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Abstract

The local structure of hydrogenated amorphous Si–C alloy films, a-Si$_{1-x}$C$_x$:H, has been studied by measuring the extended X-ray absorption fine structure at the Si K edge. The first-coordination-shell average bond lengths are found to be 2.35 Å for Si—Si and 1.86 Å for Si—C and are constant with concentration to within ± 0.015 Å. By comparing the composition of the first coordination shell around silicon with the average concentration, it is shown that the alloy tends to be chemically ordered, in that heteroatomic bonds are preferred.

1. Introduction

Recently there has been a considerable increase in interest in hydrogenated amorphous Si–C alloys (a-Si$_{1-x}$C$_x$:H) because of the properties which make them technologically interesting [1]. As in other amorphous semiconductor alloys, it is possible to tailor the optical gap by changing the carbon concentration. Moreover, they show attractive diamond-like properties such as high transparency, hardness and resistivity. They are extensively used as the p window layer in p–i–n heterojunction solar cells [2].

Besides technological applications, this material is interesting also from a fundamental point of view, in regard to understanding the effect of local silicon, carbon and hydrogen bonding configurations on the film properties. Moreover, the ability of carbon to have twofold, threefold and fourfold coordination adds a degree of freedom in local structural arrangement which is absent in other amorphous semiconductor alloys. In this context, of special interest is the problem of chemical ordering, i.e. the relative arrangement of silicon and carbon atoms on the sites of the amorphous network.

Much information on the local structure in a-Si$_{1-x}$C$_x$:H derives from the study of optical properties [3–6]. Results are consistent with a complex picture in which the macroscopically homogeneous films are microscopically heterogeneous and composed of different phases: an amorphous polymeric tissue (only carbon and hydrogen atoms), amorphous graphitic clusters (only carbon atoms [7]), an amorphous alloy component of silicon, carbon and hydrogen atoms, and voids. An important issue for a-Si$_{1-x}$C$_x$:H is the nature of the bonding of the silicon and carbon atoms in the amorphous alloy component.

There are very few direct structural studies of these films. An extended X-ray absorption fine structure (EXAFS) study at the Si K edge [8, 9], performed on alloys prepared by glow discharge decomposition, yielded average first-coordination-shell bond lengths. It was found that the average Si—Si bond length was equal to the crystalline value of 2.35 Å, while the Si—C bond length was slightly lower than the c-SiC value of 1.88 Å, with an average of 1.86 Å. An electron diffraction study [10] showed that under certain deposition conditions and for a nearly equiatomic composition a completely chemically ordered structure was obtained; films prepared under other conditions with similar as well as different compositions were described as partially chemically ordered. Finally, an electron energy loss fine structure study [11] on stoichiometric films pre-

pared by r.f. reactive sputtering in an argon atmosphere indicated that in a-SiC, hydrogenated or not, each silicon atom is surrounded by nearly four carbon atoms and vice versa.

In this work we report first-shell structural information (bond lengths and coordination numbers) on a series of glow discharge a-Si$_{1-x}$C$_x$:H samples. On one of the samples second-shell results are also reported.

2. Experiment and results

The a-Si$_{1-x}$C$_x$:H samples were prepared by r.f. glow discharge decomposition of SiH$_4$ and CH$_4$ and were deposited at a substrate temperature of 200 °C. The gases were mixed to the desired ratio in a separate gas-handling system and delivered at a constant flow rate of 20 standard cm^3 min^{-1} (sccm); the pressure during deposition was kept constant at 0.2 Torr. Four different alloy compositions were investigated as well as pure a-Si:H. Samples were transferred in ultrahigh vacuum (10^{-9} Torr) to an analysis chamber (10^{-11} Torr), where Auger measurements were performed to obtain average concentration values. The compositions of the five samples are listed in Table 1.

X-ray absorption measurements at the Si K edge were performed at the PULS synchrotron radiation facility of the Laboratori Nazionali di Frascati. The Si K edge absorption spectra were analysed according to standard procedures [12]. Raw EXAFS oscillations obtained are reported in the left panel of Fig. 1.

To yield a qualitative picture of local coordination around silicon, the Fourier transforms (FTs) of the EXAFS spectra are shown in the right panel of Fig. 1. The FT of sample 1 (a-Si:H) shows a single peak at a distance $R = 1.99$ Å, which is equal to the value obtained by analysing

a crystalline sample of silicon using the same procedure. This peak corresponds to the Si—Si bond distance of 2.35 Å (once the phase shift is taken into account) and is consistent with previous measurements [9]. The FT of sample 5 ($x = 0.86$) also shows a single peak, at $R = 1.45$ Å. By comparing this FT with the spectrum obtained on tetramethylsilane gas, Si(CH$_3$)$_4$, we have determined that this peak is due to an Si—C bond with interatomic distance 1.87 Å [13], which compares well with the c-SiC value of 1.88 Å. A careful analysis was performed to test for the presence of Si—Si bonds in this sample, but there was no evidence for this.

