Distribution of Pores in \( a\text{-Si}_{1-x}C_x:H \) Thin Films


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Abstract

The aim of this paper is to compare the optical, compositional and morphological properties of \( a\text{-Si}_{1-x}C_x:H \) films deposited by plasma enhanced chemical vapour deposition (PECVD) using different mixtures of silane (\( \text{SiH}_4 \)) and methane (\( \text{CH}_4 \)) under minimum attainable deposition pressure. Films deposited at lower silane flow present a higher carbon content and larger optical gap. The morphology of the films was investigated by small-angle X-ray scattering (SAXS) using two different light sources: (i) conventional tube and (ii) synchrotron radiation. The analysis of the data from both experiments was performed in order to determine a size distribution for spherical pores. The results obtained with both light sources are consistent: the increase in the \( \text{CH}_4 \) concentration implies broader size distribution functions, with an increase of the pore size up to 10 nm. Larger pores are found in films deposited at lower silane flow. For all samples, the density of the smaller pores dominates the size distribution. The relative microvoid density is not proportional to the carbon concentration but presents a maximum for the low carbon content films.

1. Introduction

Thin films based on hydrogenated amorphous silicon and its alloys are used in several opto-electronic devices (Madan & Shaw, 1988; LeComber, 1989). The growth of \( a\text{-Si}_{1-x}C_x:H \) thin films with very low conductivity \( \left( <10^{-14} \text{ } \Omega^{-1} \text{ } \text{cm}^{-1} \right) \) and high optical gap (higher than \( -3 \text{ eV} \)) is particularly important for thin-film transistor (TFT) technology based on amorphous materials (Madan & Shaw, 1988). It is well known that the increase in optical gap is limited by the formation of graphite-like carbon clusters, which provoke a decrease in the optical gap (Sussmann & Ogden, 1981; Bullot & Schmidt, 1987; Mui, Basa & Smith, 1987). Furthermore, hydrogenated amorphous silicon and its alloys, grown as thin films by different methods, present pores in the nanometer size range (Bullot & Schmidt, 1987; Mahan, Williamson, Nelson & Crandall, 1989). In earlier works (Onmori, Pereyra, Sassaki & Carreño, 1989; Carreño, Pereyra, Fantini, Takahashi & Landers, 1994; Mastelaro et al., 1995), we reported the growth of \( a\text{-Si}_{1-x}C_x:H \) thin films having an optical gap as high as \( \approx 4 \text{ eV} \), resistivity higher than \( 10^{15} \text{ } \Omega \text{ } \text{cm} \), carbon content up to 70 at.\% with relatively smaller microvoid concentration, being chemically and structurally similar to crystalline SiC. This unusual material is obtained with very special deposition conditions, known as ‘starving’ plasma, that is a combination of low silane flow, high \( \text{CH}_4 \) partial pressure and low radio frequency (RF) power density (Solomon, Schmidt & Tran-Quoc, 1988; Carreño & Pereyra, 1996).

2. Experimental

The \( a\text{-Si}_{1-x}C_x:H \) samples were deposited with methane concentrations of 40, 80 and 90\% using low silane flow and high silane flow, as shown in Table 1. The gaseous concentrations were adjusted with mass-flow controllers. The substrate temperature was kept constant at 573 K and the RF power density was maintained at 50 mW cm\(^{-2}\). The optical gap \( (E_0) \) is also presented.

The films were simultaneously deposited on different substrates to perform the optical, compositional and morphological characterizations. The thickness of the samples was measured with an Alpha-step profile meter. Spectrophotometric measurements were performed with a Varian Cary-2315 spectrometer to determine the optical gap (Bullot & Schmidt, 1987) of the films deposited on glass substrates.

The atomic concentrations of Si, C and O contamination were determined in films deposited on carbon slides covered with a 60 nm Mo film, by Rutherford back scattering (RBS), using a 2.3 MeV He\(^+\) beam, with scattering angle of 170\°. Forward recoil spectrometry, FRS, was used for H analysis with a target tilt angle of 75\° and a 30\° detection angle. A 7 \( \mu \)m thick Al absorber was adapted to filter the recoiled H from the scattered He beam. Both analyses were carried out at the IBM-Almaden Research Center, San Jose, California, using a 3UH NEC Pelletron Accelerator.

