# Positron study of defects in a-$Si_xC_{1-x}$ films produced by ion beam deposition method

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## Abstract

Amorphous $Si_xC_{1-x}$ (a-$Si_xC_{1-x}$) films with $x$ ranging from 0 to 0.4 have been produced using a high energy ion beam deposition method. The resulting films have been characterized by Raman annihilation spectroscopy and positron annihilation spectroscopy (PAS). Hardness and wear resistance have also been measured. It has been shown that the open volume defects and their distribution through the films have an important role in determining the mechanical behavior of the as-deposited and thermal treated films. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Amorphous $Si_xC_{1-x}$ (a-$Si_xC_{1-x}$) films have attracted attention because of their electrical, optical and mechanical properties. These films can be obtained in a variety of ways and their characteristics are greatly influenced by the degree of hydrogenation and by the Si/C ratio. The advantage of the high energy ion beam deposition method is that the silicon content can be varied with the gas mixture composition, obtaining the desired Si/C ratio. In addition, these films can be grown over different substrates. In recent papers we have studied changes in the structure, as a function of temperature (thermal behavior), and mechanical properties of a-$Si_xC_{1-x}$ films obtained using high energy ion beam deposition methods [1,2].

Many experimental techniques have been applied in order to characterize the different films so obtained. Raman spectroscopy is probably the most common technique employed to evaluate the amorphous character of these films. It provides bulk information about the bonding character of the atoms (i.e. coordination and bond-angle disorder).

Positron annihilation spectroscopy (PAS) has demonstrated to be a powerful technique to characterize the homogeneity of amorphous films concerning the distribution of open volume defects [3]. It allows a non-destructive analysis of films as a function of depth from the first surface layer to the interface with the

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substrate. The knowledge of the voids distribution is important to understand the mechanical properties of these films.

The most adequate positron techniques to study open volume defects in solids (lifetime and Doppler-broadening positron annihilation spectroscopy) have been applied on irradiated single-crystal 3C–, 2H–, 4H–, 6H–, SiC polytypes (see [4] and references therein). Only a few works have dealt with amorphous SiC (a-SiC) [5,6] deposited by electron cyclotron resonance chemical vapor deposition.

In this paper we have studied a-$Si_xC_{1-x}$ films with $x$ up to 0.4, obtained with controlled incorporation of silicon in a high energy ion deposition system. The open volume defects distribution was measured by PAS, in the as-deposited films and in films thermally treated up to 900°C. These results were correlated with Raman data and with electrical resistivity, hardness and wear resistance measurements.

## 2. Experimental

### 2.1. Film preparation

The films of a-$Si_xC_{1-x}$ were obtained using high energy (30 keV) ion beam deposition methods. Carbon and silicon incorporation in silicon wafers is achieved from the decomposition of different methane–silane gas mixtures. The ion beam is obtained from the decomposition of the precursor gases in the ion source by means of an electronic arc. The ions are accelerated through an extracting electrode and then go through a magnetic steerer in order to separate the $H^+$ ions from the remaining heavier ions. Finally, they arrive at a stainless steel deposition chamber kept under a vacuum of $10^{-5}$ mbar, where the sample to be coated is located. No external heating is provided [2]. Films of ∼1 μm thickness were grown.

The samples of a-$Si_{0.3}C_{0.7}$ were annealed in vacuum (∼$10^{-5}$ mbar) in 100°C steps, from 500 to 900°C, for 30 min in order to analyze their thermal stability.

### 2.2. Film characterization

The composition characterization was made using XPS. The measurements were carried out using the Mg Kα line (1253.6 eV) as incident radiation. The binding energies were calibrated considering the Au $4f_{7/2}$ peak at 84.0 eV with respect to the Fermi level. Depth profiles were carried out using sputtering with an Ar beam of 4 keV incident at an angle of 60° from the surface normal.

Microhardness of the coatings was measured by the dynamical indentation technique using a commercially available apparatus (NanoTest 550, MicroMaterials Ltd., UK). The resolutions are 1 nm in depth and 1 μN in load.

