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**AMORPHOUS HYDROGENATED ALLOYS: A COMPARATIVE EXAFS
STUDY OF $a\text{-Si}_{1-x}\text{C}_x\text{:H}$, $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$, $a\text{-SiN}_x\text{:H}$ AT THE SILICON K-
EDGE**

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AMORPHOUS HYDROGENATED ALLOYS : A COMPARATIVE EXAFS STUDY OF

 $a\text{-Si}_{1-x}\text{C}_x\text{:H}$, $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$, $a\text{-SiN}_x\text{:H}$ AT THE SILICON K-EDGE⁽¹⁾A. FILIPPONI, P. FIORINI, F. EVANGELISTI, A. BALERNA* and
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ABSTRACT

$a\text{-Si}_{1-x}\text{C}_x\text{:H}$, $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$, $a\text{-SiN}_x\text{:H}$ alloys have been studied at the Si K-edge. Si-Si and Si-A (A being C, N, Ge) bond lengths have been determined as a function of composition. The Si-C distance was found to vary significantly, while the Si-Ge and Si-N distances remain almost constant. A high frequency signal has been detected in the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ and $a\text{-SiN}_x\text{:H}$ films at large x due to a second shell contribution. The compositions of the first coordination shell are also reported and discussed in terms of different local coordination models.

INTRODUCTION

The study of semiconducting binary alloys is of great interest from the fundamental as well as applied point of view. This is even more true for the hydrogenated amorphous alloys based on a-Si due to the flexibility of the deposition processes, e.g. glow discharge, and an apparent continuous miscibility of the elements. This seems to be the case also for silicon-carbon and silicon-nitrogen that in the crystalline phase form a definite compound and are not miscible. Up to now no direct structural measurements have been reported on $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ and $a\text{-SiN}_x\text{:H}$ while $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ has been already studied at the Ge K-edge [1,2].

In this paper we report the first EXAFS study performed at the Si K-edge on three silicon based alloys: $a\text{-Si}_{1-x}\text{C}_x\text{:H}$, $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$, $a\text{-SiN}_x\text{:H}$.

EXPERIMENTAL AND DATA ANALYSIS

Three series of samples of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$, $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$, $a\text{-SiN}_x\text{:H}$ were deposited by glow-discharge from binary gas mixtures of SiH_4 , GeH_4 , NH_3 , CH_4 on beryllium, quartz and silicon substrates.

⁽¹⁾ Work partially supported by PFE II-ENEA

Thickness, optical gap and refractive index were determined by optical spectroscopy. The hydrogen content was determined by IR spectroscopy integrating the intensity of Si-H and Ge-H wagging mode and C-H and N-H stretching mode. The atomic concentration of a-SiN_x:H and a-Si_{1-x}Ge_x:H was determined from calibration curves obtained from ESCA and Auger measurements on previous series of samples deposited in similar conditions. The atomic concentration of a-Si_{1-x}C_x:H was instead estimated from the optical gap and therefore is less reliable.

The Si K-edge absorption spectra were measured at LURE (Orsay) using the ACO X-ray beam, monochromatized by a InSb(111) double crystal at step of 1.eV.

The EXAFS signal was extracted subtracting an atomic-like polynomial background from the spectra and normalized by $[J*(1-8*(E-E_0)/3E_0)]^{-1}$ [3]. The origin E_0 of the k scale was placed at the inflection point of the absorption coefficient. The jump J was determined as the mean value of the absorption coefficient above and below the white line, both extrapolated at E_0 . The EXAFS multiplied by k^2 were Fourier transformed in the range 2-9 Å⁻¹ with a 0.5 Å⁻¹ wide Hanning window.

The results are shown in Fig. 1, 2 and 3. We have attributed the first two peaks in the Fourier transforms of the a-SiN_x:H and a-Si_{1-x}C_x:H alloys to the Si-A and Si-Si distances in the first coordination shell. The relative weight of the two peaks changes gradually with the composition. A further peak at higher R is also visible at high A concentration which has been attributed to a second shell contribution. In a-Si_{1-x}Ge_x:H the two peaks due to the first shell are not separated because of the small difference in the bond distance.