The SAXS experiments were performed on films deposited on Kapton, stacked in a pack of ten foils in order to increase total thickness. The scattered intensity of the Kapton itself was used to remove the parasitic scattering. Transmission-geometry measurements were performed with two different light sources: (i) conventional copper tube \( (\lambda = 0.1542 \text{ nm}) \); and (ii) synchrotron radiation \( (\lambda = 0.1378 \text{ nm}) \) at beam line D22 at LURE, Orsay, France.

The experiments with a conventional copper tube were carried out with 1.2 kW power (40 kV and 30 mA), line-focus geometry, using a Kratky camera and a linear position-sensitive detector (PSD). The acquisition
Table 1. Deposition parameters: \( g \) is the deposition rate, \( t \) is the film thickness and \( E_0 \) is the optical gap

<table>
<thead>
<tr>
<th>Sample</th>
<th>CH(_4) conc. (%)</th>
<th>SiH(_4) flow (scm)</th>
<th>( g ) (nm s(^{-1}))</th>
<th>( t ) (nm)</th>
<th>( E_0 ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI20</td>
<td>0</td>
<td>20</td>
<td>418</td>
<td>1253</td>
<td>1.90</td>
</tr>
<tr>
<td>C5440</td>
<td>40</td>
<td>5.4</td>
<td>238</td>
<td>476</td>
<td>2.02</td>
</tr>
<tr>
<td>C2040</td>
<td>40</td>
<td>20</td>
<td>760</td>
<td>1390</td>
<td>1.98</td>
</tr>
<tr>
<td>C3650</td>
<td>50</td>
<td>3.6</td>
<td>121</td>
<td>343</td>
<td>2.10</td>
</tr>
<tr>
<td>C3680</td>
<td>80</td>
<td>3.6</td>
<td>183</td>
<td>550</td>
<td>2.53</td>
</tr>
<tr>
<td>C3690</td>
<td>80</td>
<td>3.6</td>
<td>184</td>
<td>644</td>
<td>2.75</td>
</tr>
<tr>
<td>C2090</td>
<td>90</td>
<td>20</td>
<td>233</td>
<td>350</td>
<td>2.47</td>
</tr>
</tbody>
</table>

Another check was performed, which simulates the experimental data from calculations obtained with GNOM, involving the particle-size-distribution function up to different maximum values of \( R \) (\( R_{\text{max}} \)), convoluted with the experimental geometry. The results, in this case, showed that the whole \( D(R) \) has to be considered in order to obtain a complete coincidence between experimental data and the GNOM scattering intensities.

The data collected with synchrotron light, in point-focus geometry, are depicted in Fig. 3 for the set of samples specified in Table 1. The data obtained with the conventional X-ray source were corrected

time varied from 50 to 86 h, such that a minimum of 1000 counts channel\(^{-1}\) was achieved. The maximum value for the modulus of the scattering vector, \( q \), was 0.27 A\(^{-1}\); where \( q = (4\pi/\lambda)\sin \theta \), \( \lambda \) is the X-ray wavelength and \( 2\theta \) is the scattering angle. Measurements at larger \( q \) values, up to 0.8 A\(^{-1}\), were also performed in order to check for scattering from smaller voids. In this case, the background and the sample scattering intensity were equal for \( q \geq 0.3 \) A\(^{-1}\).

The experiments with synchrotron radiation were carried out with point focus, PSD detection, an acquisition time of 10 min and a maximum \( q \) value of 0.23 A\(^{-1}\).

The data obtained with synchrotron radiation were normalized by the measured sample transmittance, while the data collected with the conventional tube were corrected, supposing that the scattering intensities vanish for larger values of \( q \). It is important to point out that both data-reduction methods gave similar results.

3. Results

Fig. 1 presents the carbon incorporation (\( x \)) versus the CH\(_4\) concentration in the \( a\)-Si\(_{1-x}\)C\(_x\):H films.

The Guinier plots (Guinier & Fournet, 1955) of the scattering intensities of the film showed continuous straight lines in the \( qR < 1 \) region (\( R_g \) is the radius of gyration), characteristic of a polydisperse system. Therefore, the SAXS data were analyzed with the computer program GNOM (Svergun, 1992), modeling the particle-size-distribution function, \( D(R) \), of spherical pores of radius \( R \). In order to correct the measured data, a series of tests was performed with the computer program GNOM. In this case, a QBASIC computer routine was created, which generates theoretical scattering curves due to a given size-distribution function of spherical particles, as shown in Fig. 2. The tests comprised two steps:

(a) Generation of a theoretical scattering-particle-size distribution, \( D(R) \), with different numbers of points, followed by the calculation of the scattering intensity, which is analyzed by GNOM, in order to determine the ideal numbers of points in \( D(R) \) and \( N(R) = D(R)/V \).

