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Short Range Order In a-Ge_xSi_{1-x}:H Alloys

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1 Introduction

The possibility of "tailoring" optical and electronic properties makes the study of the semiconducting binary alloys of great interest. In particular the hydrogenated amorphous silicon-germanium alloys (a-Ge_xSi_{1-x}:H) have been recently extensively studied and applied in efficient photovoltaic devices [1]. It is the aim of the present work to perform a structural characterization of these alloys by means of EXAFS spectroscopy.

2 Experimental

The samples were grown in a R.F. capacitively coupled glow discharge apparatus by a mixture of SiH₄ and GeH₄. The gas composition $r = \text{GeH}_4 / (\text{SiH}_4 + \text{GeH}_4)$ was varied in the range 0-0.93. The deposition temperature was 250°C, but a few samples were also deposited at 190°C. The chemical composition x was determined by plasma emission spectroscopy at CISE Laboratories, Segrate (MI). The X ray absorption spectra at the Ge K-edge were taken at room temperature at the Frascati Synchrotron Radiation facility.

3 Results and Discussion

In Fig. 1 we show some EXAFS spectra of the samples studied. It is apparent that the lineshapes of the two extreme cases (spectra (a) and (f) corresponding to x=0.07, and x=1 respectively) are quite different: spectrum (a) having a monotonically decreasing envelope function, spectrum (f) a nearly gaussian envelope function with a maximum at 7 Å. This dissimilar k-dependence results from the different backscattering function of the atoms which form the first coordination shell in the two cases: Ge in spectrum (f) and predominantly Si in spectrum (a). With decreasing Ge concentration the remaining spectra of Fig.1 exhibit a progressive evolution toward a higher backscattering amplitude at low k and a decrease of the maximum at 7 Å. This behavior confirms a smooth variation of the first shell composition from pure Ge to pure Si.

Therefore at intermediate composition the spectra result from a contribution of Ge-Ge and Ge-Si pairs whose bond lengths and relative weight should be determined. To this end we performed a complete k-space analysis by Fourier filtering the experimental data. The EXAFS spectra of the samples with the two extreme compositions x=1 and x=0.07 are the obvious representative of Ge-Ge and Ge-Si pair, respectively. These two samples match all the conditions required to be good models for investigating the alloys with intermediate compositions.

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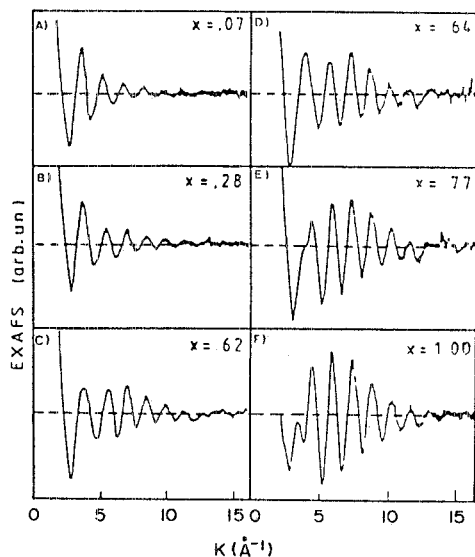


Fig. 1

Figure 1 Experimental $\chi(k)$ at different Ge concentrations.

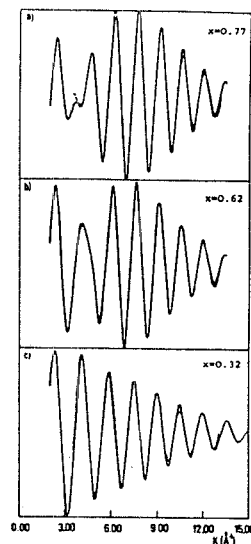


Fig. 2

Figure 2 Comparison of the experimental Fourier filtered $k\chi(k)$ with the result of the fit (dashed line).

A fitting function was built in k -space to be compared to the Fourier filtered $k\chi(k)$ by using the phases and amplitudes derived from these model samples, as reported in Ref.2. The only assumption we made was that the average coordination number around the Ge atoms does not vary as a function of the concentration. This hypothesis is reasonable since in both the two extreme cases considered ($x=1$ and $x=0.07$) the coordination number was equal to four. Therefore we performed a two shells fit by keeping fixed the total coordination number around Ge atoms, but varying the relative concentration of the two components, their σ^2 factors and R values. In Fig.2 we show the excellent quality of the fits obtained, and in Table 1 we report the numerical results. We want to stress here that:

- the bond lengths are equal to 2.45 Å for the Ge-Ge pair and to 2.38 Å for the Ge-Si pair and both remain constant over the whole concentration range;
- the relative concentrations of the Ge-Ge and Ge-Si pairs are in excellent agreement with the results of the chemical analysis (compare columns one and two);
- σ^2 values obtained are so small that the disorder factor can be considered constant over the whole range of concentration and equal to the value of the two models, namely $\sigma^2=0.5 \times 10^{-2} \text{Å}^2$.

