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STRUCTURAL PROPERTIES OF a-$Si_{1-x}C_x$:H BY SAXS AND IR SPECTROSCOPY

DAVOR GRACIN[1] and PAVO DUBČEK

"R. Bošković" Institute, POB 1016, Bijenička 54, 10000 Zagreb, Croatia

Dedicated to Professor Boran Leontić on the occasion of his 70$^{\text{th}}$ birthday

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The a-$Si_{1-x}C_x$:H thin films, with carbon concentrations up to $x = 0.3$ deposited by means of a DC magnetron sputtering source, using benzene vapour as the origin of carbon atoms, were analysed by small-angle X-ray scattering (SAXS) and IR spectroscopy. The incorporation of carbon atoms in a-Si:H results in the appearance of IR absorption related to the Si-C and C-H bonds and a slight decrease of absorption related to Si-H bonds. By increasing the carbon concentration, stretching frequency of Si-H bonds increases. This frequency, which is related to the described changes, is considered to be the consequence of an increasing void volume ratio and/or void volume per each Si-H oscillator. The SAXS data of pure a-Si:H indicate "particles" with the giro radius $R_G = 1.27$ nm, which increases with the carbon content up to $R_G = 2.05$ nm. These "particles" are attributed to the clusters of small voids with dimensions up to several silicon vacancies.

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1. Introduction

Amorphous silicon carbide has been produced by a variety of preparation techniques, using different methods to introduce carbon atoms into the silicon matrix. They result in different properties, depending not only on the composition but also

[1]Corresponding author, E-mail: gracin@rudjer.irb.hr tel. (+385-1) 456-0970,

on different distributions of inhomogeneities from the atomic level to the nanometer scale [1]. We have studied some properties of a-$Si_{1-x}C_x$:H deposited by sputtering, where the source of carbon atoms was benzene vapour added into the vacuum chamber during the film growth.

Some of the structural properties of the samples were reported earlier. In particular, by an analysis of the optical properties in visible and near IR part of the spectrum, it was concluded that the samples contain voids whose volume fraction increases with carbon concentration [2,3].

On the nanometer scale, as verified by Auger spectroscopy, carbon is homogeneously distributed. However, above $x = 0.2$, a certain amount of C-C bonds in the σ and π configurations has been observed by Raman spectroscopy [2,4].

Here, we report on the small angle X-ray scattering (SAXS) measurements using the same type of samples. The SAXS results are discussed together with those derived from IR data, in the framework of the previously proposed structural model [5].

2. Experiments

Thin amorphous hydrogenated silicon-carbide films, of a thickness of about 0.8 μm, were deposited by DC magnetron sputtering in an argon-hydrogen gas mixture, onto non-heated monocrystalline silicon and glass substrates. The benzen vapour was introduced near the surface of the growing film whithout interfering in the discharge processes.

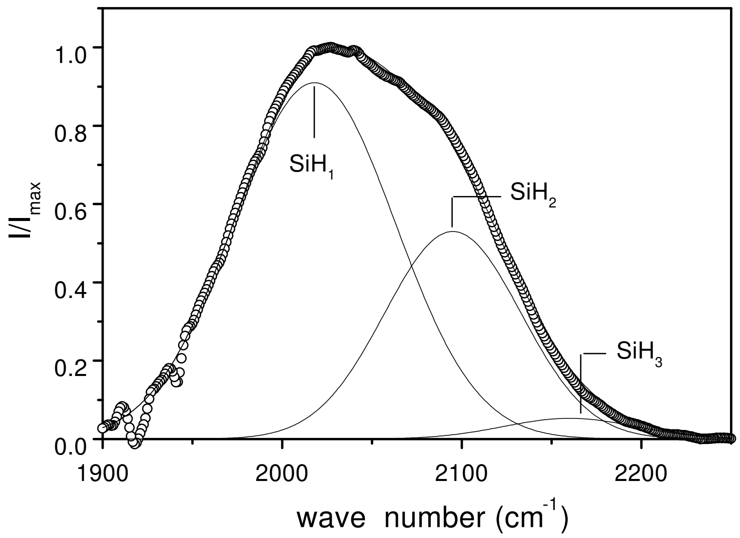

Fig. 1. Deconvolution of the absorption band corresponding to the stretching vibration of Si-H *bonds; the open circles are experimental points.*

The IR transmittance measurements were performed by using a Perkin Elmer 17110 FTIR spectrometer. The spectra were converted into absorption spectra by standard methods [6]. The deconvolution of absorption bands was done by the least-squares fitting, assuming a Gaussian intensity distribution. A typical result obtained by using this procedure is plotted in Fig. 1 for the Si-H stretching-related absorbtion line which has been deconvoluted into 3 bands: SiH_1, SiH_2 and SiH_3.

