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Structural studies of amorphous semiconductor–metal alloys

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It is well known that a semiconductor to metal transition may be induced in amorphous semiconductor–metal alloys by increasing the metal concentration above a critical limit. However, without a knowledge of the atomic scale structure of the alloy it is difficult to ascribe a mechanism to this process. Three alloy systems (a-$Si_{1-x}Ni_x$–H, a-$Ge_{1-x}Au_x$ and a-$Si_{1-x}Sn_x$–H) have been prepared as thin films by rf reactive co-sputtering over pertinent composition ranges. The micro-structure of these alloys has been investigated using EXAFS. Both a-$Si_{1-x}Ni_x$–H and a-$Ge_{1-x}Au_x$ appear to consist of two separate phases, regions of an amorphous Ni–Si alloy and a crystalline Ge–Au alloy being embedded in an amorphous matrix provided by a-Si and a-Ge, respectively. In contrast, however, Sn atoms are substituted randomly into the a-Si tetrahedral random network.

1. Introduction

Non-crystalline semiconductors are of immense technological interest, having many and varied applications. However, potentially of even greater significance are materials formed by alloying a-Si–H with metals (M). By careful control of the composition of the materials formed (a-Si–M–H), it is possible to regulate the electrical conductivity and for certain metal impurities, e.g. noble and transition metals, to induce a transition from semiconducting to metallic-type behaviour above a certain critical limit. The electronic properties of such alloys have been extensively studied[1] and the MITs are usually decribed in terms of an Anderson-type transition where electrons at the Fermi level become delocalised and extended state conduction can occur. However, this approach relies on the assumption that the impurity atoms are incorporated randomly into the structure. If clustering of metal atoms occurs it is more appropriate to describe the electrical conductivity in terms of classical percolation theory[2].

In contrast to the behaviour described above, alloying a-Si–H with the group IV metal, tin, does not induce an MIT. As the metal concentration is increased the optical bandgap smoothly decreases along with a concomitant increase in dark conductivity[3]. However, above about 5 at% Sn, the conduction process changes from n-type to p-type and the photoconductivity falls[4]. This latter phenomenon has been attributed to the non-substitutional inclusion of impurity atoms.

It is clear that to clarify our understanding of the conductivity processes in a-Si–M alloy it is advantageous to have a knowledge of the atomic scale structure of the materials and the way in which the impurity atoms are included in the tetrahedral random network (TRN) of the host semiconductor. To this end we have investigated the structure of three alloy systems of interest (a-Si–Ni–H, a-Ge–Au and a-Si–Sn–H) over pertinent composition ranges using the technique of extended X-ray absorption fine structure (EXAFS).

2. Sample preparation

Thin film samples were deposited onto substrates by reactive co-sputtering. Argon (99.998% purity) was used as the sputtering gas with H_2 (99.993% purity) added in the ratio 10/1-Ar/H_2, to saturate dangling bonds in the samples[5]. The total pressure was 7.3×10^{-3} mbar with a constant rf power of 200 W. The composition of the samples was controlled by varying the number of small metal discs arranged on the crystalline semiconductor target to give a homogeneous distribution at the substrate. However, the a-Ge–Au samples were not hydrogenated to aid qualitative comparison with previous work on this system. Compositional analysis was performed using an electron microprobe and later verified using α-particle Rutherford backscattering. Each sample was also found to contain an approximately constant proportion (8 at%) of Ar incorporated during the sputtering process. The amount of H_2 incorporated in the hydrogenated samples was not quantitatively evaluated; however, ir absorption spectroscopy shows the presence of Si–H bonds at all compositions. The optical and electronic properties of the samples are also being measured as part of a parallel study and the findings will be published elsewhere[6].

3. Structural measurements

EXAFS allows the average local environment of individual atomic species to be evaluated. To obtain maximum information, we have performed EXAFS experiments at the absorption edges of both the semiconductor and metal atoms present in the samples. The experiments were performed using the synchrotron radiation source (SRS) at Daresbury Laboratory (DL), UK. Experiments on the Ge, Au, Ni and Sn edges were performed using standard transmission geometry with beam intensities, and hence absorptions, being measured with ionisation chambers. This type of experiment necessitated the use of low absorping polypropylene substrates. The optimal ratio of post to pre-edge absorption (approximately 1.5) was achieved by stacking several layers of sample. Due to the low X-ray energies and high absorption at the Si K-edge, it was necessary to measure Si K-edge absorption using the electron drain current method, a variation on the total electron yield method[7]. For this type of measurement the samples were deposited to a thickness of approximately 1.5 μm on conducting (stainless steel) substrates.

