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ABSTRACT

Results of the data analysis of x-ray absorption spectra of several amorphous silicon films are presented. We have used an unconventional fitting procedure that allows to determine the bond length variances and the bond-angle standard deviations. We found that increasing the substrate deposition temperature there is a continuous ordering of the first neighbors while the second neighbors show an higher level of disorder.

Introduction.

In this contribution we present a XAS (X-ray Absorption Spectroscopy) investigation on several amorphous silicon (a-Si) films prepared by using the ion beam sputtering technique. Multiple scattering (MS) theory has been used for data analysis in order to extract information on the modifications of the local structure.[1] It has been shown that a-Si K-edge x-ray absorption spectra contain, besides the trivial first-shell dominant wave, a detectable high frequency signal which is due to the MS contributions and to the second-shell single-scattering signal.[2-6] The high-frequency signal has been interpreted as due mainly to the first peak of the three-body correlation function.[2,3] Bond, angle variances and bond-angle correlations, have been extracted directly from the experiment revealing the different structural properties of each sample.

Data analysis.

Experimental details can be found on ref. 5. Here we report the data analysis of Si K-edge absorption measurements on a set of three thin a-Si films prepared by ion-beam sputtering for three different substrate deposition temperature: room temperature (RT), 200°C and 440°C bombarded during the growth by an argon gun (Ar-B).[7] The Si K-edge EXAFS (Extended X-ray Absorption Fine Structures) spectra are characterized by a very good signal to noise ratio (less than 0.1%).

The a-Si EXAFS spectra are dominated by the first-shell low-frequency contribution while a weak but detectable high-frequency signal represents the contribution, mainly in the XANES (X-ray Absorption Near Edge Structures) part, of longer scattering paths.[8,2-5] The Fourier transform (FT) of each a-Si spectrum shows that the high-frequency harmonics are nearly suppressed but a small residual signal is shifted, compared to to the c-Si case, toward higher distances.[2-6,9] The differences in the XANES spectra are mainly due to the high-frequency components of the absorption signal. Residual high-frequency signals can be easily extracted from these spectra by subtracting the first-shell signal but are difficult to analyze quantitatively. In fact besides a damped second-shell single scattering signal they contain also multiple scattering contributions. In this case the usual FT procedure can not be used for extracting quantitative information because of the interference
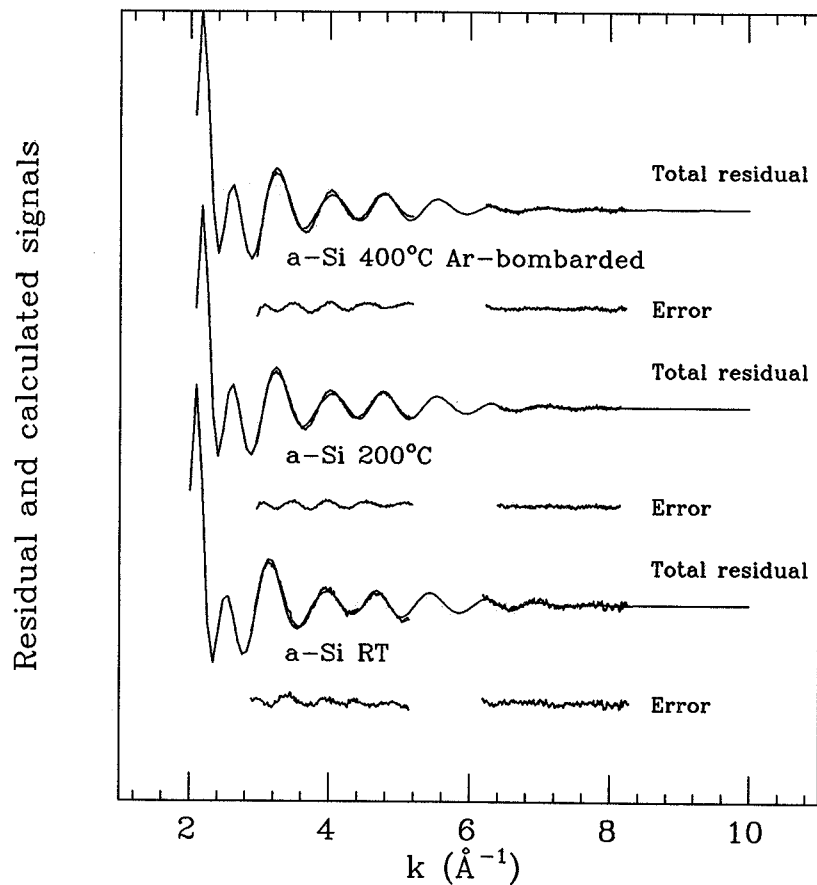
Figure 1: In this figure we show for each sample the experimental and calculated modulating signals free from the dominant first-shell contribution. There is an excellent agreement between the experimental high-frequency total residuals and the calculated ones (smooth curves) which take account of the MS contributions associated to the first peak of the g_3 and to the second-shell g_2 one.

