On the structural properties of \( a\text{-Si}_{1-x}C_x :H \) thin films

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The structural and chemical properties of hydrogenated amorphous silicon carbide \( (a\text{-Si}_{1-x}C_x :H) \) thin films, deposited by plasma-enhanced chemical-vapor deposition, were determined by extended x-ray absorption fine structure (EXAFS), x-ray-absorption near-edge spectroscopy (XANES), small-angle x-ray scattering, Fourier transform infrared (FTIR) spectroscopy, Auger electron spectroscopy, and visible spectrometry. The EXAFS and XANES results show the crucial influence of the “starving” plasma deposition conditions on the structural properties of wide-gap \( a\text{-Si}_{1-x}C_x :H \) films and are consistent with the FTIR and optical-absorption data. The first-neighbors distance for alloys with smaller carbon content or deposited at higher silane flow are very close to the mean Si–Si distance obtained for \( a\text{-Si}:H \). On the other hand, the EXAFS spectra of films with higher carbon content \((x>50\text{ at. \%})\) and deposited under “starving” plasma regime show Si–C distances similar to crystalline SiC \((c\text{-SiC})\). The presence of a typical \( c\text{-SiC} \) resonance in the XANES spectra of the same samples is evidence that the material has a chemical order close to that of \( c\text{-SiC} \). © 1996 American Institute of Physics. [S0021-8979(96)04702-X]

INTRODUCTION

Hydrogenated amorphous silicon alloys obtained by the plasma-enhanced chemical-vapor deposition technique are used in many different optoelectronic devices, mostly due to the possibility of tailoring the optical gap with variations in the gas mixture composition. In particular, hydrogenated amorphous silicon carbide thin films, \( a\text{-Si}_{1-x}C_x :H \) are used in solar cells and thin-film transistors, always tailoring the optical gap by varying the methane concentration in the gas mixture. However, for high CH\(_4\) partial pressures, these materials generally show a decrease in the optical gap, which is related to the formation of graphitelike \( sp^2 \) C–C bonding instead of diamondlike \( sp^3 \) C–C bonding.

In a previous work we demonstrated that it is possible to obtain hydrogenated amorphous silicon carbide thin films with optical gap as high as 3.7 eV, resistivity higher than 10\(^{15}\) Ω cm, very low refractive index, and high carbon content \((x\sim70\text{ at. \%})\), suggesting the presence of a diamondlike C–C structure. The growth of \( a\text{-Si}_{1-x}C_x :H \) films with these unusual properties is achieved under special deposition conditions, known as the “starving” plasma regime. At this regime, the deposition rate is strongly dependent on the silane flow and it is characterized as a combination of a low rf power density with a very low silane flow and high methane concentration.

In this work we extend the previous investigation on \( a\text{-Si}_{1-x}C_x :H \) films, studying the dependence of their structural properties with the two deposition parameters in question: The silane flow and the methane concentration. These parameters determine the carbon incorporation form and the structural, electronic, and optical properties of the material. Various techniques were used to analyze the films: extended x-ray-absorption fine structure (EXAFS) and x-ray-absorption near-edge spectroscopy (XANES) to explore the structural characteristics, small-angle x-ray scattering (SAXS) to detect the formation of microvoids, Auger electron spectroscopy (AES) to determine the alloy chemical composition, and visible and infrared (IR) spectrometry to find the optical gap and atomic bonds inside the material.

The structural features of amorphous Si-based alloys have been addressed by means of EXAFS and XANES experiments. A previous study of \( a\text{-Si}_{1-x}Ge_x \) alloys found that Ge–Ge and Ge–Si distances are independent of concentration \( x \) and equal to 2.45 and 2.38 Å, respectively. The results point out that the first coordination shell around Ge is consistent with a random mixing of the two species in the alloys. The total disorder factors have been determined for both Ge–Ge and Ge–Si, being constant and equal to each other in the whole analyzed concentration range.