The dielectric constant for long wavelengths, ϵ, was calculated from the interference fringes in transmission IR spectra [7].

The hydrogen content, C_H, was obtained from the integral absorption in the wagging-twisting-rocking band of IR spectra, using the value 1.6×10^{19} cm^{-2} as the proportionality constant [5]. The carbon content, C_C, was estimated by Auger spectroscopy.

The SAXS data were step-scanned using a standard Kratky camera with a modified sample carrier, which make possible a precise positioning of the sample and accurate determination of the primary and reflected beam angle at small ("grazing") incidence angles. In this geometry, the line-collimated X-rays are totally reflected on the sample surface, and only a part of the primary beam enters the film (due to the roughness of the surface). Therefore, a nonstandard raw-data treatment is applied [8].

3. *Results and discussion*

3.1. *Infrared spectroscopy (IR)*

The incorporation of carbon atoms in a-Si:H results in an increase of absorbtion of IR radiation related to atom groups containig carbon. By increasing the carbon concentration, the Si-C related absorption (750 – 800 cm^{-1}) gradually increases (see Fig. 2). The absorption related to silicon-hydrogen bonds slightly decreases in favour of C-H bonds (see stretching vibrations of Si-H bonds in the 2000 – 2200 cm^{-1} region in Fig. 2). The C-H bonds absorption frequencies are around 1000 cm^{-1} and between 2800 and 3000 cm^{-1}, indicating $CH_{2,3}$ bonds in the sp^3 configuration.

Special attention is paid to the stretching frequencies of Si-H bonds which are used for the estimation of the size of voids. The stretching frequency of Si-H bonds increases as the carbon content is increased (Fig. 3). This shift reveals severall effects. The first effect is the change in the bond forces due to the substitution of Si-atoms by C-atoms. The second one is the appearance of Si-H bonds at a frequency above the peak absorption (SiH_2 and SiH_3) and the third one is the increase of volume around each Si-H oscillator of the same SiH_x atom group [5].

For a quantitative analysis of the IR spectra, a simple model from Ref. [2] was adopted, where a-$Si_{1-x}C_x$:H was assumed to be a network of silicon and carbon atoms interrupted by voids. The hydrogen atoms are placed presumably in voids, decorating completely internal surfaces of voids. In this model, Si-H stretching frequency, determinated by the "solid state effect", mostly depends on the size of voids and changes in "matrix effects" induced by the substitution of a certain number of Si atoms by carbon and/or $CH_{1,2,3}$ atom groups. In general, a-Si alloys contain all types of Si-H bonds, SiH_1, SiH_2 and SiH_3, each occupying a different

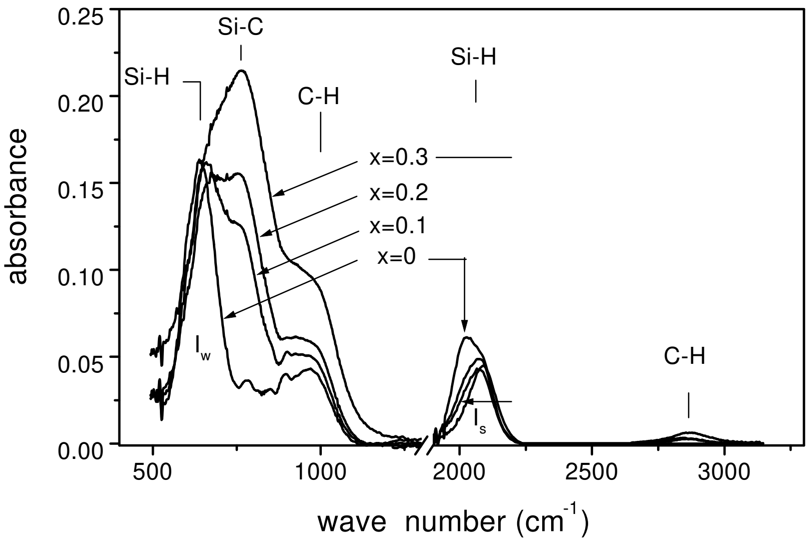

Fig. 2. Infrared absorption spectra of a series of a-$Si_{1-x}C_x$:H *samples; the typical assignations of absorption bands are marked.*