The two peaks of the first shell were back-transformed into k -space. Each spectrum has been fitted with a model EXAFS as follows. Experimental amplitudes and phases for the Si-Si and Si-A pairs were obtained from the EXAFS of pure a-Si:H and of the sample with the highest A content, respectively. The Si-Si and Si-C models were also compared with crystalline Si and SiC in order to have an absolute reference for distance, coordination number and mean square relative displacement σ^2 . The Si-N distance in the model was assumed to be 1.73 Å, i.e. equal to that in β -Si₃N₄. With these functions the model spectra were built, by assuming a constant coordination around the silicon atom at any composition. Fitting parameters were the two distances, the two $\Delta\sigma^2$ values and the relative coordination $C_r = N_A / (N_A + N_{Si})$ of atom A around the Si atom. The results are reported in Tab. 1,2,3, where x is the atomic concentration and R are the average bond lengths. Only the $\Delta\sigma^2$ which could be determined with a significant accuracy are reported.

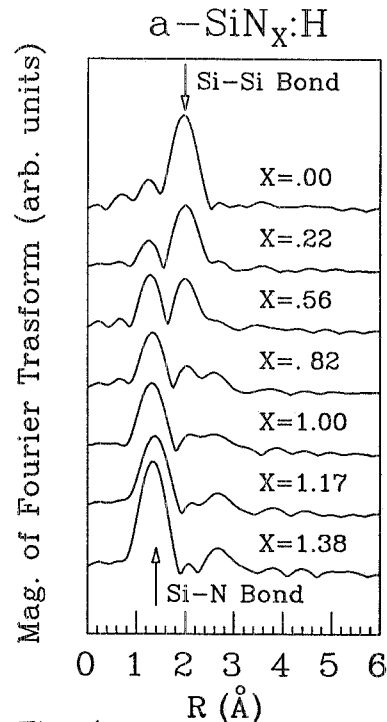
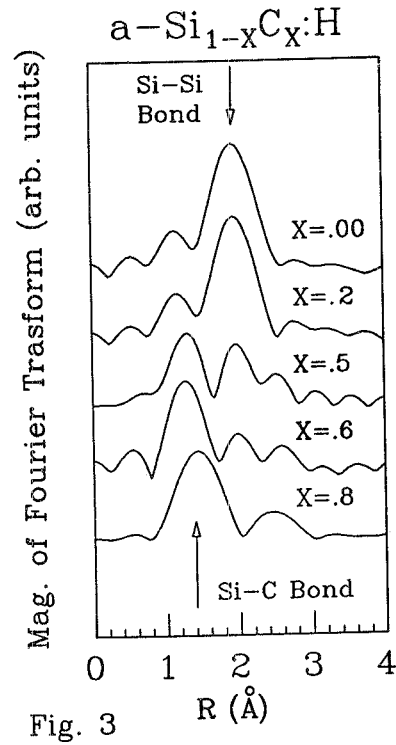
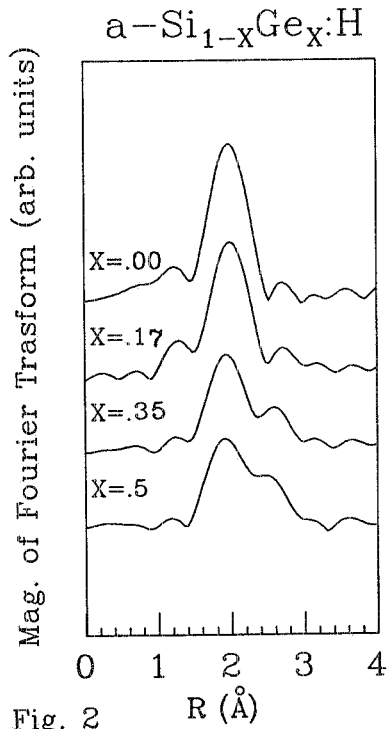


Fig. 1

TABLE 1 $a\text{-SiN}_x\text{:H}$

X	C _T	R(Si-N)(Å)	R(Si-Si)(Å)	$\Delta\sigma^2(\times 10^{-3}\text{Å}^2)$
.22(3)	.17(3)	1.73(2)	2.37(1)	2.(1)
.56(5)	.36(3)	1.74(2)	2.37(1)	1.(2)
.82(7)	.54(4)	1.75(1)	2.38(2)	
1.00(8)	.65(4)	1.73(1)	2.36(2)	
1.17(9)	.74(4)	1.74(1)	2.40(3)	
1.38(9)	.92(4)	1.73		

TABLE 2 $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$

X	C _T	R(Si-Si)(Å)	$\Delta\sigma^2(\times 10^{-3}\text{Å}^2)$	R(Si-Ge)(Å)	$\Delta\sigma^2(\times 10^{-3}\text{Å}^2)$
.17(6)	.10(5)	2.37(1)	3.(1)		
.35(8)	.49(5)	2.36(2)		2.40(2)	2.(1)
.5(1)	.65(5)	2.36(3)		2.41(2)	2.(1)
.8(1)	.85(5)			2.40(1)	2.(1)