4. Data analysis

The EXAFS data were analysed in the standard way using the suite of programs available at DL. Pre and post-edge backgrounds were removed by fitting smooth, low order polynomials to the appropriate regions of the experimental spectra using the program EXBACK[8]. Structural parameters were evaluated by non-linear least squares fitting of the theoretical EXAFS function ($\chi(k)$) to the experimental data using the rapid curved wave theory[9] as implemented in the program EXCURV88[10]. As an illustration of the information available from EXAFS we show a much simplified version of the EXAFS function in equation (1).

$$\chi(k) = -\sum_{i=1}^{n} \frac{N_i}{kR_i^2} \sin(2kR_i + 2\delta + \psi_i)|F_i(\pi, k)| \times \exp(-A_i k^2)\exp\left(-\frac{2R_i}{\lambda}\right). \qquad (1)$$

Here k is the photo-electron wavevector; N_i is the number of neighbouring atoms of type i in a shell of radius R_i having an electron backscattering amplitude of $F_i(\pi, k)$. The term A_i is a Debye–Waller factor giving a measure of the static and thermal disorder present in the system. The sine term accounts for phaseshifts experienced by the photo-electrons on their passage through the potentials of the emitting and scattering atoms. Phaseshifts and backscattering factors were calculated theoretically and then verified by evaluating the structural parameters of a series of standard samples. Finally, λ is the elastic mean free path of the photo-electron.

The deviation of the theoretical model from the experimental result can be quantified in terms of a fit index (*FI*) as shown in equation (2).

$$FI = \frac{1}{NPTS} \sum_{i=1}^{NPTS} (\chi(k)_{\text{exp}} - \chi(k)_{\text{theory}})^2. \qquad (2)$$

Here *NPTS* is the number of data points. Addition of an extra shell in the fitting procedure will decrease *FI* simply because of the increase in the number of variable parameters. We have therefore applied rigorous statistical tests in order to estimate the validity of addition of extra shells to the model[11]. The same approach is applied in the evaluation of experimental errors. For a full discussion of these techniques the reader is referred to the paper by Joyner *et al*[12].

5. Results

5.1. a-Ge–Au. The structural parameters obtained from the fitting procedure are shown in Table 1. From the Au edge data we see that Au atoms are co-ordinated to both Ge and Au atoms at all compositions. The presence of definite Au–Au co-ordination, even at low Au concentrations, suggests that the Au atoms are clustering. However, at low Au concentrations (< 20 at%) the Au–Au co-ordination number is low and similar to the Au–Ge co-ordination number, suggesting the formation of regions of a Ge–Au alloy. When the Au concentration increases above 20 at% the Au–Au co-ordination number increases above the Au–Ge equivalent and the Au–Au near neighbour distance approaches that of bulk Au (2.88 Å) suggesting that sizeable clusters of Au are now formed in addition to the Ge–Au alloy. The Ge K-edge results show that Ge–Ge co-ordination is dominant with no Au being visible. The Ge–Ge interatomic spacing and co-ordination is that expected for a-Ge, i.e. 4 Ge atoms at a distance of 2.45 Å.

Table 1. Ge K-edge (upper), and Au L_3-edge (lower), EXAFS results for a-$Ge_{1-x}Au_x$. N_{i-j} gives the average number of atoms of type j at a mean distance R_{i-j} (in Angstrom Å) from an atom of type i

x ±0.02	N_{Ge-Ge} ±0.5	R_{Ge-Ge} ±0.005
0.00	4.1	2.45
0.03	4.3	2.46
0.09	4.1	2.45
0.12	3.8	2.45
0.15	3.7	2.45
0.21	3.8	2.46
0.27	3.8	2.46
0.33	3.8	2.46
0.37	3.3	2.45

x ±0.02	N_{Au-Ge} ±1.0	R_{Au-Ge} ±0.02	N_{Au-Au} ±1.0	R_{Au-Au} ±0.02
0.03	1.3	2.58	1.0	2.84
0.09	2.1	2.59	1.8	2.84
0.12	2.4	2.59	2.2	2.84
0.15	1.3	2.59	2.2	2.84
0.21	2.4	2.59	2.6	2.84
0.27	1.9	2.59	5.6	2.85
0.33	3.4	2.62	5.1	2.86
0.37	1.3	2.62	4.9	2.96

We are thus drawn to the conclusion that the a-Ge–Au system consists of at least two phases; regions of a Ge–Au compound being embedded in an a-Ge TRN. Preliminary X-ray diffraction work suggests that the Ge–Au alloy is at least partially crystalline. There is also the possiblity that Au clusters appear when the concentration of Au in the sample is increased above 20 at%. This type of behaviour has been observed previously in the a-Ge–Mo alloy system[13].