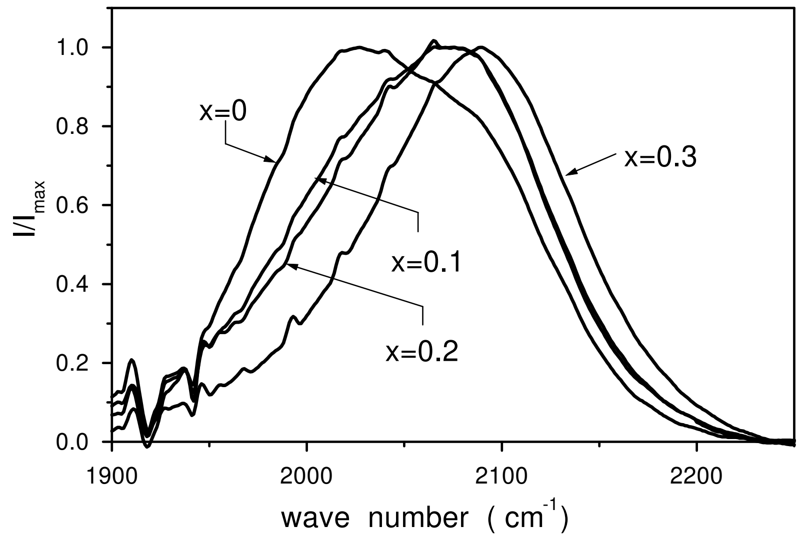

Fig. 3. Absorption bands, normalised to the peak values, corresponding to the Si-H *stretching vibrations of* a-$Si_{1-x}C_x$:H *specimens; the carbon content of the samples is indicated.*

volume per Si-H bond. This volume, V_i in nm^3, can be estimated [5] using the equation

$$V_i = 0.20F^{*2}\,(F^* - 1)\,(\omega_{\mathrm{G}\,i} - \omega_{\mathrm{S}\,i})^{-1} \tag{1}$$

where $\omega_{\mathrm{G}\,i}$ and $\omega_{\mathrm{S}\,i}$ are the stretching frequencies of the corresponding type of Si-H oscillator in gaseous (G) and solid (S) phase. F^* is the local field correction that can be estimated [5] by the semi-empirical equation

$$F^* = \sqrt{10\,\varepsilon^{\frac{1}{2}}\,\frac{I_s}{I_w}} \tag{2}$$

where ε is the dielectric constant. I_s and I_w are the integrated absorption in stretching (s) and wagging-twisting-rocking (w) mode in IR spectra (see Fig. 2). Since $\omega_{\mathrm{S}\,i}, \omega_{\mathrm{G}\,i}, I_{s,w}$ and ϵ are measured values, using Eqs. (1) and (2), volume per one Si-H oscilator, V_i, can be estimated. Consequently, the total contribution of the void volume can be estimated by a summation over all Si-H oscillators

$$v = \sum \frac{V_i C_{\mathrm{H}\,i}}{V_0}\,, \tag{3}$$

where $C_{\mathrm{H}\,i}$ is concentration of Si-H bonds of i-th type and V_0 is average volume occupied by silicon atom (about 0.020 nm^3). The results of estimations obtained by using of above relations are listed in the second and third columns of Table 1. Both sets of values, the volume per Si-H oscilator, V_i (second column), and the volume void ratio, v (third column) show, more or less, a gradual increase with the carbon concentration. The increase of V_i and v is possibly a consequence of the Si network deformation in the vicinity of voids, due to the substitution of Si atoms by the smaller ones, the carbon atoms. Also, the growth kinetics changes somewhat as the carbon content increases.

