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LNF-87/109

S. Mobilio and A. Filipponi:
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Estratto da:
Journal of Non-Crystalline Solids 97 & 98, 365 (1987)

Servizio Documentazione
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EXAFS IN AMORPHOUS SILICON ALLOYS

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I. INTRODUCTION

The oscillations observed in the absorption coefficient above the X-ray edge of each atomic species present in a given material are today interpreted in terms of local average structural properties and referenced as Extended X-ray Absorption Fine Structure (EXAFS)^{1,2}. At energies well above the edge (>15-20 eV) the absorption cross section can be interpreted by a single scattering theory. The photoelectron, excited by the X-ray, emerging from the absorbing atom is treated as a free wave partially backscattered by the potential of the surrounding atoms. In this single scattering energy range, the interference between outgoing wave and the backscattered component $\chi(k)$ is described by the formula:

$$(\mu - \mu_0)/\mu_0 = \chi(k) = \sum_j 4\pi \int \rho |f_j(k, \pi)| e^{-2r/\lambda} g_{ij}(r) \sin(2kr + \phi_{ij}(k)) dr ; \quad (1)$$

the sum running over all the atomic species in the sample. ρ is the atomic density and $g_{ij}(r)$ is the pair correlation function between atomic species i and j . k is the photoelectron wavevector given by $(\hbar^2/2m(E-E_0))^{1/2}$ where E is the photon energy and E_0 is the edge energy, λ is the mean free path of the photoelectrons in the material. $|f_j(k, \pi)|$ and $\phi_{ij}(k)$ describe the scattering process undergone by the photoelectron, the former depending only on the scattering atomic species j , the latter on both the absorbing and the scattering ones.

It is quite evident from eq. (1) that EXAFS spectra carry a lot of local structural information and is well suited for describing the surrounding of the absorbing atom. The presence of the damping term due to the photoelectron mean free path and the weight $1/r^2$ generally limit the detectable contributions to the first 3-4 coordination shells.

The scattering functions $|f_j(k, \pi)|$ and $\phi_{ij}(k)$ in eq. (1) greatly complicate the data analysis since they must be accurately known, in order to determine the $g_{ij}(r)$ correlation function from the spectra. Theoretical tabulation is available³, but up to now the best approach is the experimental one. In fact, it has been proved that these functions can be determined from measurements of a known structure where the same pair i - j of atoms is present and then used in analysing the data of the unknown structure^{4,5}. Accuracies as high as .02 Å in distances and ≈10% in coordination numbers are routinely achieved in this way. A crucial point in such phase

and amplitude transferability is the chemical similarity between model and unknown: as will be shown later, one order of magnitude higher accuracy can be obtained in determining the variation of the structural parameters brought about by changes induced on a given chemical system since in such a case model and unknown are chemically identical.

In multicomponent systems a peculiarity of EXAFS is its capability to provide independent pictures of the environment of each atomic species: in binary systems (AB), for example, while X-ray scattering measures a weighted sum of the three correlation functions A-A, A-B and B-B, EXAFS measures only the correlation functions involving the excited atomic species. Moreover the k dependence of the scattering functions varies strongly with the Z of the scattering atom. This gives the opportunity to distinguish the contribution of different backscattering atomic species

and therefore to unambiguously sort out the individual $g_{ij}(r)$ contributing to eq.(1). As an

example, in fig. 1 we show the EXAFS spectra⁶ of the $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ grown by glow discharge, taken at the K edge of Ge. These spectra reflect the evolution of the mean coordination around the Ge atoms. Note that with increasing Ge concentration the spectra exhibit a smooth evolution from the situation in which the amplitude of the oscillations decreases monotonically, typical of Si as backscatterer, towards a situation in which the amplitude has a maximum at $\approx 7 \text{ \AA}^{-1}$, as expected when Ge is the backscatterer. Such strong difference in the backscattering amplitude allows one to separate unambiguously the Ge-Ge correlations from the Ge-Si ones at any Ge concentration. A point to stress is that eq. 1 does not hold for k values lower than $\approx 2.5 \text{ \AA}^{-1}$, since for low energy photoelectrons the assumption of single scattering is too crude an approximation. In this region, generally referred as XANES (X-ray Absorption Near Edge Structure), multiple scattering terms (i.e. terms in which the