Filiponi et al. studied, using EXAFS at the Si K edge, the structure of three series of hydrogenated amorphous Si-based alloys. Average bond lengths and first shell compositions were determined. Concerning particularly the \( a\text{-Si}_{1-x}C_x :H \) system, it was found that the Si–Si average distance \( R_{\text{Si-Si}} \) is independent of \( x \) and equal to 2.35 Å, whereas the Si–C average distance \( R_{\text{Si-C}} \) undergoes a more complicated behavior, exhibiting a minimum at \( x=0.5 \) and an overall variation of more than 0.1 Å. According to the authors, the results on \( R_{\text{Si-C}} \) should be carefully analyzed due to the poorer quality of the experimental data.
TABLE I. Silane flow $F$ and methane concentration of the studied samples with the obtained values for their optical gap $E_o$ and the carbon concentration in the solid phase $x$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$F$ (SiH$_4$) (sccm)</th>
<th>$[\text{CH}_4]$ (%)</th>
<th>$E_o$ (eV)</th>
<th>$x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MVC2</td>
<td>10</td>
<td>98</td>
<td>3.7</td>
<td>0.66</td>
</tr>
<tr>
<td>MVC1</td>
<td>10</td>
<td>92</td>
<td>3.4</td>
<td>0.70</td>
</tr>
<tr>
<td>MVC4</td>
<td>10</td>
<td>80</td>
<td>3.0</td>
<td>0.55</td>
</tr>
<tr>
<td>MVC3</td>
<td>10</td>
<td>72</td>
<td>3.0</td>
<td>0.56</td>
</tr>
<tr>
<td>MVC5</td>
<td>10</td>
<td>50</td>
<td>2.0</td>
<td>0.46</td>
</tr>
<tr>
<td>MVC6</td>
<td>50</td>
<td>72</td>
<td>2.8</td>
<td>0.54*</td>
</tr>
<tr>
<td>MVC7</td>
<td>100</td>
<td>72</td>
<td>2.6</td>
<td>0.51*</td>
</tr>
<tr>
<td>MVC8</td>
<td>150</td>
<td>72</td>
<td>2.5</td>
<td>0.50*</td>
</tr>
</tbody>
</table>

*Estimated from $E_o$ values.

More recently, Laffon, Flank, and Lagarde$^{15}$ presented XANES studies of some silicon compounds. They compared the x-ray-absorption near-edge structure of c-Si, c-SiO$_2$, and c-SiC (all crystalline compounds) and provided a qualitative analysis concerning the energy shifts and the presence of some particular features. In these compounds, each silicon atom is four coordinated, but the spectra are very different. The energy of the white line maximum depends on the electronegativities of the bonded elements. A large resonance was observed at about 15 eV from the absorption edge in all these samples. The values of $\Delta E$, which is the energy between the absorption edge and the resonance, are somewhat imprecise due to the width of the resonance (except in the case of c-SiC), but for all these structures the relation $(\Delta E) R^2 = \text{const}$ is verified. The resonance at about 15 eV does not exist in the Si(CH$_3$)$_4$ molecule and is spread out for amorphous silicon carbide, a-SiC. They infer that this resonance is characteristic of a structural order which extends up to the Si–Si second shell and its carbon neighbors. The presence of this feature is not related to a particular shell, but to the whole set of atoms in the structure taking into account the carbon neighbors.

These previous EXAFS and XANES results serve as guidelines for the data analysis presented in this work.