TABLE 1. The average volume per Si-H *bond, V_i, the void volume ratio, v, the average electron density in void-rich region, ρ_0, the electron density difference between the void-rich and the void-free regions, $\Delta\rho$, the calculated right-hand side of Eq. (4), I_{calc} and the giro radius, R_G, of* a-$\mathrm{Si}_{1-x}\mathrm{C}_x$:H *for different carbon concentrations (x).*

x	V_i (nm^3)	v	ρ_0	$\Delta\rho$	I_{calc}	R_G (nm)
0.0	0.010	10	4	10	9	12.7
0.1	0.011	13	3.8	9.4	10	18.4
0.2	0.021	19	2	10.5	17	20.5
0.3	0.023	19	1.8	9.8	15	17.3

3.2. Small-angle X-ray scattering (SAXS)

The SAXS data, desmeared and corrected for the background scattering, are shown in Fig. 4 in the so-called Guinier plots (logarithm of intensity vs. the square of the scattering angle[2]), along with the calculated best fit. According to the Guinier approximation, the gradient of this fit gives the radius of gyration (R_G), which indicates the dimension of detected "particles". The obtained results for R_G are listed in Table 1 in the last column. The giro radius increases with the concentration up to the 20% of carbon. Further increase in carbon content results in a decrease of R_G.

A similar result, the well-defined gyro radius, was already observed in a-Si:H

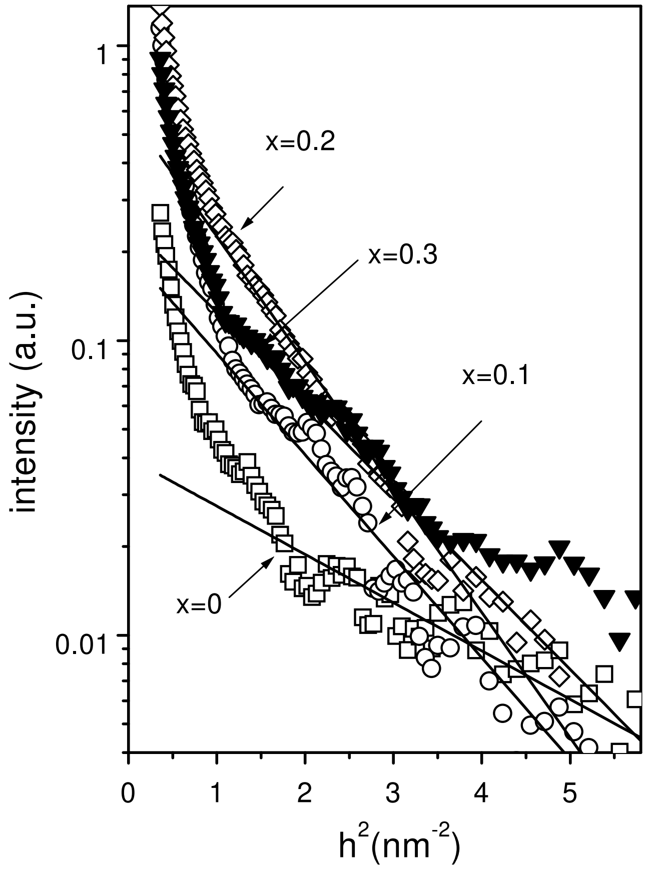

Fig. 4. Guiner plots of a-$Si_{1-x}C_x$:H *specimens (logarithm of intensity vs. the square of the angle); the squares are for pure* a-Si:H *($x = 0$), open circles for $x = 0.1$, open diamonds for $x = 0.2$ and triangles for $x = 0.3$. The full lines represent the best linear fits. The gradients were used to determine the radii of gyration, R_G.*

[2]We use the term "scattering angle" for $h = 4\pi \sin\Theta/\lambda$.

and a-$Si_{1-x}C_x$:H by SAXS. It reveals the presence of "particles" of the specific size and electron density, different from the rest of the material. It was found that the R_G values have variations from about a nanometer [1 – 1.4 nm] to several tens of nm [15]. One of the most frequent assignation of "particles" was single void. By using this interpretation, a single cavity with our R_G values (between 1.2 and 2.0 nm) corresponds to a hundred or even thousands of missing Si and/or C atoms. The formation of such large cavities in sputtered samples seems to be extremely unlikely. Besides, in such large voids, the frequency of stretching vibrations of Si-H bonds should be much higher than the measured ones.