Our results on distances are the first direct determination of first-nearest neighbour bond length in Ge-Si:H amorphous alloys. They confirm previous results of a diffraction study of $\text{Ge}_x\text{Sn}_{1-x}$ at $x=0.5$ and $x=0.75$ [3] and suggest that a concentration-independent bond distance is probably a general feature of the disordered alloys.

The excellent agreement found between the relative number of Ge-Ge and Ge-Si pair in the first coordination shell and the overall chemical composition of the alloy demonstrates the presence of a large compositional disorder superimposed to the topological one. This conclusion is in agreement with results obtained by the analysis of Raman data [4].

In order to understand point c) we examine separately the thermal and the structural contribution to the disorder factors. As for the thermal component, only the uncorrelated motion of the atoms contribute to the EXAFS. By representing this motion with an Einstein model one gets:

$$\frac{\Delta\sigma^2_{\text{Ge-Ge}}}{\Delta\sigma^2_{\text{Ge-Si}}} = \frac{\langle u^2 \rangle_{\text{Ge-Ge}}}{\langle u^2 \rangle_{\text{Ge-Si}}} = \frac{(\langle n \rangle + \frac{1}{2})_{\text{Ge-Ge}}}{(\langle n \rangle + \frac{1}{2})_{\text{Ge-Si}}} \cdot \frac{\mu_{\text{Ge-Si}} \omega_{\text{Ge-Si}}}{\mu_{\text{Ge-Ge}} \omega_{\text{Ge-Ge}}} \sim 1$$

where $\langle n \rangle$ is the Bose-Einstein occupation number, $\mu_{\text{Ge-Ge}}$ and $\mu_{\text{Ge-Si}}$ are the reduced masses of the Ge-Ge and Ge-Si pair and $\omega_{\text{Ge-Si}}$ and $\omega_{\text{Ge-Ge}}$ are the frequencies of the phonon modes localized on the Ge-Si and Ge-Ge pairs, equal to 400 and 290 cm^{-1} respectively as shown from Raman measurements [5]. Therefore we conclude that the thermal contribution in all alloys is equal to that of a-Ge:H, i.e. $\sigma^2 = 0.33 \times 10^{-2} \text{ \AA}^2$.

As a consequence of the above result the structural contribution is the same for the Ge-Ge and Ge-Si pair over the whole concentration range studied and equal to $0.16 \times 10^{-2} \text{ \AA}^2$. This means that the rms fluctuations of the bond distances are the same for the two pairs and equal to $4 \times 10^{-2} \text{ \AA}$. The explanation of its constancy with concentration is to be found in the likeness of the interaction elastic potentials in these materials, a consequence of their very close electronic structure. This closeness is reflected in the nearly equal values of the Keating potentials in pure Ge and Si.

Table 1 Numerical values of the parameters obtained from the fitting procedure.

% Ge	%Ge by EXAFS	$R_{\text{Ge-Ge}} (\text{\AA})$	$\Delta\sigma^2_{\text{Ge-Ge}} (10^{-3} \text{ \AA}^2)$	$R_{\text{Ge-Si}} (\text{\AA})$	$\Delta\sigma^2_{\text{Ge-Si}} (10^{-3} \text{ \AA}^2)$
28	26	2.45	-0.21	2.37	-0.03
32	30	2.45	0.42	2.37	-0.20
62	62	2.45	-0.05	2.37	0.17
64	65	2.45	-0.73	2.38	0.74
77	89	2.45	-0.11	2.38	2.7
89	100	2.45	-0.09	--	--

- 1 Y.Yukimoto: Jarect Vol.6 "Amorphous Semiconductor Technology and Devices", Ed. Y.Hamakawa, North Holland Publ. Co. 1983.
- 2 L.Incoccia, S.Mobilio, M.G.Proietti, P.Fiorini, C.Giovannella and F.Evangelisti: to be published.
- 3 R.J.Temkin, G.A.N.Connel and W.Paul: Solid State Commun. 11, 1591 (1978).
- 4 B.K.Agrawal: Solid State Commun. 37, 271 (1981).
- 5 S.Minomura, K.Tsugi, M.Wakagi, T.Ishidate, K.Inoue and M.Shibuya: J. Non-Cryst. Solids 59-60, 541 (1983).