**EXPERIMENT**

The amorphous silicon carbide films were deposited by the PECVD method, currently referred as the radio-frequency glow discharge technique, from gaseous mixtures of silane and methane, in a capacitively coupled reactor. The substrate temperature was fixed at 250 °C, the deposition pressure was 1 Torr, and the power density was 150 mW/cm$^2$. The total pressure inside the chamber was kept constant by varying the gas flows and the pumping speed. In order to analyze separately the influence of the silane flow and the gas mixture concentration on the a-Si$_{1-x}$C$_x$:H properties, two sets of samples were deposited: a first set, changing the CH$_4$ concentration, maintaining the silane flow constant, and a second one, changing the SiH$_4$ flow for a constant (72%) CH$_4$ concentration. Table I depicts the deposition parameters for the produced films, the optical gap $E_o$ and the carbon content in the solid phase $x$. The gyration radius and relative microvoid volume fraction of the samples were determined by SAXS, using part of the white x-ray spectrum or Mo $K\alpha$ radiation. The carbon, silicon, and hydrogen incorporation form in the different films were determined by Fourier transform infrared (FTIR) spectrometry.$^{16}$

The EXAFS and XANES data were collected at the Si $K$ absorption edge ($E=1.839$ keV) at the SUPERACO ring (SA32 station) at the LURE synchrotron radiation facility in Orsay, France. The beam was monochromatized using a double-crystal monochromator, equipped with two InSb monocrystals. The detection was performed in the total electron yield mode, so that the requirement of a clean surface is not a very critical issue. The $K$ edge EXAFS and XANES spectra were analyzed by subtracting a linear background, computed by least-squares fitting from the pre-edge region. All the XANES spectra were arbitrarily normalized on the maximum $K$ edge peak. The EXAFS oscillation curves $\chi(k)$, with $k=\sqrt{m/4\pi^2(E-E_0)}$, were obtained by a standard procedure,$^{17}$ normalized, background removed, and Fourier transformed using the available programs for Macintosh computers.$^{18}$ After a $k^3$($k$) weighting, a Kaiser apodization function was applied over 3.6 and 10.6 Å$^{-1}$, with $\tau=2.5$.

Crystalline and amorphous samples were taken as structural references: a-Si:H (for Si–Si bonds), c-SiC (for Si–C and Si–Si bonds), and c-SiO$_2$ (for Si–O bonds). In a-Si:H, due to the low H concentration, more than 90% of the silicon atoms are coordinated by other four silicon atoms situated at about 2.35 Å. In c-SiC, each silicon atom is surrounded by four carbon atoms forming the first shell (at 1.89 Å) and 12 silicon atoms forming the second shell (at 3.08 Å). In c-SiO$_2$ compound, each silicon atom is surrounded by four oxygen atoms situated at an average distance of 1.61 Å.$^{14}$

**RESULTS**

The results presented in Table I show that for films of the first set of samples, deposited under the same silane flow and different methane concentration, the optical gap increases monotonically with the increase of carbon content in the material up to a maximum of approximately 4 eV attained for a carbon incorporation of about 70 at. %. On the other hand, the films of the second set of samples, deposited with in-

FIG. 1. FTIR absorption spectra of a-Si$_{1-x}$C$_x$:H samples deposited under starving regime (10 sccm of SiH$_4$) at different methane concentrations.
creasing silane flow, but with the same methane concentration in the gas mixture, show a decrease in the optical gap for higher silane flows.

Figure 1, related to the first set of samples, depicts the infrared-absorption spectra for three samples grown at different methane concentration (50%, 72%, and 92%) and constant (10 sccm) silane flow. For increasing methane concentration in the gas mixture, there are lower levels of carbon incorporation in the Si–C form and a nonsurprising decrease in the SiH$_n$ band, while the CH$_n$ ($n=1,2,3$) and Si–CH$_n$ bands remain almost invariant. For higher CH$_4$ concentrations, the lower availability of silicon justifies the decrease of the Si–C band but, as the other detectable carbon incorporation forms remain essentially constant, the extra carbon atoms must be incorporated through C—C bonds, which are not detectable with FTIR spectrometry.

Figure 2, related to the second set of a-Si$_{1-x}$C$_x$:H films, depicts the infrared-absorption spectra of samples deposited at constant methane concentration (72%) and variable silane flow. The Si–C band is higher and the SiH$_n$ band is smaller, for samples grown at lower silane flow, the difference being more pronounced for samples deposited at the lowest flow (10 sccm), which corresponds to the starving plasma regime.