That is why we assume as a better interpretation, at least for our samples, the somewhat older model, proposed also by Petrich et al. [16] in a discussion on the results of single and multiple quantum nuclear magnetic resonance measurements. That model predicts a columnar structure: the material consist of regions of lower and higher density. Lower density regions contain agglomerates of small voids (clusters of voids), with single voids of the size up to the silicon multivacancy. The higher-density part is assumed to be free of voids.

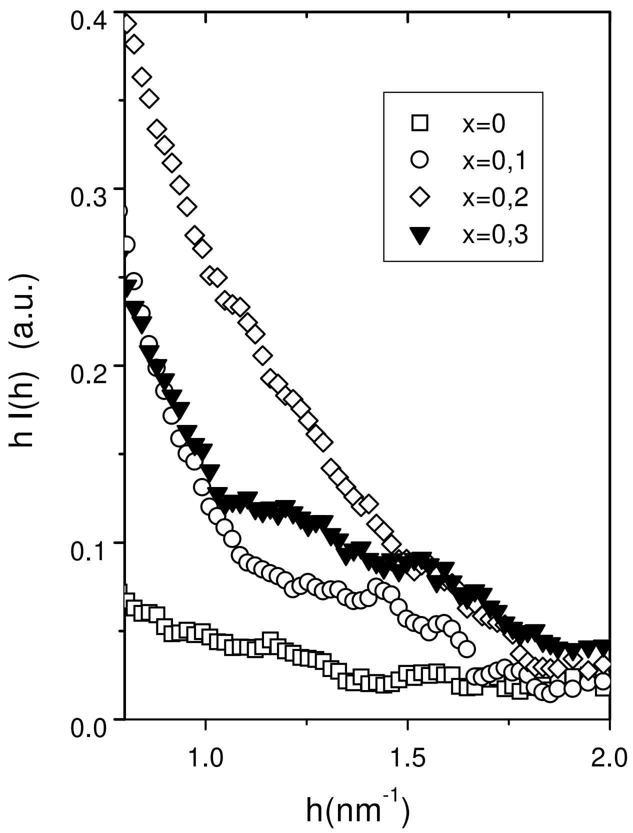

Fig. 5. The product of the scattered intensity and angle, hI, versus the scattering angle, h, for a-$Si_{1-x}C_x$:H *samples.*

Another way to present the SAXS data is illustrated in Fig. 5 where the product of the scattering intensities, I, and the scattering angle, h, is plotted versus the scattering angle. The area below the plotted points is proportional to the volume contribution of the detected "particles". It increases with the carbon concentration up to $x = 0.2$ and then decreases. According to Refs. [10–12,17], since we have line focus rather than a point one, the folowing relation is valid:

$$k \int h\, I(h)\, \mathrm{d}h = (\Delta\rho)^2\, v_f\, (1 - v_f)\,, \tag{4}$$

where v_f is "particle" volume fraction and $\Delta\rho$ the difference in electron density between "particles" and the remaining material. If the "particles" are voids clusters, as proposed above, v_f can be replaced with the void fraction, v, estimated from IR measurements. Futhermore, according to the assumptions of our model, the voids are completely decorated with hydrogen. Therefore, the IR-estimated values for volume corresponding to each Si-H oscilator, V_i, can be used to estimate $\Delta\rho$. Assuming that the carbon atoms are placed substitutionally, deforming the Si-network at isolated places, the difference in electron density is given by the relation (see Ref. [11]):

$$\Delta\rho = [(1 - x)\, n_{\mathrm{Si}} + x\, n_{\mathrm{C}}] - \rho_0\,, \tag{5}$$

where n_{Si} is the electron density of silicon in an average volume which corresponds to a Si atom in the silicon matrix (e.g. $V_0 \approx 0.020$ nm^3), n_{C} the electron density of carbon in the same volume and ρ_0 the electron density in the voids-rich region normalised to the Si vacancy. Since every Si-H bond corresponds to one hydrogen

