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STRUCTURE AND LOCAL ORDER IN AMORPHOUS $\text{Si}_{1-x}\text{Sn}_x$ SEMI-CONDUCTOR ALLOYS

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Résumé - La structure atomique d'alliages amorphes $\text{Si}_{1-x}\text{Sn}_x$ ($x = 0$ à $0,50$) obtenus par coévaporation sous ultravide a été étudiée par diffraction électronique, spectrométrie Mössbauer et mesures de densité. Les alliages montrent une nette tendance à l'ordre, les atomes d'étain évitant de se placer en position de proches voisins pour des raisons d'encombrement stérique. L'analyse des spectres Mössbauer en fonction de la température donne des informations sur le spectre de vibration des noyaux ^{119}Sn .

Abstract - The atomic structure of co-evaporated amorphous $\text{Si}_{1-x}\text{Sn}_x$ alloys has been studied by electron diffraction, Mössbauer spectroscopy and density measurements. The alloys show a tendency to ordering, Sn atoms avoiding to be in close contact. The analysis of the temperature change of Mössbauer spectra provides some information about the vibration spectrum of ^{119}Sn in the alloys.

I - INTRODUCTION

The aim of this paper is to provide some information on the structure of $\text{Si}_{1-x}\text{Sn}_x$ amorphous alloys by means of diffraction experiments, density and hyperfine parameters measurements, in order to obtain a coherent picture of their atomic structure. The random network model of Polk /1/ and the model developed by Connell and Temkin /2/, based on tetrahedral units, account for the experimental observations made in amorphous group IV semi-conductors using X-ray, electron and neutron diffraction, namely /3/ :

- i) the average number of nearest neighbours to a given atom is slightly smaller than four and the n. n. distance is close to that observed in the crystalline phase,
- ii) the number of second neighbours is close to twelve, as in the crystal.

These models have been used to interpret the physical properties of some semi-conductor compounds /4/ and it was interesting to investigate the structure of a IV-IV amorphous alloy in a large composition range. The Si Sn system has been chosen because it is possible to incorporate up to 50 % of Sn in amorphous homogeneous Si Sn alloys. Moreover the optical band gap continuously changes with composition, so that it is possible, by monitoring the preparation conditions, to fabricate layers or multilayers to be used in photovoltaic conversion devices or in imaging systems.

Si Sn amorphous alloys, prepared by rf or dc sputtering, have been studied by Vérié et al. /5,6/ and by Williamson and Deb /7/. This method of preparation leads to the introduction of gaseous impurities in the alloys, that may alter their atomic and electronic structure. In order to accurately control the purity of the samples, we have constructed an apparatus for preparing Si Sn amorphous alloys by co-evaporation in a high vacuum /8/. Electron diffraction, Mössbauer spectrometry experiments and density measurements have been made to investigate the structure of the amorphous films obtained by this procedure.

II - EXPERIMENTAL RESULTS

$\text{Si}_{1-x}\text{Sn}_x$ samples were prepared in an ultrahigh vacuum chamber (3×10^{-8} Torr), by simultaneous condensation of silicon and tin on substrates held at 77 K. Two quartz monitoring systems were used to control the evaporation rate of each constituent. For $x < 0.5$ perfectly homogeneous amorphous alloys were obtained. In the concentration range $0.50 < x < 0.75$ small β - Sn crystallites are observed, by dark field electron microscopy, in a matrix that remains amorphous. For $x > 0.75$ the amorphous phase disappears and a mixture of β - Sn and Si crystallites is observed.

2. 1 - Electron diffraction

Electron diffraction patterns have been obtained using a scanning high energy electron diffraction apparatus /9/. As in pure amorphous silicon or germanium, the structure factor exhibits two well-defined peaks and a third peak with a very small intensity. The ratio $y = k_2/k_1$ of the values of k at the first two maxima of $S(k)$ continuously changes from $y_1 = 1.81$ for pure a-Si to $y_2 = 1.63$ for $x = 0.57$ (table I). This can be taken as an indication that the atomic structure of the alloys evolves from a Polk-like structure for $x = 0$, towards a structure where odd-membered rings are excluded for $x = 0.5$. As shown in table I, elemental semi-conductors are correctly described by the Polk model ($y = 1.80 - 1.82$) while the Connell-Temkin model ($y = 1.67 - 1.76$) seems more appropriate for amorphous compounds.

	Polk model	Connell-Temkin model		
<hr/>				
Model values				
unrelaxed	1.80	1.67	$\text{a-Si}_{1-x}\text{Sn}_x$	
relaxed	1.82	1.76	Present work	
<hr/>				
Experimental values			x	y
a-Si	1.81		0	1.81
a-Ge	1.77		0.10	1.75
a-Ga-As		1.71	0.13	1.74
a-Ga-P		1.70	0.22	1.72
a-Ga-Sb		1.70	0.32	1.70
a-In-P		1.67	0.38	1.70
a-In-Sb		1.59	0.47	1.67
A-Ge _{0.5} -Sn _{0.5}	1.76		0.57	1.63

Table I - The ratio $y = k_2/k_1$ of the values of k at the first and second diffraction peaks (from ref. /3/).