The FTs relative to the alloys with intermediate composition can be viewed in the range $0.0 \leqslant R \leqslant 2.4$ Å as a combination of the two configurations corresponding to the Si—Si and Si—C bonds. Starting from sample 1, we notice how the Si—Si peak gradually disappears as the Si—C peak rises. Signals relative to higher coordination shells ($R > 2.4$ Å) are present in the FTs of samples 3 and 4.

Quantitative data analysis has been performed in k space, comparing the Fourier-filtered data,
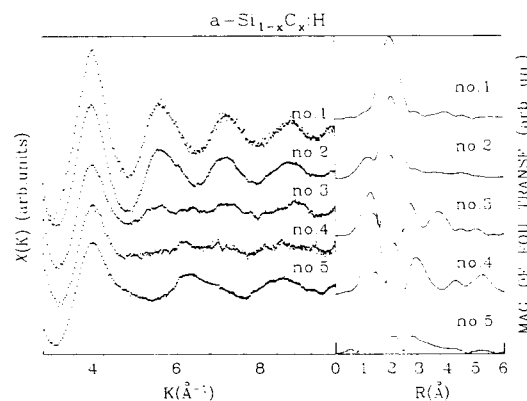

Fig. 1. The left panel shows the raw EXAFS data. Magnitudes of the Fourier transforms are shown on the right.

TABLE 1

Columns 2 and 3 contain the values of x and x' as explained in the text. Columns 4–12 contain the values of the structural parameters obtained from the best fits of the filtered EXAFS signal. N_{Si-C}, N_{Si-Si} and $N_{Si-C-Si}$ are the coordination numbers relative to the model compounds. $\Delta\sigma_{Si-C}^2$, $\Delta\sigma_{Si-Si}^2$ and $\Delta\sigma_{Si-C-Si}^2$ are the disorder factors relative to the model compounds

Sample no.	x	x'	N_{Si-C}	R_{Si-C} (Å)	$\Delta\sigma_{Si-C}^2$ (10^{-3}Å^2)	N_{Si-Si}	R_{Si-Si} (Å)	$\Delta\sigma_{Si-Si}^2$ (10^{-3}Å^2)	$N_{Si-C-Si}$	$R_{Si-C-Si}$ (Å)	$\Delta\sigma_{Si-C-Si}^2$ (10^{-3}Å^2)
1	0.00	0.00	0.00			1.00	2.35	0.0			
2	0.26	0.26	0.17	1.85	−3.1	0.79	2.35	−0.6			
3	0.44	0.38	0.41	1.84	2.2	0.28	2.34	−1.0	0.15	3.11	4.6
4	0.57	0.40	0.63	1.87	3.1	0.23	2.36	6.3			
5	0.86	0.65	1.00	1.87	0.0	0.00					

obtained by inverse Fourier transforming the FTs in the R range 1.0–2.4 Å (1.0–3.3 Å when including second-shell contributions), with model EXAFS spectra. The model signals for the Si—Si and Si—C pairs have been obtained from model compounds in which bonding configurations similar to those being investigated are present. The obvious choice for the models in our case are samples 1 and 5 respectively: in the former the silicon atom is surrounded only by silicon atoms at a distance of 2.35 Å, and in the latter it is surrounded only by carbon atoms at a distance of 1.87 Å. A linear combination of the signals is then used in a least-squares-fitting routine with interatomic distances R_{Si-Si} and R_{Si-C}, coordination numbers (numbers of silicon or carbon atoms surrounding the central silicon atom N_{Si-Si} and N_{Si-C} and disorder factors (mean square relative displacements) $\Delta\sigma_{Si-Si}^2$ and $\Delta\sigma_{Si-C}^2$ as free parameters. If a third contribution is added, i.e. an Si—Si pair in an Si—C—Si configuration, a third signal is added to the linear combination.

A second-shell analysis was performed on sample 3: we tested for the various bonding configurations and the best fit was obtained for an Si—C—Si second-shell contribution. The best-fit parameters obtained are reported in Table 1. In Fig. 2 we show the comparison between the fits and the Fourier-filtered data.

3. Discussion

From the values reported in Table 1 we note that the first-shell average bond lengths do not
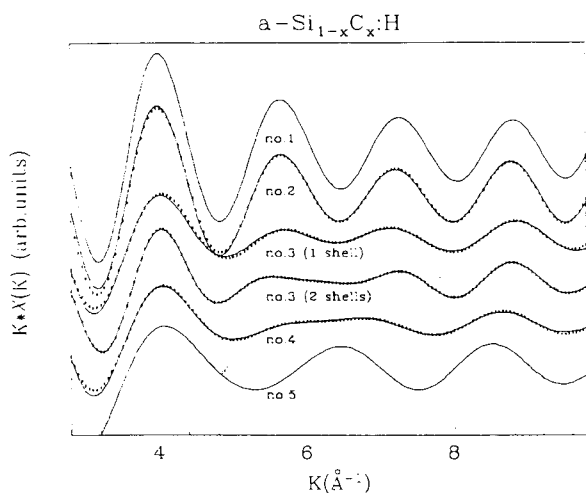

Fig. 2. Best fits (dotted curves) to the filtered EXAFS signals (full curves), obtained as explained in the text.

change with composition to within ±0.015 Å. Constancy in interatomic distances has already been observed in amorphous semiconductor alloys [9, 14, 15] and is attributed to the lack of long-range order which allows relaxation of the distances to their "molecular" values. As for second-shell interatomic distances, the value of 3.11 Å obtained for the Si—Si pair in an Si—C—Si configuration compares well with the crystalline value of 3.08 Å for the same configuration in cubic SiC.