5.2. a-Si–Ni–H. The results obtained from curve fitting to the Si and Ni K-edge data are displayed in Table 2. The a-Si–Ni–H system shows similar behaviour to the a-Ge–Au alloys discussed above in that Ni atoms are co-ordinated to both Ni and Si atoms at all compositions. Si K-edge data show no evidence of Si–Ni correlations, again suggesting phase separation into regions of an intermetallic alloy contained in an a-Si TRN. The apparent decrease in the Si co-ordination is due to the backscattering factors of Si and Ni atoms being approximately π out of phase in the energy region under consideration[11].

Table 2. Si K-edge (upper), and Ni K-edge (lower), EXAFS results obtained from a-$Si_{1-x}Ni_x$–H. Notation follows that used in Table 1

x ±0.02	$N_{\text{Si-Si}}$ ±1.0	$R_{\text{Si-Si}}$ ±0.02
0.00	4.0	2.35
0.03	3.0	2.35
0.06	2.6	2.36
0.09	2.7	2.34
0.13	3.4	2.34
0.16	2.2	2.35
0.19	2.4	2.35
0.22	1.8	2.36

x ±0.02	$N_{\text{Ni-Si}}$ ±1.0 ±0.02	$R_{\text{Ni-Si}}$ ±0.01	$N_{\text{Ni-Ni}}$ ±1.0	$R_{\text{Ni-Si}}$
0.03	7.4	2.33	1.5	2.55
0.06	7.5	2.33	2.3	2.54
0.09	9.0	2.37	4.9	2.51
0.13	9.3	2.36	3.5	2.52
0.14	9.1	2.36	4.0	2.52
0.16	8.8	2.35	3.3	2.53
0.19	8.6	2.34	2.8	2.54
0.22	8.7	2.35	2.6	2.54
0.25	8.5	2.35	2.7	2.54

Table 3. Si K-edge (upper), and Sn K-edge (lower), EXAFS results obtained from a-$Si_{1-x}Sn_x$–H. Notation follows that used in Table 1.

x ±0.02	$N_{\text{Si-Si}}$ ±1.0	$R_{\text{Si-Si}}$ ±0.01	$N_{\text{Si-Sn}}$ ±0.5	$R_{\text{Si-Sn}}$ ±0.02
0.00	4.1	2.34		
0.02	4.0	2.34		
0.04	4.2	2.35		
0.05	4.3	2.35		
0.06	4.0	2.35		
0.07	3.8	2.35		
0.09	3.1	2.34		
0.18	2.9	2.35	0.6	2.61

x ±0.02	$N_{\text{Sn-Si}}$ ±1.5	$R_{\text{Sn-Si}}$ ±0.03
0.02	3.3	2.60
0.03	4.2	2.59
0.04	3.5	2.60
0.05	3.3	2.61
0.06	4.2	2.59
0.07	3.6	2.59
0.08	4.7	2.59
0.12	3.9	2.60

This system also shows similarities to the properties observed when thin layers of Ni are deposited on both crystalline[14] and amorphous[15] Si substrates. Here an interfacial layer of an amorphous Ni–Si compound is formed; this amorphous material rearranges to give crystalline $NiSi_2$ on annealing. Thermal analysis[16] of our samples shows a recrystallisation at a temperature of approximately 450°C (similar to that observed in the thin layers) with the appearance of a Bragg diffraction pattern characteristic of $NiSi_2$. There is a further recrystallisation at 650°C which has been interpreted as the crystallisation of the a-Si.

5.3. a-Si–Sn–H. The Si and Sn K-edge results are tabulated in Table 3. In contrast to the two cases discussed above there is no evidence of metal–metal correlations. However, at the highest Sn concentration studied (18 at% Sn) Si–Sn correlations can be observed. Both Si and Sn atoms retain a total co-ordination of 4 at all compositions and the interatomic spacings agree with those suggested by a naive addition of the covalent atomic radii (Si-1.18 Å, Sn-1.40 Å) to within experimental error. We are therefore led to the conclusion that Sn atoms are substituted randomly for Si atoms in the a-Si TRN.