To test the wear resistance of the films, the samples were polished with 3 μm diamond paste on a polishing pad. The silicon substrates were masked during deposition in order to leave half of their surface without the a-$Si_xC_{1-x}$ coating. The thickness reduction caused by wear in the a-$Si_xC_{1-x}$ coating and in the uncoated silicon substrate was measured.

Raman spectra were obtained using an Ar laser operating at 514.5 nm; the dispersed beam was analyzed in a 90° geometry. A typical Raman analysis penetration depth, with this excitation wavelength is about 500 nm.

The electrical resistivity was determined from *I–V* measurements.

Positron measurements were carried out with an electrostatic slow positron beam using the Doppler-broadening technique. Details about the apparatus and the measurements can be found in [7,8] and in the references therein. Here, we only report a brief description of the experiment. Positrons injected in a solid reach the thermal equilibrium in a few picoseconds then, after a diffusion path annihilate with an electron of the medium. In PAS with the Doppler-broadening technique, the shape of the 511 keV annihilation line recorded by a high purity germanium detector (resolution 1.2 keV at 511 keV), is characterized by the so-called *S* parameter. The *S* parameter is calculated as the ratio of the counts in the central area of the peak ($|511 - E_\gamma| \leq 0.85$ keV, where $E_\gamma$ is the energy of the Doppler shifted gamma ray) and the total area of the peak ($|511 - E_\gamma| \leq 4.25$ keV). The Doppler-broadening of the 511 keV annihilation line $\Delta E_\gamma = |511 - E_\gamma|$ is related to the electron–positron annihilating pair momentum component $p_z$, in the detector direction, by the relation $\Delta E_\gamma = p_z c/2$. The *S* parameter reflects the fraction of positrons annihilating with low-momentum electrons. An increase of

the $S$ parameter values with respect to a non-defected sample is an indication of the positron annihilation in open volume defects. In condition of trapping saturation, the higher the $S$-value, the larger the open volume defects (i.e. vacancy, divacancy, voids) in which positrons annihilate. The $S$ parameter was measured as a function of the positron implantation energy in the 0.15–20 keV energy range. In SiC this range corresponds to a mean positron implantation depth ranging from 1 to 2500 nm. For each positron implantation energy, $3 \times 10^5$ counts in the 511 keV annihilation line were accumulated. It corresponds to a statistical error of 0.1% on the measured $S$ parameter.

## 3. Results

XPS results show that the as-deposited films are homogeneous and that the composition remains constant up to the interface. The measured Si/C ratios in the films are correlated to the methane–silane gas mixture. Films a-$Si_xC_{1-x}$ with $x = 0$, 0.1, 0.2, 0.3 and 0.4 were obtained with 0, 10, 20, 30 and 40% silane content in volume (see Table 1). The electrical resistivity of the samples increases with the silicon content from about $10^{10}\ \Omega$ cm for the a-C sample to $10^{14}\ \Omega$ cm for the a-$Si_{0.4}C_{0.6}$ sample (see Table 1).

Hardness measurements are also shown in Table 1. It can be seen that these values are almost constant up to a silicon concentration of 20% and then decrease with the silicon content. The wear test indicates that these films are much more resistant than silicon: the diamond paste polishing pad produces several times a deeper erosion depth in the uncoated silicon substrate than in the film. After 6 h polishing procedure, the uncoated silicon substrates showed an erosion thin-ness of about 20 μm, but the film coatings showed a scratched surface and a thickness diminution inferior to 10% of their original thickness. This slight decrease made impossible the distinction of the erosion resistance among the a-$Si_xC_{1-x}$ samples with different compositions.

The wear test for annealed a-$Si_xC_{1-x}$ samples showed that wear resistance properties are not substantially altered up to 700°C. For comparison, a-C samples showed a high wear resistance up to 500°C.