(b) The ideal \( D(R) \) or \( N(R) \) are chosen and scattering intensity plots are calculated for different maximum values of \( q \) (\( q_{\text{max}} \)).
using the computer program Gnom for the line-focus geometry using two different approaches: (i) calculating the correction for the measured height of the slit at the detector position; and (ii) assuming the infinite-slit approximation, dividing the scattering intensity \( I(q) \) by \( q \), followed by data treatment as point focus. Fig. 4 shows the results obtained with the first data treatment. The agreement between the two data-reduction methods was remarkable, showing that, in our experimental conventional X-ray source set-up, the infinite beam height is a good approximation.

The relative microvoid volume fraction \( \eta \) was calculated for the experimental data, considering \( \eta \propto \int I(q)q^2 dq / (\Delta \rho)^2 \) and \( \eta \propto \int I(q)q dq / (\Delta \rho)^2 \) for, respectively, the synchrotron-radiation and conventional X-ray-source measurements. Fig. 5 depicts the relative microvoid volume fraction \( \eta \) for the samples deposited under different silane flows as a function of carbon concentration in the film (\( x \)).

![Graphs showing the normalized particle-size-distribution function](image-url)
4. Discussion

The RBS and FRS results showed that the amount of H incorporated into the films is around 50 at.% and the O content is not larger than 3 at.%, which is probably trapped at the microvoids. The carbon incorporation is more effective for samples deposited at lower silane flow, as shown in Fig. 1.

The optical gap increases with the carbon content but, as shown in Table 1, only samples grown under 'starving' conditions lead to optical gaps greater than 2.5 eV, in agreement with our earlier results (Carreño,
The tests with the GNOM software showed that it fails in describing size-distribution functions of small particles ($R < 10 \text{ Å}$), as pointed out by other authors (Mulato & Chambouleyron, 1996). The results are strongly dependent on $q_{max}$, as depicted in Fig. 2. The larger $q_{max}$ is, the better is the agreement between the theoretical particle-size-distribution function and the GNOM results. In the case of our experimental data, since $q_{max} \approx 0.3 \text{ Å}^{-1}$, only values of $R > 10 \text{ Å}$ were considered. It is important to point out that the results with both light sources gave identical $D(R)$ functions. Therefore, the use of conventional sources in the analysis of materials showing low scattering intensities is possible, provided there is enough data-collection time. Of course, the use of synchrotron radiation is recommended, since the point-focus data-normalization procedure with GNOM software is straightforward and time-consuming experiments, where stability precautions have to be taken into careful account, are avoided.

The particle-size distribution showed that the increase in carbon content promotes broadening in $D(R)$ towards larger particle sizes, besides an increase in the value of $R_{max}$. These results indicate that the microvoid size distribution depends on the carbon content, independently of the silane flow. Considering the number of particles with a given particle size, $N(R)$, the relative number of particles with smaller sizes, with good precision for $R > 10 \text{ Å}$, is higher particularly for low carbon content samples.

The results concerning the relative microvoid volume fraction ($\eta$) showed that $\eta$ is not an increasing function of $x$, which agrees with our previous data about the morphology of $a$-$\text{Si}_{1-x}$-$\text{C}_{x}$:$\text{H}$ deposited under ‘starving’ plasma conditions (Carreño, Pereyra, Fantini, Takahashi & Landers, 1994).

5. Conclusions

The optical, compositional and morphological properties of $a$-$\text{Si}_{1-x}$-$\text{C}_{x}$:$\text{H}$ thin films, deposited by PECVD under ‘starving’ plasma regime with two different silane flows, depend on the silane flow. The higher optical gaps (>3 eV) are achieved for larger carbon incorporation ($x > 0.5$) at the lowest $\text{SiH}_4$ flow [3.6 sccm (where sccm is standard cubic centimetres per minute)]. The morphological characteristics of the films, obtained from SAXS experiments, showed that the increase in the carbon concentration in the solid phase implies broader spherical-particle-size-distribution functions, with an increase of the pore size up to 10 nm. Larger pores are found in films deposited at lower silane flow, which always lead to higher carbon content. For all samples, the density of the smaller pores dominates the particle-size-distribution function. The relative microvoid density is not proportional to the carbon concentration but presents a maximum for low carbon content films.

References