THE EFFECT OF THE SUBSTRATE TEMPERATURE AND THE ACCELERATION POTENTIAL DROP ON THE STRUCTURAL PROPERTIES OF SIC THIN FILMS DEPOSED BY TVA METHOD

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Abstract. *Crystalline Si-C thin films were prepared at substrate temperature between* 200 °C *and* 600 °C *using Thermionic Vacuum Arc (TVA) method. To increase the acceleration potential drop a negative bias voltage up to* -1000 V *was applied on the substrate. The 200 nm thickness carbon thin films was deposed on glass and Si substrate and then* 200-500 nm *thickness Si-C layer on carbon thin films was deposed. Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM), X-Ray and Photoelectron Spectroscopy (XPS) techniques was performed to characterize the structure of as-prepared SiC coatings. At a constant acceleration potential drop, the crystallinity of the Si-C films deposed on C, increase with increasing of substrate temperature. On the other part, significant increases in the acceleration potential drop at constant substrate temperature lead to a variation of the crystallinity of the SiC coatings XPS analysis was performed using a Quantera SXM equipment, with monochromatic AlKα radiation at* 1486.6 eV.

Keywords: TVA method, Si-C coating, TEM, HRTEM, XPS

1. Introduction

Silicon carbide (SiC) is recognized as an important non-oxide ceramic material, that has some exclusive properties as high hardness, high melting point chemical and thermal stability, oxidation resistance, and suitable electrical and thermal conductivity. On the other hands is considerate as a wide band gap semiconductor. All of these properties determine extensive applications of silicon carbide in

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several technologies, for instance high power, high temperature electronic devices, abrasion and cutting techniques, UV detectors [1,2], chemical sensors [3], micromechanical systems (MEMS)[4,5], nanoelectronics [6] and also an important category of biomedical applications[7]. Additionally, it can be doped both n-type and p-type for the purpose of certain optical and electrical applications [8]. Several methods can be used to syntheses SiC thin films such as Chemical Vapor Deposition (CVD) [9], Molecular Beam Epitaxy (MBE), Electron Cyclotron Resonance (ECR) [10] or Thermionic Vacuum Arc (TVA) method [11,12]. The purpose of this paper is to synthesize Si-C composite thin films at different substrate temperatures and at different acceleration potential drops using TVA method.

Experimental set-up

The proposed method to obtain Si-C is Thermionic Vacuum Arc, which is characterized by high voltage (0.3-4kV), low current (0.1-4A) discharge, ignited in the pure vapors of materials to be deposited. One significant advantage of this method is the lack if any buffer gas inside the coating chamber but also the possibility to control the ions energy using acceleration or deceleration potential drop on the substrates during the deposition of by means of a bias DC supply [13-16].

The evaporation of desired materials takes place in high vacuum conditions (about 10^{-4} Pa). An external heated tungsten (W) grounded cathode having 0.8-1.2 mm in diameter produces thermal electrons by a 20-60 A current passing through it. These electrons are accelerated and focused through a Wehnelt cylinder towards the anode by the applied high voltage (0.3-4 kV). The electron beam focus is necessary to ensure melting and evaporation of the material's atoms. The high voltage also ensures the ionization of the evaporating atoms and the ignition of the electrical discharge. The ions are directed with high energies (200-1000 eV) towards the substrates. TVA plasma is localized within 5-10 cm from the anode-cathode system. This make possible the ignition of multiple TVA sources simultaneously (in our case C and Si plasma sources) [17]. TEM and HRTEM analysis was performed on Philips Tecnai F30G2 (300 kV setup) and Philips CM120ST (at 100kV). Surface analysis performed by X-Ray Photoelectron Spectroscopy (XPS) was carried out on a Quantera SXM equipment, with a base pressure in the analysis chamber of 10^{-9} torr. The X-ray source was Al K_α radiation (1486.6 eV, monochromatized) and the overall energy resolution is estimated at 0.65 eV by the full width at half maximum (FWHM) of the $Au4f_{7/2}$ line. In order to take into account the charging effect on the measured Binding Energies (BEs), the spectra were calibrated using the C1s line (BE = 284.8 eV, C-C (CH)n bonding's) of the adsorbed hydrocarbon on the sample surface. A dual beam neutralizing procedure (e^- and Ar^+ ion beams) has been used to compensate the charging effect in insulating samples.

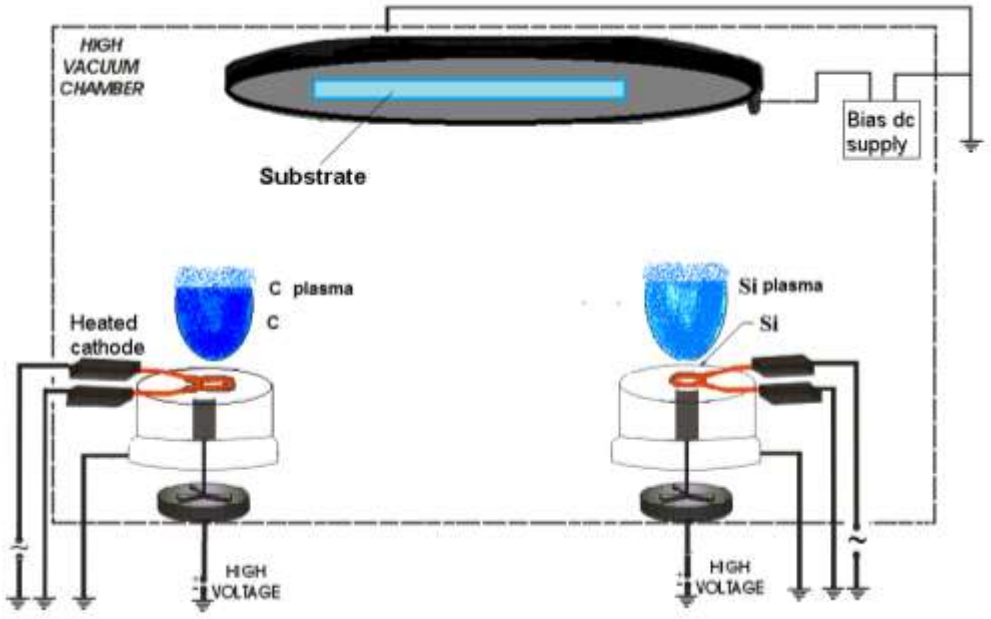

Fig. 1. Thermionic Vacuum Arc set-up.

