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STRUCTURAL STUDY OF a-$Si_{1-x}C_x$:H BY EXAFS AND X-RAY SCATTERING

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We present a comprehensive study of short range order in a-$Si_{1-x}C_x$:H using X-ray scattering and Si K-edge EXAFS. The X-ray scattering probes the total radial distribution function; by detailed fitting in R-space we measure short range order parameters around C and Si for the first and second shell. The C-C distances in first and second shell indicate that both carbidic and graphitic configurations are present. The coordination numbers indicate that there is a tendency to chemical order; at high C concentrations there is evidence for chemical order with phase separation. The EXAFS measurements probe local order in the Si-C alloy phase; there is clear evidence that even this phase is chemically ordered.

1. INTRODUCTION

As in all semiconductor alloys, of special importance in a-$Si_{1-x}C_x$:H is the issue of chemical ordering of the atomic species. In general, the atomic arrangement of an alloy can exhibit clustering, a random arrangement, chemical order with homogeneous dispersion or chemical order with phase separation[1,2]. It is interesting to note that the ability of carbon to have twofold, threefold and fourfold coordination adds a degree of freedom to local structural arrangement which is absent in other amorphous semiconductor alloys.

a-$Si_{1-x}C_x$:H has been the subject of many investigations[2-10]. Although the literature is sometimes contradictory, the following general picture emerges: a-$Si_{1-x}C_x$:H is a microscopically heterogeneous material which is composed of four different phases[3]: a Si-C alloy component, graphitic carbon, polymeric carbon and voids.

X-ray scattering (XRS)[11] and EXAFS[12] are powerful complementary techniques in the study of amorphous materials. While XRS probes the total radial distribution function (RDF), EXAFS is chemically specific, being sensitive to the RDF around the excited atom. We have applied both techniques to obtain quantitative information on structure in a-$Si_{1-x}C_x$:H. The EXAFS results have been reported previously[5].

2. EXPERIMENTAL AND DATA ANALYSIS

a-$Si_{1-x}C_x$:H\samples were prepared by PE-CVD from SiH_4 and CH_4 mixtures in standard conditions. Due to the different requirements on sample characteristics for XRS and EXAFS the samples were prepared in different chambers but with similar deposition conditions. The main difference was a reduced substrate temperature for the XRS samples (110 °C versus 200 °C), required to increase the deposition rate of the high C content films. While the deposition parameters are not strictly the same for XRS and EXAFS, useful information is obtained from the measurements and it can be rationalized within the same framework. Sample compositions were determined separately for the two sets of samples with Auger spectroscopy and Secondary Neutral Mass Spectrometry.

XRS measurements were performed using a conventional Mo x-ray tube and a quartz monochromator on the incident beam; the maximum value of the scattering vector was 16 $Å^{-1}$. Quantitative analysis of XRS results was performed by fitting the experimental RDF following the "exact"

