between that for proustite and smithite but similar to that for $Ag_2S$. The lack of second shell as seen in the latter rules this out as a model for the coordination. However there is gooed similarity between the films and the bulk glass in which no second shell is observed. To reinforce this a comparison of the XANES is shown and that of the films is almost identical to that of the glass.

## CONCLUSION

It is clear that phase-separation and inhomogeneity can be a problem in these photodoped films, and yet most of the films we have studied have been reasonably homogeneous. The environment of the silver is closest to that found in the bulk glass. An improved understanding of the glasses will be of great importance in determining the structure of the films. An important question that may be answered by using EXAFS is whether the glass-forming composition region is significantly extended in these thin films.




XANES comparison of the films and the model compounds.

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