6. Discussion

Inclusion of Au into a-Ge and Ni into a-Si leads to the formation of regions of Ge–Au and Si–Ni alloys that are embedded into a matrix provided by the persisting amorphous semiconductor TRN. There is evidence that suggests that at higher Au concentrations clusters of Au may also exist. These results may have important consequences on the interpretation of the electrical properties of this type of material; specifically it may be necessary to apply classical percolation theory in order to explain the MIT that is known to occur in both of these systems.

The electrical conductivity of sputtered a-Si–Ni–H has recently been documented[17] and measurements on our samples suggest that metallic conduction may occur for nickel concentrations as low as 5 at%. We interpret this result in terms of regions of a (weakly) conducting intermetallic Si–Ni compound embedded in an a-Si dielectric. If we assume that the Si–Ni compound is a highly disordered form of $NiSi_2$, a hypothesis that is supported by the thermal analysis, then there is approximately twice as much Si in the clusters as there is Ni. Thus, for a system containing 5 at% Ni there is approximately 15 at% of the sample contributing to the conducting regions—approximately the proportion needed to induce a MIT from percolation theory[18].

A similar interpretation is possible for the a-Ge–Au alloys. Bragg peaks observed in initial X-ray diffraction spectra[19] suggest the existence of regions of the metastable phase $Au_{60}Ge_{40}$[20] in the sample. However, more work needs to be performed to ascertain the precise nature of the Ge–Au clusters.

In contrast to a-Si–Ni–H and a-Ge–Au, there is little evidence to suggest local rearrangement of the TRN by the inclusion of Sn atoms. Rather, the Sn atoms substitute randomly for Si atoms with the result that no sharp MIT occurs in this system.

7. Conclusions

Inclusion of Ni into a-Si and Au into a-Ge leads to local reordering of the TRN. Small regions of intermetallic compound are formed and are surrounded by the matrix provided by the persisting amorphous semiconductor. The behaviour of a-Si–Sn–H appears to be fundamentally different; here Sn atoms are substituted for Si atoms and tetrahedral co-ordination is preserved.

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References

[1] K Morigaki, *Phil Mag*, **B42**, 979 (1980).
[2] R Zallen and H Scher, *Phys Rev*, **B4**, 4471 (1971).
[3] H Itozaki, N Fujita, T Igarishi and H Hitotsuyanagi, *J Non-Cryst Solid*, **50/60**, 589 (1983).
[4] A Mahan, D L Williamson and A Madan, *Appl Phys Lett*, **44**, 220 (1984).
[5] J D Joannopoulos and G Lucovsky, *The Physics of Hydrogenated Amorphous Silicon I*. Springer, Berlin (1984).
[6] E A Davis, S C Bayliss, R A Asal and M I Manssor, To be published.
[7] W T Elan, J P Kirkland, R A Neiser and P D Wolf, *Phys Rev*, **B38**, 26 (1988).
[8] C Morrel, J T M Baines, J C Campbell, G P Diakun, B R Dobson, G N Greaves and S S Hasnain, *Daresbury Laboratory EXAFS Users Manual* (1989).
[9] S J Gurman, N Binsted and I Ross, *J Phys C*, **17**, 143 (1984).
[10] N Binsted, S J Gurman and J C Campbell, SERC Daresbury Laboratory EXCURV88 Program (1988).
[11] A M Edwards, M C Fairbanks, R J Newport, S J Gurman and E A Davis, *J Non-Cryst Solid*, **113**, 41 (1989).
[12] R W Joyner, K J Martin and P Meehan, *J Phys C*, **20**, 4005 (1987).
[13] J B Kortright and A Bienenstock, *Phys Rev*, **B37**, 2979 (1988).
[14] R T Tung, J M Gibson and J M Poate, *Phys Rev Lett*, **50**, 429 (1983).
[15] M O Aboelfotoh, H M Tawancy and F M d'Heurle, *Appl Phys Lett*, **50**, 1453 (1987).
[16] S C Bayliss, Private Communication (1988).
[17] N A Rogachev, V Smid, J J Mares and J Kristofik, *J Non-Cryst Solid*, **97/98**, 955 (1987).
[18] R Zallen, *The Physics of Amorphous Solids*. Wiley, New York (1983).
[19] G Bushnell-Wye, Private Communication (1988).
[20] T R Anantharaman, H-L Luo and W Klement, *Trans Met Soc AIME*, **233**, 2014 (1965).