From this discussion we can draw the conclusion that in Si Sn alloys, chemical and size constraints are large enough to induce a well-characterized chemical short range order. Sn atoms show a tendency to be selectively surrounded by Si atoms so that, as x increases, the number of odd-membered rings decreases.

2.2 - Mean interatomic distance

The mean interatomic distance is determined as follows. The thickness of the amorphous films is measured by Tolansky interferometry and the number of atoms of each species that are deposited per unit area is determined by the frequency shift of the oscillators. Assuming a tetrahedral network it is possible to calculate $\bar{d}$ the average nearest neighbour distance (fig. 1) ; $\bar{d}$ is found to vary linearly with x from $\bar{d} = 2.41$ in pure a-Si, a figure 2.5 % larger than in pure c-Si. We may therefore assume that $\bar{d}$ would increase by 2.5 % when (hypothetical) crystalline $\text{Si}_{1-x}\text{Sn}_x$ alloys are made amorphous. The interatomic distance in c-alloys would then change with x

according to curve (b) in fig. 1. The linear variation of $\bar{d}$ with x is consistent with the assumption that Sn atoms avoid close contacts. With $d_{\text{SiSi}} = 2.35 \text{ \AA}$ as in c-Si, the experimental data lead to $d_{\text{SiSn}} = 2.53 \text{ \AA}$, a figure 1.5 % smaller than $1/2 (d_{\text{SiSi}} + d_{\text{SnSn}})$.

Fig. 1 - Variation with x of the average interatomic distance $\bar{d}$ in amorphous $\text{Si}_{1-x}\text{Sn}_x$ alloys

2.3 - Mössbauer spectroscopy

Conventional transmission Mössbauer spectroscopy spectra have been obtained in the temperature range 4.2 K to 400 K in alloys of different compositions, using the ^{119}Sn resonant nucleus, with a 10 mCi Ba SnO_3 source. In amorphous alloys a single resonance line is observed, which fits accurately to a Lorentzian of $\text{FWHM} = 1.16 \text{ mm.s}^{-1}$. This shows i) that there is only one site for Sn atoms in our alloys, unlike in dc sputtered alloys /7/ where the association with oxygen leads to three lines, ii) Sn atoms tend to avoid themselves because, if the distribution of Sn atoms were random, a broadened line would be observed.

The Debye-Waller and the second-order Doppler shift have been measured as a function of temperature in three different alloys, to determine the dynamics of Sn atoms.

a - The total shift of the absorption line is made up of two components :

$$\delta_{\text{mes}} = \delta_{\text{IS}} - \frac{\langle v^2 \rangle}{2c} \quad (1)$$

where δ_{IS} , assumed to be independent of T , is the chemical shift and the second term is due to the second-order Doppler effect. According to the conventional theory of lattice vibrations, $\langle v^2 \rangle$ can be written ;

$$\langle v^2 \rangle = \frac{3}{2} \frac{\hbar}{m} \int_0^\infty g(\omega) \coth\left(\frac{\hbar\omega}{2kT}\right) \omega d\omega \quad (2)$$

Our results show that the density of states $g(\omega)$ (normalized to unity) can be approximated by a superposition of a Debye band with Debye frequency ω_D , and an Einstein level at the frequency ω_E :

$$g(\omega) = \frac{3}{2} \frac{\omega^2}{\omega_D^3} (1 - Y(\omega - \omega_D)) + \frac{1}{2} \delta(\omega - \omega_E) \quad (3)$$

where Y is the heaviside function.

In order to determine δ_{IS} , we notice that the Debye band contributes by $3 kT/4mc$ to δ_{mes} at high temperature. A plot of

$$Y = \delta_{mes} + \frac{3 kT}{4 mc} + \frac{3 \hbar \omega_E}{8 mc} \coth \frac{\hbar \omega_E}{2kT}$$

as a function of $1/T$, extrapolated at infinite temperature, provides the value of δ_{IS} . The extrapolation process is not sensitive to the value of ω_E and the value $\omega_E = 8 \times 10^{13} \text{ s}^{-1}$ has been selected for this purpose. According to table II δ_{IS} is observed to increase with x , which can be ascribed to the decrease of the number of p -like electrons concentrated in covalent bonds when the concentration of tin increases.

When δ_{IS} is determined, the variation of $\langle v^2 \rangle$ with T can be obtained from eq. (1) (fig. 2).