TABLE 3 $a\text{-Si}_{1-x}\text{C}_x\text{:H}$

X	C _T	R(Si-C)(Å)	R(Si-Si)(Å)
.2(1)	.06(5)	1.84(4)	2.36(1)
.3(1)	.22(5)		2.36(1)
.5(1)	.60(7)	1.79(3)	2.37(2)
.6(1)	.73(8)	1.84(2)	2.39(2)
.7(1)	.9(1)	1.86(3)	
.8(1)	1.0(5)	1.89(1)	

RESULTS and DISCUSSION

No significant variation of the bond lengths was detected in $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$, in agreement with previous results obtained at the Ge K-edge [1]. In $a\text{-SiN}_x\text{:H}$ the Si-N bond distance remains constant. In $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ a gradual change of 0.1 Å in the Si-C distance occurs at high C concentrations. Finally a slight increase of 0.02 Å of the Si-Si distance is observed both in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ and in $a\text{-SiN}_x\text{:H}$.

By comparing the average composition of the first-neighbour shell as seen by EXAFS with the atomic concentration in the sample it is possible to derive information on the compositional disorder of the material [1]. Two extreme cases are considered and reported in Fig. 4 and 5 for the $a\text{-SiN}_x\text{:H}$ and $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ films whose atomic concentration was known.

In one case the films are considered chemically ordered, i.e. the tendency to form a compound is supposed dominant over disordering effects. For x varying from zero to the stoichiometric value ($X=0.5$ for $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ and $X=4/3$ for $a\text{-SiN}_x\text{:H}$), the atom A would be surrounded by Si atoms only, while the environment of Si is not constrained. In order to have larger values of x the role of the two atoms must be reversed. The estimated coordination of atom A around the Si atom as a function of the atomic concentration is reported in Fig. 4 and 5 for the two materials (dotted line). The dashed line in

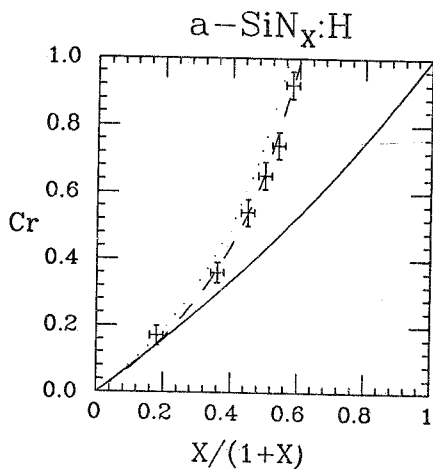


Fig. 4

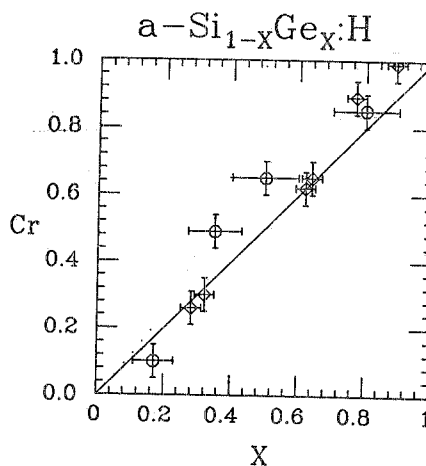


Fig. 5 Diamonds are experimental points from ref. 1 measured at the Ge K-edge.

Fig. 4 shows the change brought about by taking also account of the presence of hydrogen.

While still keeping constant the coordination of the different atoms (4 for Si and Ge and 3 for N) the opposite hypothesis considers negligible any other chemical constraint, so that the distribution is completely random. As a consequence the probability for any atom to form a bond with a given species is proportional to the atomic concentration of that species times its valence. The relative coordination of Si for this random bonding model is reported as a full line in Fig. 4 and 5.

The experimental points show that the above two extreme hypothesis closely reproduce the situation of a-SiN_x:H and a-Si_{1-x}Ge_x:H, respectively. The random composition of the silicon-germanium films agrees with the complete miscibility of the two elements already established in the crystalline alloys. On the other hand the tendency to local chemical order that the silicon-nitride films seems to display is not surprising keeping in mind that in the crystalline phase they are hardly miscible but form stoichiometric Si₃N₄ compounds. Finally it is worth mentioning that this tendency toward the chemical order is also found by analysing the IR absorption spectra of a-SiN_x and a-SiN_x:H [4].

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