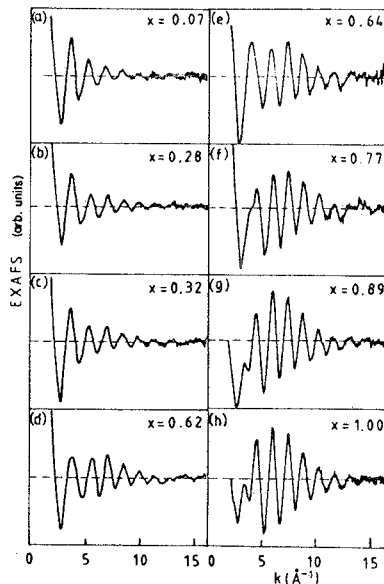


FIGURE 1
Experimental $\chi(k)$ of amorphous silicon germanium alloys at different Ge concentrations.

photoelectron is scattered two or more times by the neighboring atoms) contribute significantly to the cross section. XANES is potentially a source of unvaluable structural information since it is sensitive to three body and even higher order correlation functions. A considerable progress has been done in interpreting such region in ordered systems as well as in single shell systems, but up to now no successful quantitative application to amorphous materials has been reported.

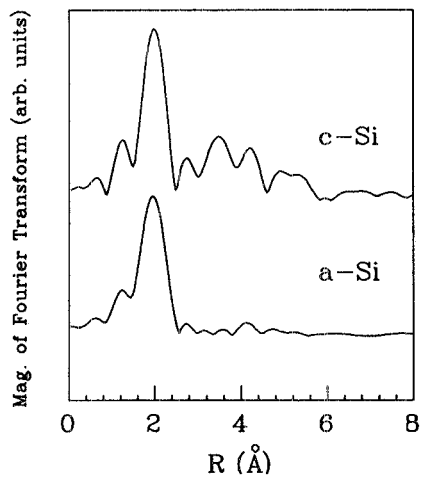


FIGURE 2
Fourier transform of crystalline
and amorphous silicon.

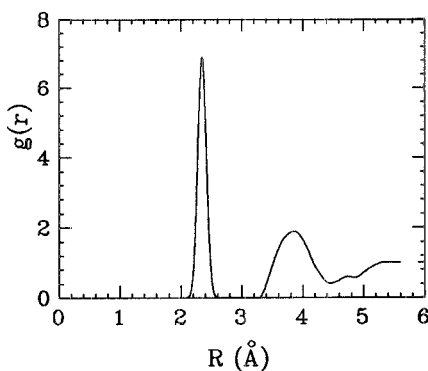


FIGURE 3
 $g(r)$ of amorphous silicon deduced
from EXAFS data.

EXAFS data analysis is typically performed by isolating each shell contribution to the $\chi(k)$ by means of Fourier filtering techniques and then interpreting such contributions by means of least square fittings using model spectra. The lack of low k values implies that in the Fourier Transform (FT) any broad structure in $g_{ij}(r)$ is lost⁷. In ordered material the structures in $g_{ij}(r)$ have a typical Debye-Waller broadening of $\approx 10^{-1} - 10^{-2}$ Å, which corresponds to a lowering of the corresponding FT peaks of about 10%: that means that no information is lost in the region $0 - k_{\min}$ ⁸. On the contrary in disordered systems broad peaks are generally present in the $g_{ij}(r)$ beyond the first coordination shell. It is well known, for example, that in a-Si the second shell peak has a rms broadening of $\approx .27$ Å, mainly due to the fluctuations of the tetrahedral angle. A reduction of about 80% occurs in the corresponding FT peak⁸ (fig. 2) therefore this peak is not revealed by EXAFS, while it is well present in the X-ray deduced $g_{ij}(r)$. This feature has been interpreted as a weakness of EXAFS when applied to amorphous systems. However it can be often overcome by performing very accurate data analysis directly in k -space. In fact in a-Si the second shell contribution to the spectrum amounts to $\approx 5\%$ at k_{\min} so that it can be detected. To this end a promising regularized least square method has been proposed by Babanov et al.⁹ to solve the integral equation (1) and get $g_{ij}(r)$. We have applied such method in a-Si, using experimental amplitude and phase functions of c-Si. A satisfactory agreement between the calculated and experimental a-Si:H spectrum was obtained. The obtained $g_{Si-Si}(r)$

is shown in fig. 3¹⁰. Note that in such a way the correct second shell peak is obtained, with a maximum at 3.83Å and a broadening of .28Å, in excellent agreement with X-ray scattering results. A different approach is to subtract from experimental spectra the dominant

contribution of the first coordination shell and then to interpret the residual one in terms of more distant atoms and multiple scattering effects. Using such an approach we have shown how multiple scattering contributions in a-Si:H are negligible, since they are smeared out by the disorder¹¹.