Fig. 2 - Mean square amplitude ($\langle x^2 \rangle$) and velocity ($\langle v^2 \rangle$) of ^{119}Sn nuclei in $\text{Si}_{54}\text{Sn}_{46}$ amorphous alloys.

b - The Debye-Waller factor is determined from the Lamb-Mössbauer f -factor. The intensity factor $E(0)$ is defined as

$$E(0) = \frac{I(\infty) - I(0)}{I(\infty)}$$

where $I(\infty)$ and $I(0)$ are respectively the background intensity and the peak intensity of the absorption line. It is well known that $E(0)$ can be written :

$$E(0) = f_s [1 - e^{-0.5 T_A} J_0(0.5 T_A)] \quad (4)$$

where f_s is the recoilless fraction of the Ba Sn O_3 source ($f_s = 0.6$), $T_A = n \sigma_0 f$ where n is the number of resonant nuclei per unit surface, σ_0 is the maximal resonance cross-section and J_0 is the Bessel function of zero order. From the experimental absorption spectra we have determined f and the mean-square amplitude of the oscillations of Sn nuclei from the equation

$$\ln f = -k^2 \langle x^2 \rangle$$

where k is the wave-number of the incident γ -rays.

Experimental values of $\langle x^2 \rangle$ are given in fig. 2. For each concentration investigated the Debye and Einstein frequencies defined by eq. (3) have been determined through a least square fitting of the experimental results to the theoretical expressions for $\langle x^2 \rangle$ and $\langle v^2 \rangle$.

$$\langle x^2 \rangle = \frac{\hbar}{2m} \int_0^\infty g(\omega) \coth \frac{\hbar\omega}{2kT} \frac{d\omega}{\omega}$$

$$\langle v^2 \rangle = \frac{3\hbar}{2m} \int_0^\infty g(\omega) \coth \frac{\hbar\omega}{2kT} \omega d\omega$$

The values obtained for ω_D and ω_E are recorded in table II.

x	$\delta_{\text{mes}} (300 \text{ K})$ mm.s^{-1}	δ_{IS}^{-1} mm.s^{-1}	ω_D 10^{13} s^{-1}	ω_E 10^{13} s^{-1}
0.19	2.008	2.14	3.0 ± 0.2	8.0 ± 0.2
0.23	2.016	2.15	2.1 ± 0.2	8.1 ± 0.2
0.46	2.063	2.19	2.2 ± 0.2	8.2 ± 0.2

Table II - Values of the Debye frequency ω_D and of the Einstein frequency for ^{119}Sn in $\text{Si}_{1-x}\text{Sn}_x$ amorphous alloys

The fact that δ_{IS} increases with x can be ascribed to the decrease in the number of p-like electrons concentrated in covalent bonds when the concentration of tin increases /10,11/.

The values obtained for ω_E are consistent with the Einstein frequency $\omega_E \sim 8.8 \times 10^{13} \text{ s}^{-1}$ in pure silicon /12/. The softening of the Debye frequency ω_D when the concentration of Sn increases can be attributed to the weakening of the force constants for ^{119}Sn in Si /12/ and to the presence of impurity modes around $\omega_E \sim 1.2 \times 10^{13} \text{ s}^{-1}$. Detailed calculations of the vibration spectra in ordered $\text{Si}_{50}\text{Sn}_{50}$ crystalline alloys are currently in progress, to obtain values of the interatomic force constants.

REFERENCES

- /1/ Polk, D. E., J. Non-Cryst. Solids, 5 (1971) 365.
- Polk, D. E. and Boudreaux, D. S., Phys. Rev. Lett., 31 (1973) 92.
- /2/ Connell, G. A., and Tenkin, R. J., Phys. Rev. B 9 (1974) 5323.
- /3/ Dixmier, J., Gheorghiu, A. and Theye, M. L., J. Phys. C 17 (1984) 227.
- /4/ Etherington, G., Wright, A. C., Wenzel, J. T., Dore, J. C., Clarke, J. H. and Sinclair, R. N., J. Non-Cryst. Solids, 48 (1982) 265.
- Sinclair, R. N., Desa, J. A. E., Etherington, G., Johnson, P. A. V. and Wright, A. C., J. Non-Cryst. Solids 42 (1980) 107.
- /5/ Vérié, C., Rochette, J. F. and Rebouillat, J. P., J. Phys. Paris 10 C 4 (1981) 667.
- /6/ Vérié, C., Proc. 17th I. E. E. E., PVSC (to be published).
- /7/ Williamson, D. L. and Deb, S. K., J. Appl. Phys. 54 (1983) 2588.
- /8/ Vergnat, M., Thesis (1983) Nancy (unpublished).
- Vergnat, M., Marchal, G., Piecuch, M., Gerl, M., Solid St. Comm. 50 (1984) 237.
- /9/ Vergnat, M., Piecuch, M., Marchal, G., and Gerl, M., Philos. Mag. 51 (1985) 327.
- /10/ Antončík, E., Phys. Stat. Sol. (b) 79 (1977) 605.
- /11/ Weyer, G., Nylandsted-Larsen, A., Deutch, B. I., Andersen, J. V., and Antončík, E., Hyperfine Interactions, 1 (1975) 93.
- /12/ Nielsen, O. H., Phys. Rev. B 25 (1982) 1225.