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effects and of the limited amplitude and energy-extension of the signals. Moreover the opening of a KL double electron excitation channel affects the FT spectrum.[4]

In order to overcome the intrinsic limitations of the standard EXAFS analysis we have developed a fitting procedure where a model theoretical signal is compared directly with the experimental spectra. The fitting program follows a previously presented scheme, taking into account also the KL-edge,[2] which has been adapted to employ ab-initio theoretical phase-shifts instead of experimental ones.[6] The model signal is composed of the first-shell single-scattering signal, an appropriate atomic background and an higher frequency contribution. The high-frequency contribution is limited by Fourier analysis to 4.5Å and this upper value sets a serious bound to the length of the MS paths which may contribute to the spectrum. As already discussed [2] the paths contributing to the high-frequency signal originate from the first two peaks of the pair distribution function $g_2(r)$ and from the first peak of the three-body correlation function $g_3(r_1,r_2,\theta)$. We have found [6] the relevant paths associated to the first peak of the g_3 and calculated their high-frequency undamped contribution to the x-ray absorption spectrum of a-Si. Our fitting procedure treats the $g_2(r)$ and $g_3(r_1,r_2,\theta)$ peaks as Gaussian functions and performs the configurational average. The validity of the Gaussian approximation is supported by the analysis of several computer models of a-Si built using empirical potentials [10]. Recent ab-initio molecular dynamics models [11] show asymmetry effects connected both with defects and tetrahedrally coordinated sites. Possible asymmetry effects, not considered in this analysis, are *not* expected to affect the covariance matrix diagonal parameters, but only the mean values of the bond length and angle.

In figure 1 we report for each sample the various high frequency contributions as indicated before and the residual signal with the total model signal. We note that the error corresponds to a precise frequency already identified as a complex contribution of the third neighbors in the $g_2(r)$ and in the third g_3 peak.[6]

TABLE 1	N	σ^2_r (10^{-3}Å^2)	σ_θ (deg)	$\rho_{r\theta}$
a-Si RT	4.0(1)	6.2(1)	9.2(3)	0.17(3)
a-Si 200°C	3.8(1)	4.2(1)	10.0(3)	0.19(3)
a-Si Ar-B	3.8(1)	3.6(1)	10.4(3)	0.13(3)
a-Si:H (14%)	3.8(1)	4.5(1)	8.9(3)	0.07(3)

Table 1:
We report for each sample: the first-shell coordination number N, the bond length variance σ^2_r, the bond-angle standard deviation σ_θ and the bond-angle correlation $\rho_{r\theta}$. We show for comparison the results obtained for a-Si:H. The bond length variance σ^2_r approaches the value of $\sigma^2_r = 3.4 \times 10^{-3}$ Å² (found for crystal silicon and due to thermal disorder) as the deposition temperature is increased.

Results.

In table 1 we report the results of the Gaussian analysis. The a-Si:H results are shown for comparison. Within our confidence level several differences of structural order are evident among the samples. The resulting values for the first-shell bond variance σ^2_r are in agreement with what was previously found with the standard analysis. [5] The ordering process of the first-shell atoms is *continuous* .

In table 1 we show also the bond-angle standard deviations σ_θ for each sample which show a different behavior. There is evidence of an increase of the disorder at the second-shell level as the strain were transferred gradually from the bond length distortion to the bond-angle one. This trend is found also by neutron diffraction experiments on a-Si deposited at 100°C and on the same sample annealed at 600°C by Fortner and Lannin. [12]

The bond-angle correlation $\rho_{r\theta}$ is unchanged within the errors in each sample. Therefore in this case we do not get any additional information from this parameter. It confirms only that the first peak of the g_3 has its principal axis tilted respect to the angle one and that the angle distribution remains broad varying the deposition temperature.

Conclusions.

We have shown that using an advanced fitting procedure and ab-initio model signals it is possible to detect structural differences in differently prepared a-Si films by using x-ray absorption spectroscopy. We have extracted the first-shell bond variance and the angle standard deviation directly from the absorption spectra with a very low statistical error. The results are in good agreement with neutron diffraction data. In this way XAS becomes competitive with the diffraction techniques to determine the structural properties of disordered systems.

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