2. ELEMENTAL AMORPHOUS TETRAHEDRAL SEMICONDUCTORS

The FT of the EXAFS (fig. 4)¹² of a-Ge shows the presence of a single peak, due to four Ge atoms at a distance of 2.45 Å, confirming that the local structure of the amorphous network is similar to that of crystal. The accuracy achieved in such determination is very high indeed: some authors¹³ claim $\approx 1\%$ accuracy in the coordination number and $\approx .003$ Å in the distance, thanks to very good spectra extending up to $k \approx 18 \text{ \AA}^{-1}$ and to a perfect phase and amplitude transferability between c-Ge and a-Ge. The absence of any second shell contribution at about 4.0 Å points to a spread in the tetrahedral angle of at least 7° rms in this material.

Interesting information was also obtained by following the ordering of a-Ge as a function of the substrate deposition temperature in a series of studies pioneered by Evangelisti et al.¹¹ and subsequently performed by many authors¹²⁻¹⁴. Looking at the behavior of the FTs it was concluded that crystallization happens through the formation of crystalline islands dispersed in a disordered connective tissue. Stern et al.¹⁴ unambiguously demonstrated the existence of such a heterogeneous phase: they showed that for substrate temperature ranging from 175°C to 250°C the shape of the second coordinating shell can be accounted for only assuming a mixture of contributions, one typical of crystalline clusters and the other typical of an amorphous state with a $\sigma^2 \approx 8 \cdot 10^{-2} \text{ \AA}^2$ corresponding to a tetrahedral angle spread of about 10° .

The effect of hydrogen has been investigated in a-Si:H¹⁵. Here too pure amorphous sample exhibits in the first coordination shell 4 Si atom at a distance of 2.35 Å as c-Si does. The incorporation of H in glow discharge films does not change such a distance; but a lowering of Si coordination is found in quantitative agreement with the number of Si-H bonds in the sample. The Debye Waller factor shows an interesting behaviour. At small H concentrations

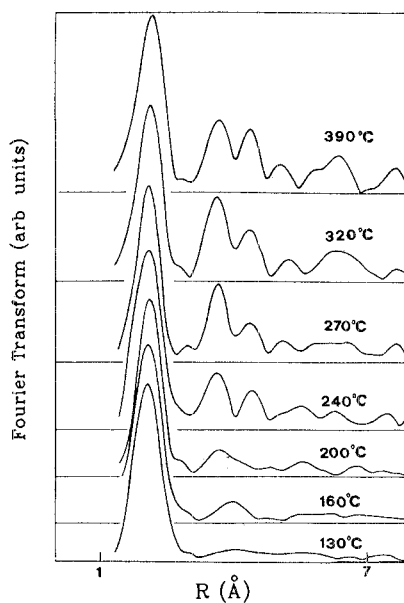


FIGURE 4
Fourier transform of the EXAFS
of Ge K edge for different
substrate deposition temperature.

a decrease of the disorder factor is found. In this range of concentrations H relieves the strain of the amorphous network. At higher H concentration (>20%) the disorder factor increases again. Sayers and Paesler¹⁶ have suggested that this behaviour may be related to the formation of a material with a significant fraction of silane-like chains $(\text{SiH}_2)_n$.

3. AMORPHOUS SILICON ALLOYS

We discuss now the results of an EXAFS investigation we have performed on the amorphous glow discharge hydrogenated alloys $a\text{-Si}_{1-x}\text{A}_x\text{:H}$, (A=Ge, C or N) to determine not only the structural parameters, like bond lengths and coordination numbers, but also their compositional character^{17,18}. The corresponding crystalline compounds show different behaviours: $\text{Si}_{1-x}\text{Ge}_x$

is compositionally disordered with each Si atom surrounded by both Si and Ge atoms in a completely random way; c-SiC and c-Si₃N₄ on the other hand are completely ordered with Si atoms bonded only to N (or C) atoms and vice-versa. Moreover the first can be grown at any value of x, while the last two only exist at the stoichiometric compositions. As for the amorphous counterparts they can be grown for any value of x ranging from 0 up to 1 in the case of $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ and $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ and up to ≈ 0.6 for $a\text{-Si}_{1-x}\text{N}_x\text{:H}$, corresponding to a N concentration slightly richer than the stoichiometry. The existence of alloys at concentrations different from the stoichiometric values implies the presence of Si-Si and A-A bonds (A=C or N) as well as Si-A in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ and $a\text{-Si}_{1-x}\text{N}_x\text{:H}$ similarly to the $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ case. The upper limit $x \approx 0.6$ for the $a\text{-Si}_{1-x}\text{N}_x\text{:H}$ shows the impossibility of growing an alloy with a relevant fraction of N-N bonds. The existence of such N-N bonds, the distribution of Si-Si, Si-A and A-A bonds in the three alloys as well as the existence of different phases in the samples like, for example, islands of a-Si and a-Ge in $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ are questions that deserve attention.