Raman spectra of amorphous silicon carbon films present a broad band centered at about 1500 cm$^{-1}$ (G-band) with a shoulder at 1350 cm$^{-1}$ (D-band), assigned to sp$^2$ C–C bonds. No signal is observed in the 1100 cm$^{-1}$ region, corresponding to sp$^3$ C–C bonds; nor in the 600–900 cm$^{-1}$ region, corresponding to Si–C bonds. As was stated previously, the Raman efficiency for the sp$^2$ C–C band is high compared with those of the sp$^3$ C–C and Si–C bands.

Fig. 1 shows the Raman spectra of the samples with different composition ($x$ from 0 to 0.4). The results of the fittings with two Gaussian lineshapes are shown in Table 2. It can be seen that the G-peak shifts to lower frequencies and the D-peak relative intensity ($I_D/I_G$) decreases, as the silicon content increases. A similar behavior has been observed in a previous work [2] and in a-$Si_xC_{1-x}$ films obtained by a different method [1];

Table 1
Thickness, hardness and electrical resistivity measurements and Si/C ratio, for the a-$Si_xC_{1-x}$ samples[a]

|  | Thickness (nm) | Si/C | Hardness (GPa) | Resistivity ($\Omega$ cm) |
|---|---|---|---|---|
| a-C | 800 | 0 | 6.8 | $\sim 5 \times 10^{10}$ |
| a-$Si_{0.1}C_{0.9}$ | 970 | 0.11 | 6.5 | $\sim 2 \times 10^{11}$ |
| a-$Si_{0.2}C_{0.8}$ | 1300 | 0.25 | 6.7 | $\sim 1 \times 10^{13}$ |
| a-$Si_{0.3}C_{0.7}$ | 1020 | 0.43 | 5.2 | $\sim 2 \times 10^{13}$ |
| a-$Si_{0.4}C_{0.6}$ | 1500 | 0.67 | 4.6 | $\sim 3 \times 10^{14}$ |

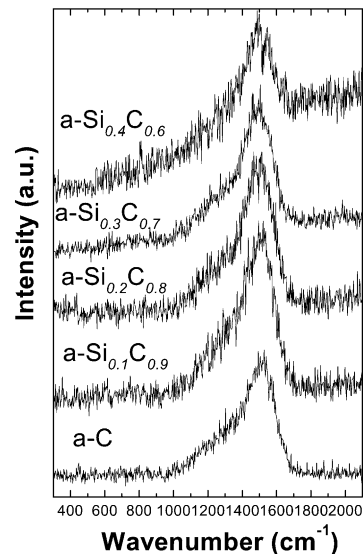[a] The error in the resistivity determination is about 30%.



Fig. 1. Raman spectra as a function of the silicon content.

Table 2
Experimental data from Raman measurements for a-Si$_x$C$_{1-x}$ samples

|  | G-peak frequency (cm$^{-1}$) | $I_D/I_G$ |
| --- | --- | --- |
| a-C | 1521 ± 1 | 1.2 ± 0.2 |
| a-Si$_{0.1}$C$_{0.9}$ | 1516 ± 2 | 1.5 ± 0.2 |
| a-Si$_{0.2}$C$_{0.8}$ | 1507 ± 2 | 1.3 ± 0.2 |
| a-Si$_{0.3}$C$_{0.7}$ | 1498 ± 3 | 0.6 ± 0.2 |
| a-Si$_{0.4}$C$_{0.6}$ | 1495 ± 5 | 0.4 ± 0.6 |

it is indicative of an increase of the sp$^3$/sp$^2$ carbon ratio, as a result of the silicon incorporation. The fluorescence background present in the spectra becomes more intense when the silicon content in the sample increases.

When thermal effects graphitize amorphous carbon samples, their Raman spectra resemble those of glassy carbon, consisting of two bands at 1580 and 1360 cm$^{-1}$. Fig. 2 shows the Raman spectra of the a-Si$_{0.3}$C$_{0.7}$ samples, annealed at different temperatures. The two peaks become narrower as annealing temperature increases but, even at 900°C, they do not reach the position characteristic of a graphitized a-C [2].