The microvoid sizes do not depend on the deposition regime. Microvoids, whose size stayed between ~2.0 and 4.0 Å, were detected for all analyzed films, from the Guinier plot of the registered data.$^{16,19}$ On the other hand, the relative microvoid volume fraction $\eta$ is larger for films grown at nonstarving plasma conditions, as shown in Table II. In the case of samples deposited at high silane flow, i.e., at nonstarving plasma regime, the analysis of the Porod’s region$^{19}$ did not show the $-3$ slope, expected for line focus geometry, indicating that the interface between the microvoids and the matrix is not abrupt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MVC1</th>
<th>MVC3</th>
<th>MVC4</th>
<th>MVC5</th>
<th>MVC6</th>
<th>MVC7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>0.02</td>
<td>0.40</td>
<td>0.68</td>
<td>0.62</td>
<td>0.36</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Figures 3 and 4 present the Fourier transform of the EXAFS data. The Fourier transforms are not corrected for the phase shift parameters, so that the maximum peak positions (corresponding to the Si–C, Si–Si, or Si–O bonds) are shifted to lower values compared to the real ones. Figure 3 corresponds to the first set of samples, grown at starving plasma conditions and different methane concentration. A qualitative interpretation of these results shows that, for a sample close to but below stoichiometry ($x=0.46$, [CH$_4$] $=50\%$), the first-neighbor distance is very similar to the Si–Si mean distance in a-Si:H. In this case a coordination number equal to four is also expected, but it is difficult to assign this distance only to Si–Si bonds, since the material has a carbon content of 46 at. %. The peak profile in the Fourier transform is asymmetric and, therefore, the peak might be a superposition of similar bonding distances related to Si–Si and Si–C. On the other hand, for films having higher carbon content ($x=0.55$ and $x=0.70$), the results demonstrate clearly the existence of Si–C distances similar to c-SiC, indicating the presence of an amorphous SiC phase with chemical order similar to c-SiC. Conversely, the Si–Si distance contributions are difficult to separate. The Si–Si bonds in the a-Si:H are situated at a distance of 2 Å, exactly between the Si–C and Si–Si second neighbors of the c-SiC (Fig. 3), making it difficult to distinguish between the differ-
ent Si–Si distances (related to $a$-Si:H and to $c$-SiC). Furthermore, Laffon showed that the imaginary part of the Si–C and Si–Si (from $c$-SiC) and Si–Si (from $a$-Si:H) peaks are in phase opposition, so that the Si–Si contribution situated at about 2 Å cannot be observed, even for a mixture of 20% of crystallized silicon and 80% of $c$-SiC. In this way, the existence of Si–Si bonds similar to $a$-Si:H cannot be ruled out in our samples which do not present the 2 Å peak in the EXAFS data.

Figure 4 presents the data related to the second set of samples, which were deposited at the same methane concentration (72%), but with different silane flow ($f=10, 50, and 100$ sccm). In this case, the number of Si–C and Si–Si bonds similar to $c$-SiC is smaller for films deposited under non-starving regime, i.e., at higher flow values. For samples deposited under the nonstarving regime (MVC6 and MVC7) a first peak situated at about 1.2 Å is observed. From Fig. 4, this peak can be attributed to an oxygen contribution, since it is located at a Si–O mean bond length similar to that in $c$-SiO$_2$. Moreover, the AES results obtained for samples deposited under nonstarving conditions (like MVC6) exhibit oxygen peaks. These samples also present higher relative microvoid densities. A close inspection of the FTIR data reveals a slight shift of the band corresponding to the Si–CH$_2$ stretching vibration (1020–1040 cm$^{-1}$), which can be attributed to the presence of Si–O–Si stretching vibrations (1075 cm$^{-1}$). Optical characterization of these samples showed an increase in the optical gap and a decrease in the refractive index for longer air exposition times. These results are compatible with the observed increase in the EXAFS peak intensity related to Si–O distances in samples that were also exposed to air for longer times. These observations are consistent with an oxidation process in which the oxygen is incorporated through the sample microvoids. Nevertheless, based on the relative peak intensities, the number of Si–O bonds is small in the studied samples as compared to the $c$-SiO$_2$ reference compound.