Several investigations have been performed by means of Raman, IR, XPS and XRD on such compounds but no direct structural investigation was reported before our study. The $a\text{-Si}_{1-x}\text{A}_x\text{:H}$

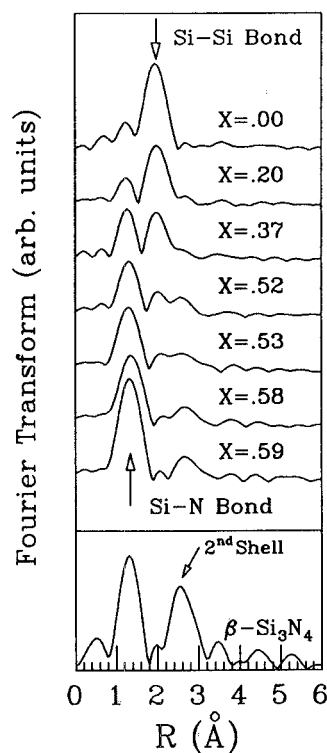


FIGURE 5
Fourier transform of crystalline and amorphous silicon nitrogen alloys at different N concentrations.

alloys are well suited for EXAFS investigations: the chemical similarity of a given kind of alloy in all the concentration range ensures high accuracy in the study of its evolution with the composition. Both Si and Ge K edges were investigated. An example of the evolution of the spectra with alloy composition was shown in fig. 1. Fig. 5 shows the FT for $a\text{-Si}_{1-x}\text{N}_x\text{:H}^{17}$. The first two peaks correspond to Si-N and Si-Si bonds in the first coordination shell: their relative weight changes gradually with the composition. At high N concentration a further peak at higher R appears, due to second shell contribution. A similar behaviour is displayed by the spectra of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$, while in $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ the two peaks due to the first shell are not resolved and no second shell peak is evident at any concentration. A quantitative analysis of the two contributions in the first coordination shell was performed by inverse transforming the two peaks back in k space and then fitting such inverse FT to eq. 1. It was assumed that both contributions Si-Si and Si-A (or Ge-Ge or Ge-Si in the Ge K edge spectra) were described by Gaussians $g_{ij}(r)$. The fitting parameters were the two distances $R_{\text{Si-Si}}$ and $R_{\text{Si-A}}$ (or $R_{\text{Ge-Ge}}$ and $R_{\text{Ge-Si}}$), the relative coordination C and the two σ^2 values. Experimental phase and amplitude functions were deduced from spectra on a-Si, c-Si, a-Ge, c-SiC and $\beta\text{-Si}_3\text{N}_4$. The

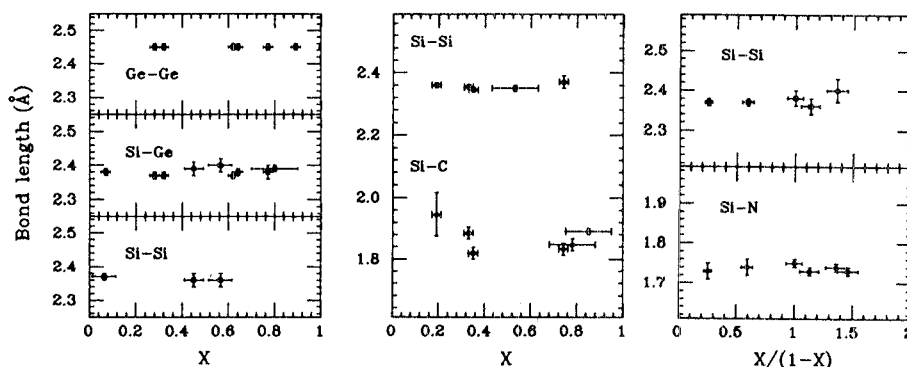


FIGURE 6
First shell bond distances at different alloy compositions for amorphous silicon germanium, silicon nitrogen and silicon carbon alloys.

average distances obtained are shown in fig.6 as a function of the atomic concentration. In $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ all the average atomic distances are practically independent of the concentration. $R_{\text{Si-Si}}$ and $R_{\text{Ge-Ge}}$ are equal to 2.35Å and 2.45Å and coincide within the experimental accuracy with the distances in elemental Si (2.35Å) and Ge (2.45Å) either crystalline or amorphous, while $R_{\text{Ge-Si}}$ is very close to the sum of the covalent radii of the two atoms (2.39Å-2.40Å). The behaviour of the $R_{\text{Ge-Si}}$ in $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ is different from the predicted behaviour in $c\text{-Si}_{1-x}\text{Ge}_x$ where an overall variation of $\approx .04\text{Å}$ has been calculated¹⁹ between the two extrema of Si impurities in Ge and Ge impurities in Si: the lack of long range order in the amorphous phase allows the $R_{\text{Ge-Si}}$ distance to relax toward its "molecular" value.