The behavior of the $S$ parameter as a function of the positron mean implantation depth for a-Si$_x$C$_{1-x}$ films
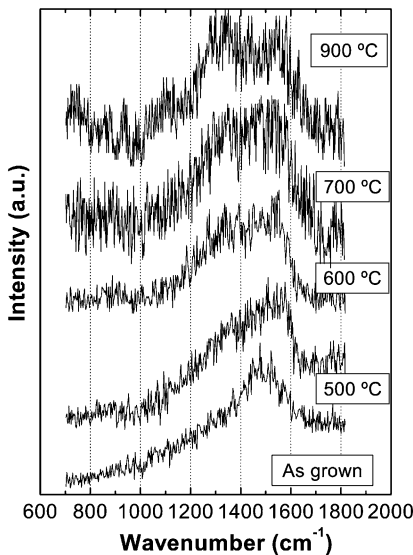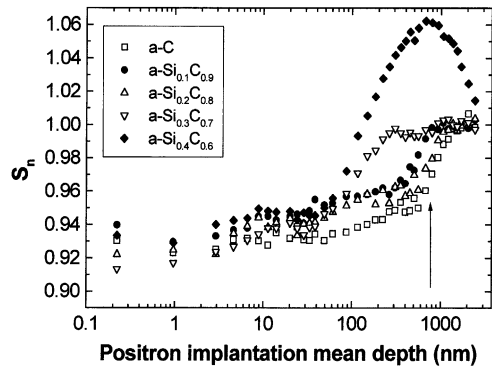


Fig. 3. Positron annihilation measurements. $S$ parameter (normalized to the $S$ bulk value of silicon) as a function of the mean positron implantation depth for the a-Si$_x$C$_{1-x}$ films. The arrow indicates the interface between the carbon film and the silicon substrate.

($x$ from 0 to 0.4) is reported in Fig. 3. The $S$ parameter has been normalized respect to the silicon $S$ bulk value.

The positron mean implantation depth, $x$, in nanometers is calculated through the equation [10]

$$x = \left(\frac{A}{\rho}\right)E^n$$

with the density of our a-Si$_x$C$_{1-x}$ film $\rho = 2.1$ g/cm$^3$, $A = 40$ and $n = 1.6$.

We start by analyzing the $S$ parameter vs. positron mean implantation depth for the a-C film (i.e. $x = 0$) in Fig. 3. The $S$-curve starts from a characteristic $S$ surface value and it remains almost constant up to 50 nm. Then the $S$-value increases slightly up to about 600–700 nm. Going deeper, the $S$ parameter increases again passing through the interface region and reaches the silicon $S$ bulk value. When silicon is added to form a-Si$_x$C$_{1-x}$ films, the $S$-values increase in all the film thickness. However, it can be seen that the $S$-curves for the films with $x = 0.1$ and 0.2 are similar to the $S$-curve of the a-C film. On the other hand, the samples with $x = 0.3$ and 0.4 present a significant increase of the $S$ parameter around 100 nm. In particular, a-Si$_{0.3}$C$_{0.7}$ sample (Si/C = 0.43), shows a small peak around 250 nm and the a-Si$_{0.4}$C$_{0.6}$ sample (Si/C = 0.67) shows a pronounced maximum. In this last sample the $S$ parameter is very high, also in the interface region SiC–Si. The results in Fig. 3 are direct evidence that with the increase of the Si/C ratio in the



Fig. 2. Raman spectra as a function of the annealing temperature for the a-Si$_{0.3}$C$_{0.7}$ sample.

film an increase of the open volume defects is produced. In a previous work [3], we have studied the microstructural modifications of a-C films as a function of the annealing temperature. The $S$ parameter decreases after annealing at 600°C, reaching a value close to that of the microcrystalline graphite ($S \sim 0.919$). As mentioned before, the $S$-values and the hardness in the as grown a-$Si_xC_{1-x}$ samples with $x = 0.1$ and 0.2 show a similar behavior to a-C, while a-$Si_{0.3}C_{0.7}$ shows a higher $S$-value and the hardness begins to decrease. This sample has been thermally annealed in order to study the changes of the voids distribution and their influence on mechanical properties.