An attempt of fitting the EXAFS data was performed for the two extreme cases, related to samples deposited at the highest and lowest methane concentration, MVC1 and MVC5, respectively. In these cases the contribution of only one kind of atom is assumed for the first peak of the Fourier transform (Fig. 3). Figure 5 presents the filtered $\chi(k)$ EXAFS spectra and the calculated curves obtained with the parameters shown in Table III. The $a$-Si:H and $c$-SiC were used, respectively, as reference compounds for the MVC5 and MVC1 fitting procedures. The fitting quality obtained for sample MVC1 [Fig. 5(a)] is very good and the results presented in Table III confirm the existence of a high local order in the film. On the other hand, for sample MVC5 [Fig. 5(b)],

![Graphical representation of EXAFS data](image)

**FIG. 4.** Fourier transform of the EXAFS data of $a$-Si$_{1-x}$C$_x$:H deposited with a methane concentration of 72% and different silane flow.

**FIG. 5.** First-shell filtered EXAFS spectra ($\cdots$) and calculated curves (O O O O) obtained with parameters from Table III: (a) MVC1 and (b) MVC5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_{Si-C}$</th>
<th>$R_{Si-C}$</th>
<th>$\Delta\sigma_{Si-C}$</th>
<th>$N_{Si-Si}$</th>
<th>$R_{Si-Si}$</th>
<th>$\Delta\sigma_{Si-C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MVC1</td>
<td>4.5</td>
<td>1.91</td>
<td>0.04</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$x=0.70$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MVC5</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>3.7</td>
<td>2.36</td>
<td>0.0002</td>
</tr>
<tr>
<td>$x=0.46$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the fitting quality is poor. In Fig. 5(b), the EXAFS experimental spectra present an intensity decrease at about 5.3 Å⁻¹ which is due to the contribution of another kind of atom, such as carbon or even silicon atoms, situated at different distances. It has been pointed out earlier that low carbon content amorphous silicon carbide films are formed by a random distribution of Si and C atoms, preserving the first neighbors distances of a-Si:H. 21,22 In order to improve the agreement with the experimental data a two-shell model should be used. Nevertheless, before attempting to obtain quantitative results from a two shell fitting, it is necessary to define the maximum number of independent parameters to be adjusted during the fitting procedure. It is a common rule for reliable simulations to take this number equal to 

\[ N_{\text{pts}} = \frac{2D_kD_R}{\pi} \]

where \( D_k \) is the \( k \) space range of the measured data and \( D_R \) is the width of the window used when Fourier transforming in \( R \) space. In this case, \( D_k = 7.4 \text{ Å}^{-1} \) and \( D_R = 1.2 \text{ Å} \) (medium value), which gives \( N_{\text{pts}} = 5.7 \). Having at least six fitting parameters, neighbor number \( N \), mean bond length \( R \), and Debye–Waller factor \( \Delta \sigma \), this value \((5.7)\) is too small to lead to an accurate determination of the structural parameters based on calculations of a two- or three-subshell model.