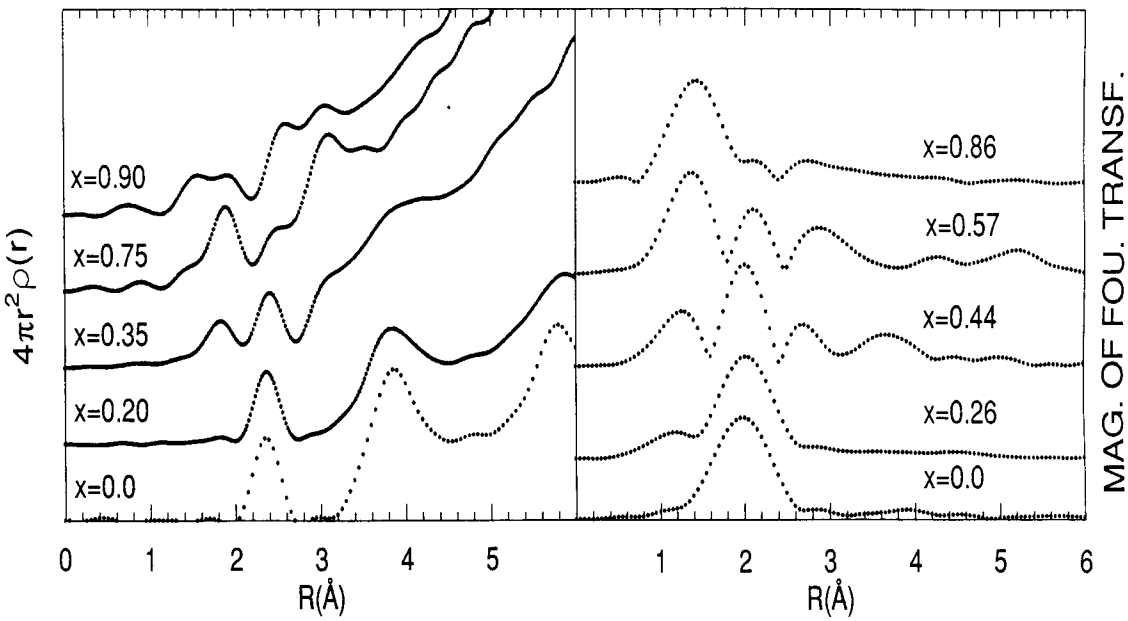

Fig. 1: In the left panel we show the total RDF's for a-$Si_{1-x}C_x$:H and on the right the magnitude of the Fourier transform obtained by EXAFS at the Si K-edge, showing the environment of Si.

method [11].

EXAFS measurements were performed in the transmission mode at the PULS X-ray beamline of the synchrotron radiation facility in Frascati (Italy) using a double crystal InSb(111) monochromator. Data were analyzed according to standard procedures[12]. The EXAFS data is available up to a maximum photoelectron wavevector of 10 $Å^{-1}$ which is equivalent to a scattering wavevector of 20 $Å^{-1}$.

3. RESULTS AND DISCUSSION

In this paper we report the most important results of the combined XRS and EXAFS analysis, leaving a detailed discussion to a longer paper.

In fig. 1 we show on the left the total RDF's of all samples studied, with x ranging from 0 to 0.9 and on the right the EXAFS Fourier transforms for an equivalent concentration range (the latter have not been corrected for phase shifts). In a-Si:H the total RDF is characterized by the well defined peaks of the first and second shell, while the third shell has a broad and structured distribution[13]; the EXAFS Fourier transform is dominated by the strong first shell signal[4]. As C is added to the a-Si:H network fig. 1 clearly shows the modifications introduced in

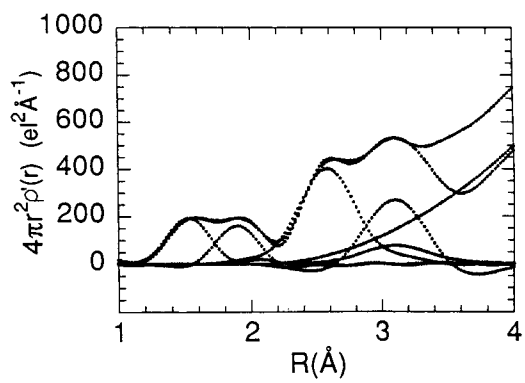

Fig. 2: RDF fit for a sample with x=0.9; components are shown and the fit is performed up to 3.2 Å.

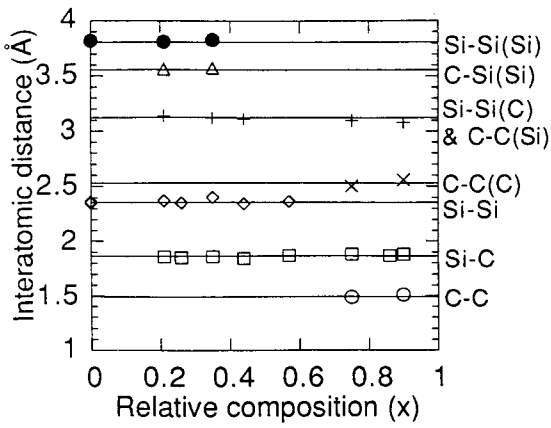

Fig. 3: Interatomic distances as a function of composition for first and second shell configurations; symbols are explained in the text.

local bonding configurations. In the first coordination shell the total RDF's show the gradual growth of Si-C bonds at ≈1.86 Å and of C-C bonds at ≈1.5 Å. The EXAFS results show that the nearest neighbor environment of Si smoothly changes from Si to C. The qualitative conclusion which can be drawn from this figure is that substantial amounts of Si-C bonding takes place.