The $S$-curves of the a-$Si_{0.3}C_{0.7}$ samples (Si/C ratio equal to 0.43), thermally annealed at different temperatures are reported in Fig. 4. Note that, differently from Fig. 3, a linear $x$-scale has been chosen to better visualize the measured $S$-values through the film. The thermal treatment has a strong effect on the film. In the region between 100 nm and the interface, where the $S$ parameter was high, a decrease of this parameter when increasing the annealing temperature from 500 to 800°C is observed. Especially in this region from 100 to 500 nm, the $S$ parameter of the film annealed at 900°C is slightly higher than those corresponding to the films annealed at 700 and 800°C, respectively.

On the contrary, looking at the region from the surface up to about 150 nm, where the $S$ parameter was low and approximately constant, $S$ increases with the increase of the annealing temperature. A peak appears in the $S$-curves with its maximum around 30 nm. The $S$-value (about 0.96) at the position of the maximum is equal for the samples annealed at 500, 600 and 700°C. With the annealing at 800°C the peak becomes more pronounced, reaching its maximum value at 900°C (about 1.03). The decrease of the $S$-parameter in the deep region of the film (from 150 nm up to the interface with the silicon substrate) is related to a decrease of the open volume defects. On the other hand, near the surface in the first 150–200 nm, a new defected region is formed, with a maximum of open defects after the 900°C annealing.

## 4. Discussion

Next, we shall give an estimation of the size of the open volume defects probed by PAS and we shall show how the mechanical behavior of the films with different Si/C ratios and the a-$Si_{0.3}C_{0.7}$ annealed samples can be well correlated with the distribution of these defects.

There is a uniform distribution of open volume defects, in the as deposited a-C films (Fig. 3, $x = 0$). The major part of these defects disappears with the graphitization process induced by the heat treatment of the material [3]. Adding silicon (Fig. 3, $x \neq 0$), there is an increase of the $S$ parameter in all the depth of the as-deposited films, indicating a more defected structure. The identification of the size of the open volume defects corresponding to the variation of the $S$ parameter can be done by cross checking the existing experimental and theoretical positron data on SiC. The calculated positron lifetime [4,9] are for positrons trapped in vacancy defects in crystalline SiC and consequently can be only used to estimate the size of the open volumes in a-$Si_xC_{1-x}$ However, being the positron lifetime directly proportional to the electron density in the defect, this estimation is expected to be more realistic as the size of the open volume defects in a-$Si_xC_{1-x}$ (or the size of the vacancy-clusters in crystalline SiC) increases. In [11], a lifetime of 260 ps obtained measuring electron irradiated 6H–SiC was attributed to defects; this observation is in correspondence with an increase of 12% of the $S$ parameter with respect to the $S$ bulk value. In [4] about the study of $Ge^+$ implanted 6H–SiC, lifetimes of
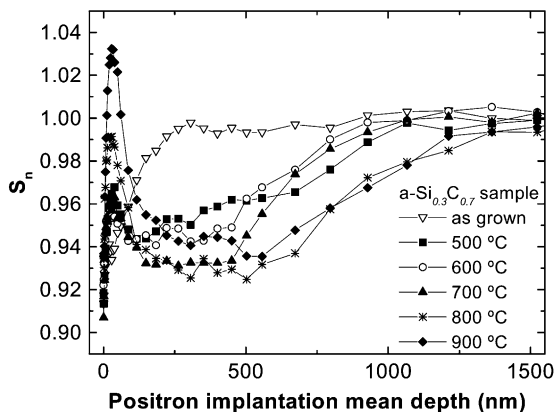


Fig. 4. Positron annihilation measurements. $S$ parameter (normalized to the $S$ bulk value of silicon) as a function of the mean positron implantation depth for the annealed a-$Si_{0.3}C_{0.7}$ films.