Figures 6 and 7 show the XANES region obtained for the two series of samples. The position of the absorption edge depends on the film composition. The higher the carbon content in the film, the closer is its absorption edge to the value obtained for c-SiC, as well as the XANES line shape. Calculations based on c-SiC XANES spectrum 23 showed that the A resonance appears when the fifth shell of atoms is included. Another feature (B), observed at about 6 eV from the absorption edge, seems to be related to a more extended SiC cluster due to the increase of the mean free path of low kinetic energy electrons. The XANES calculations determined that the B resonance should be present for a c-SiC cluster extension of at least 12 Å. The XANES results for the films deposited under the starving plasma regime (Fig. 6) do not show the B resonance, but only the A resonance, which is more pronounced for the samples having \( x = 0.7 \) and \( x = 0.55 \). The fact that this resonance is spread compared to the peak width in the c-SiC reference is attributed to the amorphous characteristics of the deposited films. 23 For the second set of samples (deposited at the same methane concentration, but with different silane flow), the A resonance in the XANES spectra is clearly observed for the film deposited at the lower silane flow and is damped for the other samples (see Fig. 7).

**DISCUSSION**

The results show that the structural, morphological, and optical properties of the hydrogenated amorphous silicon carbide alloys deposited by PECVD are strongly dependent not only on the methane concentration but also on the silane flow. As expected, the higher the methane concentration in the gaseous mixture the higher the amount of carbon incorporated in the solid phase. On the other hand, samples grown with identical methane concentration, but with different silane flows, present the same carbon content in the film matrix, but very different optical, structural, and morphological features. Increasing optical gaps for carbon-rich films are achieved only with the combination of high methane concentration and low silane flow which, in the low-power regime, determine the starving plasma conditions. The high obtained values for the optical gap can be attributed to the formation of polymerlike material but the FTIR data rule out this possibility, since all the bands related to hydrogen–carbon bonding (Si–CH₃, CH₃) decrease or remain constant.
results strongly indicate that the excedent carbon is incorporated through diamondlike C—C type of bonding.

The SAXS results demonstrate that high carbon incorporation does not necessarily mean higher microvoid volume fraction. The decrease in the relative microvoid volume fraction presented for a sample with $x\sim0.7$ when compared to samples with $x\sim0.5$ indicates that it is possible to obtain more homogeneous (in a relative scale) $a$-$Si_{1-x}C_x$:H films with high values of the carbon content in the solid phase, provided that the starving plasma deposition conditions are used. Moreover, the increase in the relative microvoid volume fraction observed for films deposited under the non-starving regime is accompanied by an increase in the number of Si—CH$_3$ bonds (see Fig. 2) which are claimed as responsible for the formation of microvoids.\textsuperscript{24,25}

The EXAFS, XANES, and FTIR results demonstrate that films with higher carbon content, deposited at the starving plasma regime, preserve the bonding distances and the chemical order of $c$-$SiC$. It is interesting to point out that the EXAFS and XANES data obtained for a sample with $x=0.46$ (below stoichiometry) show a structure similar to $a$-$Si$:H, suggesting that low carbon content material is composed by a random mixing of silicon and carbon atoms\textsuperscript{21,22} without preserving the Si—C double-layer structure of the $c$-$SiC$ lattice. Conversely, the results for carbon-rich films show that, under starving deposition conditions, an amorphous network with short-range order similar to $c$-$SiC$ is obtained. These results indicate that the deposition kinetics related to the silane flow governs the structural characteristics of the films, more than the CH$_3$ concentration.

CONCLUSIONS

The deposition of $a$-$Si_{1-x}C_x$:H films by the PECVD technique under starving plasma conditions produces films with high carbon content ($x>0.5$) which are chemically and structurally similar to $c$-$SiC$, having silicon preferentially bonded to carbon. A structure similar to $a$-$Si$:H is observed for silicon-rich films ($x<0.5$), or for films deposited with higher methane concentration but at the nonstarving regime. The change from starving to nonstarving plasma deposition conditions is deleterious, since the materials obtained at the later conditions present a higher relative microvoid volume fraction, higher density of Si—CH$_3$ bonds, and a structure less like $c$-$SiC$. Diamondlike C—C chemical bonds are suggested in films with high optical gap.

ACKNOWLEDGMENTS

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