In $a\text{-Si}_{1-x}\text{N}_x\text{:H}$ the $R_{\text{Si-N}}$ average distance remains constant and equal to that in Si_3N_4 , while $R_{\text{Si-Si}}$ is by 0.02 \AA larger than the elemental value and exhibits a tendency to increase at high x value. In $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ $R_{\text{Si-Si}}$ is again independent of x and equal to 2.35 \AA , while $R_{\text{Si-C}}$ undergoes a more complicate behaviour, with a minimum at $x \approx 0.5$ and an overall variation of more than 0.1 \AA .

From the behaviours of the relative coordination vs. the atomic concentration (fig.7)^{17,18} we can get a direct insight into the compositional disorder present in the alloys. To this end different models of average coordination have been calculated; only two extreme cases are reported in fig. 7. In one case the films are considered chemically ordered: for concentration from zero to the stoichiometric value ($x=0.5$ for $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ and $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ and $x=0.57$ for $a\text{-Si}_{1-x}\text{N}_x\text{:H}$) the minority atom Ge,C or N would be bonded only to Si, while the Si environment is not constrained. For alloys with larger values of x , the role of the two atoms must be reversed: the Si atoms are surrounded only by the other atoms A so its relative coordination is constant and equal to 1; in this region A-A bonds are present. In the other model the neighbors of each atom are not constrained: a random coordination is supposed with a coordination probability

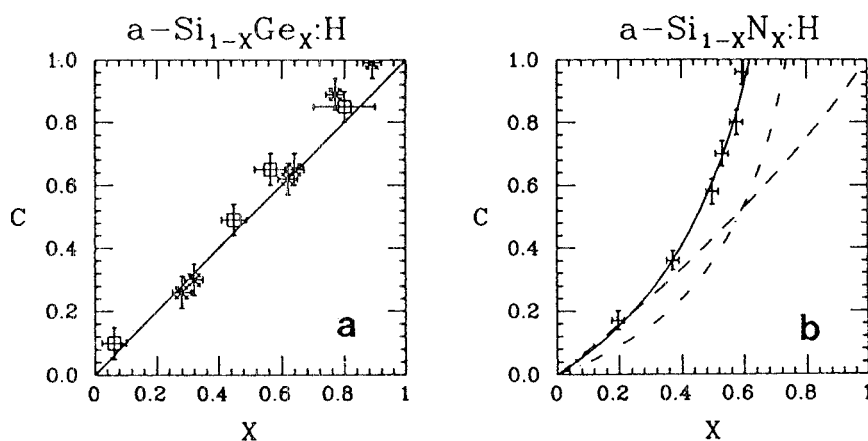


FIGURE 7

Average first shell coordination as a function of alloy concentration. a) Silicon germanium case: dotted line ordered model; solid line random model; b) Silicon nitrogen alloy: dotted line ordered model with H; dashed line random model; dot-dashed line ordered model with wrong bonds.

for each species proportional to the concentration times its valence. The experimental points show that $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ is a random alloy with random network structure, where $a\text{-Si}_{1-x}\text{N}_x\text{:H}$ on the other hand is chemically ordered. In this last case in fact the data closely follow the dotted curve of fig. 7b calculated assuming a mean valency of 2.4 for N and 3.8 for Si. These values have been derived from IR spectra, which showed that a mean number of 0.6 H atoms are bonded to N and 0.2

atoms to Si. In our model no N-N wrong bond is allowed; we can estimate an upper limit of 5% for the number of N-N bonds for each N atom since with a concentration of 15% the data would follow the dot-dashed curve of fig. 7b which is well outside the experimental indetermination. Our data on first shell coordination cannot distinguish between a random mixing of small islands of a-Si:H and a-Si₃N₄:H from more homogeneous situations in which Si is uniformly distributed in the alloys with a random bonding environment. This will be possible from the analysis of the second coordination shell, which is in progress. Anyhow some hints come out from the small increase in Si-Si distance in the first shell: this can be understood in terms of ionic repulsion between positive charged Si atoms, as it would be the case of silicon being uniformly diluted in a-Si₃N₄:H where it would be bonded to the more electronegative N. On the other hand, the distance increase is hardly understood if Si-Si first shell correlations comes out from a-Si:H islands.

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