235 and 305 ps, respectively, have been attributed to the presence of defects in defective layers in which the respective $S$ parameters increased about 5.7 and 9% from their original $S$ bulk values. On the other hand, from first principle calculations of the positron lifetimes in structures corresponding to defected 3C–SiC and 6H–SiC polytypes, a positron lifetime of 216 ps has been assigned for a $V_{Si}V_C$ divacancy complex and a lifetime ranging from 254 to 321 ps for agglomerates of 2–4 $V_{Si}V_C$ [4,9]. Comparing the above experimental results with the theoretical calculations, an increase of $S$ around 5% could be assigned to the presence of small $V_{Si}V_C$ complexes. A higher increase of the $S$ parameter necessarily must be attributed to the positron annihilation in vacancy agglomerates of increasing size. The 9% increase in $S$ and the 350 ps lifetime found in an amorphous layer [4] were attributed to the presence of vacancy clusters consisting of at least four or six vacancies and, recently, an increase in $S$ of 12–15% was attributed to agglomerates of about seven divacancies [12]. All the above quoted variations of the $S$ parameter are referred to $S$ bulk value of a crystalline SiC not normalized to the $S$ silicon bulk value usually used as a standard one.

If we take as reference the $S$-value of our material, the average of the $S$-values for the samples with $x$ equal to 0.1 and 0.2 (Si/C ratio 0.11 and 0.25) considered between 70 and 400 nm, the resulting value is $S_{ref} = 0.955$. This value, due to the presence of defects, is expected to be higher than the $S$ bulk value of a crystalline SiC. In the a-$Si_{0.3}C_{0.7}$ and in the a-$Si_{0.4}C_{0.6}$ samples (Si/C = 0.42 and 0.67), values of the $S$ parameter around 1 and 1.06, are respectively, reached (see Fig. 3): these values correspond to an increase of 4.7 and 11% of the $S_{ref}$ value. From the above considerations, it can be concluded that this variation corresponds to the presence of open volumes, which size is comparable with small divacancy complexes in the a-$Si_{0.3}C_{0.7}$ samples, and open volumes with larger size (more than four divacancies) in the a-$Si_{0.4}C_{0.6}$ sample. The presence of these open volume defects, indicates a less compact microstructure. This microstructure can be considered as the direct responsible for the decrease of hardness and the increase of the electrical resistivity in the films with Si/C > 0.25.

During the annealing process, the $S$-value corresponding to the a-$Si_{0.3}C_{0.7}$ film in the 150–1000 nm region (see Fig. 4) decreases significantly going from an annealing temperature of 500–800°C. This change could be attributed to a densification process induced by the start of the graphitization as observed by Raman (Fig. 2). At the same time, an increase of open volume defects is observed in the near surface region. The process of formation of these defects near the surface is not clear. One explanation could be that voids diffuse towards the surface during annealing, and once there, they agglomerate around impurities. A second possible explanation is that small open volumes are present in the as-deposited samples but they would not be trapping centers for positrons because they are filled by hydrogen [5], possibly incorporated in the film during deposition. When the hydrogen escapes with the thermal treatments, the small open volumes become active positron traps and they agglomerate with the increase of the annealing temperature. However, the films deposited using high energy ion beam methods, showed an hydrogen content lower than 5%, measured by ERDA [1].

As a matter of fact this defected layer is most probably responsible for the worsening of the wear resistance observed in the sample annealed at 800 and 900°C.

## 5. Conclusions

We have found that silicon incorporation in a-$Si_xC_{1-x}$ increases the thermal stability with respect to a-C films [2], but decreases the hardness when the Si/C ratio is greater than 0.4.

The mechanical properties of deposited thin films depend on the microstructure of the material. In particular, it has been shown that the open volume defects and their distribution through the films have an important role in determining the mechanical behavior of the as-deposited and thermal treated films. PAS has allowed to investigate directly these open volume defect distribution in a "not destructive way", showing that it is a valuable and complementary technique in the characterization of amorphous thin films. This technique has given results well related to the mechanical behavior of the films. In a future, this technique could also be used to predict the mechanical properties in an on-line control of the as-produced materials.

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