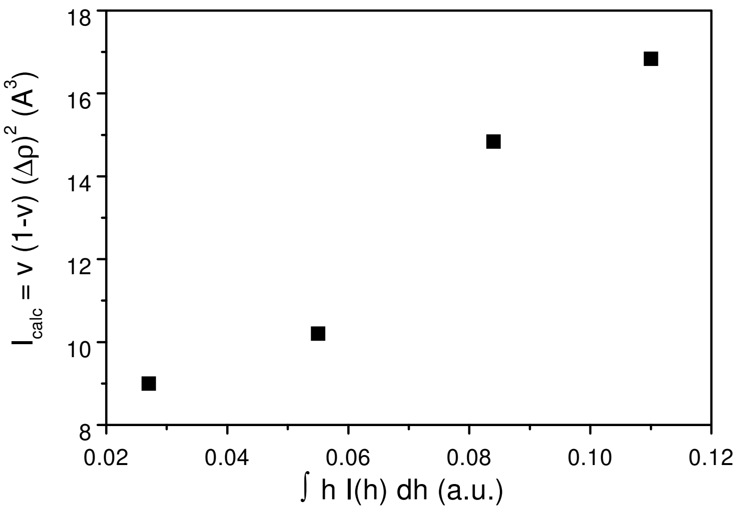

Fig. 6. Calculated values, I_{calc} (IR data, Eq. (4)) versus the integrated intensity calculated from Fig. 5 (SAXS data).

atom, e.g. 2 electrons, the electron density in voids-rich regions is approximated by the relation $\rho_0 = (2e/V_i)\,V_0$.

The calculated values of ρ_0 and $\Delta\rho$ are listed in Table 1. The values of ρ_0 decrease with increasing carbon content because the average volume of individual voids increases. On the other hand, the electron density of tissue also decreases with the carbon incorporation, since by this process the silicon atoms are replaced by carbon atoms of lower electron density. The final result is that $\Delta\rho$ undergoes relatively small changes.

Figure 6 displays the right-hand side of Eq. (4), calculated from the results of IR measurements and the proposed model (denoted by $I_{\rm calc}$, fifth column in Table 1), versus $\int h\,I(h)\,\mathrm{d}h$, eg., the results calculated from SAXS data. According to Eq. (4), a linear dependence is expected which is fulfilled reasonably well, thus confirming the model and the method of analysis.

4. *Conclusion*

The magnetron deposited a-$Si_{1-x}C_x$:H samples consist of void-free tissue and regions of lower density material. The lower-density part contains clusters of small voids decorated with hydrogen. By increasing the carbon concentration from $x = 0$ to $x = 0.3$, the void-volume ratio increases and the average volume of each void seems to become larger. The average size of clusters increases with the carbon content from 1.27 nm at $x = 0$ up to 2.05 nm at $x = 0.2$. Above that value, at $x = 0.3$, the cluster size slightly decreases to 1.73 nm.

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STRUKTURNA SVOJSTVA a-$Si_{1-x}C_x$:H SAXS-om I IR SPEKTROSKOPIJOM

Primijenili smo raspršenje rendgenskog zračenja pod malim kutom (SAXS) i infracrvenu spektrometriju (IR) za analize tankih slojeva a-$Si_{1-x}C_x$:H, napravljenih DC magnetronskim izvorom čestica u prisustvu benzenskih para, za više koncentracija ugljika do $x = 0.3$. Ugrađivanje ugljikovih atoma u a-Si:H ima za posljedicu pojavljivanje IR apsorpcije zbog Si-C i C-H vezanja i slabo smanjenje apsorpcije u području koje odgovara Si-H vezanju. S povećanjem koncentracije ugljika, povećava se frekvencija istezanja Si-H vezanja. Ta frekvencija, koja je u svezi s opisanim promjenama, smatra se posljedicom povećanog udjela praznina i/ili volumena praznine po Si-H oscilatoru. Podaci SAXS za čisti a-Si:H ukazuju na "čestice" sa žiro polumjerom $R_G = 1.27$ nm koji se poveća za veće sadržaje ugljika do $R_G = 2.05$ nm. Te se "čestice" pridjeljuju nakupinama malih praznina. Njihov je volumen reda veličine nekoliko jednoatomskih praznina u siliciju.