In fig. 2 we show an example of the fitting for the total RDF's for a sample with x=0.9. We shall indicate second shell configurations with the symbol A-B(C), meaning correlations between atoms A and B with atom C as a center. The RDF of figure 2 was fitted with the following contributions: C-C and Si-C, C-C(C), Si-Si(C) and C-C(Si). A similar fitting, using the same components but with different relative weights, was obtained for the sample with x=0.75. The main, important, conclusion which can be drawn from this figure is that the second shell can be simulated in the two samples with high C content by using only configurations expected in chemical order with phase separation[2]. Specifically, no Si-C(C) contribution at 2.7 Å was detected.

In fig. 3 we show the interatomic distances obtained for the first and second shell configurations from the EXAFS and XRS data. The first conclusion which can be drawn from this data is that first and second shell distances are independent of x; this is in agreement with previous data[5], confirms a general trend in amorphous semiconductor alloys[4] and extends that data to include second shell interatomic distances. The Si-Si and Si-C distances are found to be constant to within ± 0.02 Å at 2.36 and 1.86 Å respectively. The C-C distance obtained, 1.50 ± 0.01 Å, is in between the values expected for diamond and graphite, consistent with the expectation that both sp^2 and sp^3 C hybridizations co-exist. As for second shell bond distances, the C-C(C) distance is found to be 2.53 ± 0.03 Å; this value indicates an average bond angle of 116°, a clear indication of a mixture of graphitic and carbidic configurations. The Si-Si(Si) distance is 3.84 ± 0.01 Å and is consistent with tetrahedral coordination of Si. The peak at approximately 3.12 Å is in fact due to the sum of Si-Si(C) and C-C(Si) configurations; its position shifts

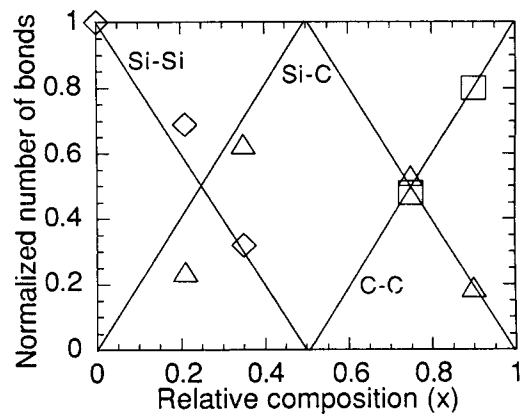

Fig. 4: Normalized number of bonds as a function of composition for the three first shell configurations. Also shown as the solid lines are the predictions of a chemically ordered model.

with concentration as C central atoms are substituted with Si central atoms and is compatible with the hypothesis of tetrahedral angles on Si and a mixture of sp^2 and sp^3 configurations on C.

We now address the question of chemical order. In fig. 4 we plot the values of the normalized first shell coordination numbers as a function of x for the XRS results. Also shown is the plot of the expected behavior of the coordination number assuming complete chemical order. It is quite clear that there is good agreement with those predictions. As mentioned by analyzing the second shell data (see fig. 2) we can further specify that we expect chemical order with phase separation to be dominant at high C content ($x \geq 0.75$); on the other hand, at lower C content (samples with $x = 0.15$ and 0.35) the mixed contribution Si-C(Si) was observed. This is compatible with the presence of C dispersed in a Si matrix and rules out macroscopic separation of SiC clusters[10].

We also adressed the problem of chemical ordering by looking only at the Si environment with Si K edge EXAFS. We expect in this way to probe relative atomic arrangement only in the Si-C alloy phase. As described in a previous paper[5] analysis of the composition of the Si first coordination shell clearly shows that the environment of Si exhibits a tendency towards chemical order in agreement with the XRS data.

In conclusion we have provided quantitative evidence that a-$Si_{1-x}C_x$:H is a complex material in which C is present in a number of configurations and in which there is a considerable tendency towards chemical ordering. This is compatible with recent molecular dynamics simulations of the material[14], and is independently confirmed by Auger measurements on our samples[10].

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