In order to check for the presence of chemical ordering in the alloy component of the material, we compared experimental relative coordination numbers $N_{Si-C}/(N_{Si-Si} + N_{Si-C})$ with theoretical values obtained for the two extreme cases: a total chemical ordering or a random distribution of the two types of bonds. In the former case homonuclear bonds between minority-type atoms are absent, while in the latter the distribution of atoms is purely statistical and all types of bonds are allowed with the same intrinsic probability. For a binary amorphous alloy with average carbon composition given by x', these values can be calculated [16] as a function of total coordination N_{Si} ($N_{Si} = N_{Si-Si} + N_{Si-C}$) and N_C ($N_C = N_{C-C} + N_{C-Si}$) and average coordination $\langle N \rangle = (1 - x')N_{Si} + x'N_C$. In our calculations we shall assume that $N_{Si} = 4$. In doing so we are committing a small error. In fact, N_{Si} is slightly smaller than 4 because of hydrogen bonding: since EXAFS is not sensitive to hydrogen, this results in a reduction of the "effective" coordination. IR measurements [5] show that the number of Si—H bonds varies with carbon content but is always quite small, i.e. lower than 10% of the total silicon bonds. Therefore the "effective" silicon coordination is within 10% equal to 4. On the other hand, the number of C—H bonds is not negligible. IR spectra [3, 5, 17] as well as mass density measurements [4] on glow discharge a-Si$_{1-x}$C$_x$:H show that carbon is incorporated mainly as methyl and methane groups and estimates for the C—H bond content are as high as 33% [5, 7] of the total carbon bonds. This would bring the "effective" coordination down to 2.7. Since it is impossible to determine the value of N_C from Si K edge results, we shall compare our experimental relative coordination numbers around silicon with the theoretical values calculated for N_C in the range 2–4.

In our case x' refers to the composition in the alloy component, which is not equal to the mean total composition x, and $x' < x$. Part of our research

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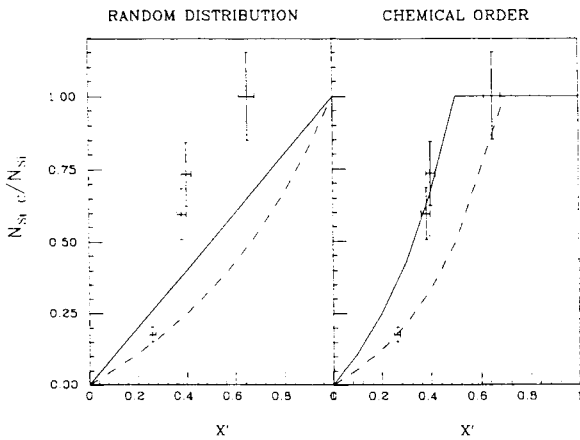RANDOM DISTRIBUTION   CHEMICAL ORDER

Fig. 3. Comparison of experimental relative coordination numbers with theoretical values obtained for the two cases of a random distribution of bonds (left panel) and a totally chemically ordered structure (right panel). Solid lines are calculated using $N_C = 4$, while dashed lines are for $N_C = 2$. Clearly the chemically ordered case fits the data best.

group is presently conducting an electron energy loss spectroscopy study on our alloys giving evidence that both graphitic and polymeric components increase with carbon content [18]. In order to estimate the fraction of segregated carbon atoms, we have used the values of Mui et al. [5]. The values of x' corresponding to our values of x are shown in Table 1. In Fig. 3 we report the comparison between our experimental values of N_{Si-C}/N_{Si} and theoretical values calculated for the two cases of a random distribution of bonds and of a totally chemically ordered structure as a function of x'.

In the random case three experimental points lie outside the physically acceptable region of N_C. On the other hand, the right panel clearly shows that there is a strong preference for heteroatomic bonding in all samples. A random distribution of bonds cannot, however, be excluded in the sample with low carbon content. This result confirms previous results on local order in amorphous semiconductor alloys. The same result was obtained for a-$Si_{1-x}N_x$:H [8, 9]. The tendency to local chemical order that these films display is not surprising bearing in mind that in the crystalline phase silicon and carbon (or silicon and nitrogen) are immiscible but form stoichiometric SiC (or Si_3N_4). On the other hand, results on a-$Si_{1-x}Ge_x$:H [9, 14] show that there is a random distribution of bonds in the films, which agrees

with the complete miscibility of the two elements already established in the crystalline alloys. Finally, the second-shell signal detected in the spectra relative to samples 3 and 4 is evidence of a higher degree of local order at compositions around stoichiometry.

Acknowledgments

We are grateful to F. Campolungo for skilful technical assistance and to the Laboratori Nazionali di Frascati machine staff for their collaboration.

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