Results and discussions

Influence of the substrate temperature

Silicon carbon films obtained without bias at 600°C (Sample S1) and 1000 °C (Sample S2) are shown in Figure 2. Both samples S1 and S2 consist by successive C-Si films on 200 nm carbon film on Si substrate.

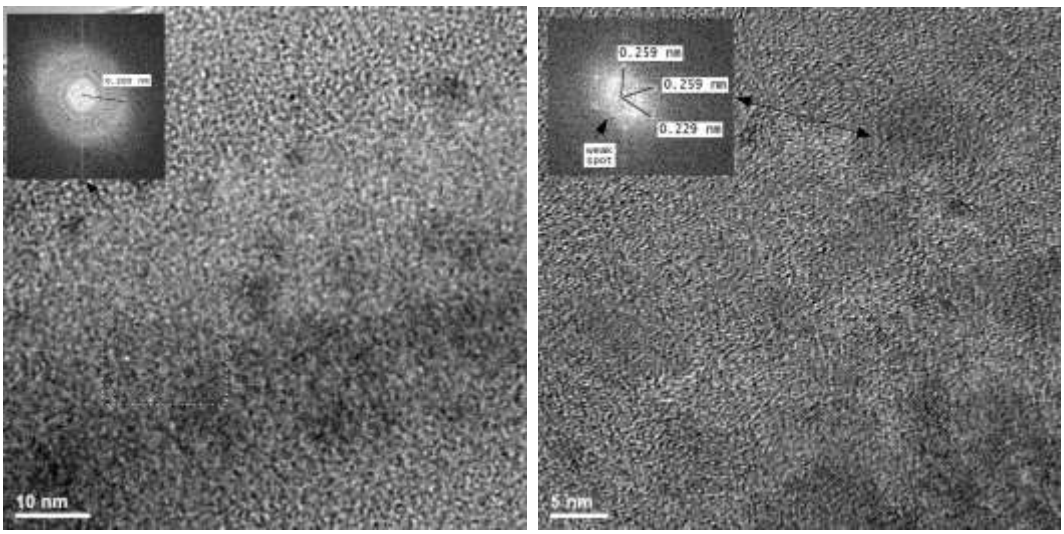

Fig. 2. HRTEM images for Si-C samples without bias, S1 (left) and S2 (right).

For sample S1 we observe a beginning of crystallization, the FFT representation (left inset Figure 2) showing that there is organization at around 0.300 nm. Instead, in the case of sample S2, we can identify using FFT representation (right inset Figure 2), SiC crystallites, the SiC crystal oriented in the [02$\underline{2}$] direction, with measured interplanar distances at 0.259 and 0.229 nm having Miller indices (111) and (200) as we determines assuming the SiC cubic structure (space group F-43m and lattice parameter a = 0.453 nm).

Influence of the acceleration potential drop

In Figure 3 are shown the HRTEM images for samples S3 and S4. The samples S3 and S4 consists both by 400 nm Si-C film on 200 nm C film on Si substrate and glass substrate respectively. The DC bias was -400 V for sample 3 and -1000 V for sample S4, and substrate temperature was maintained at 200 °C for both samples.

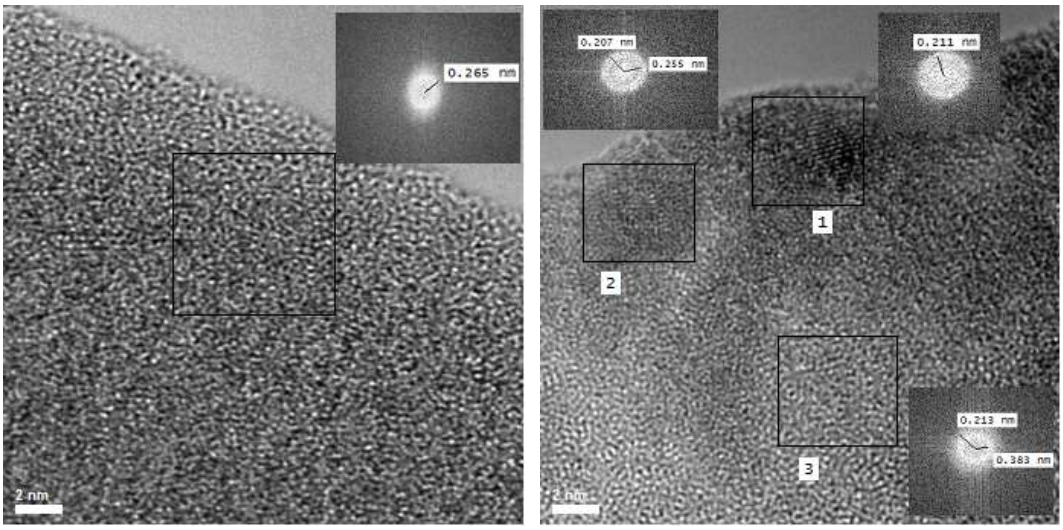

Fig. 3. HRTEM images for Si-C samples S3 (left) and S4 (right).

In the case of sample S3 we observe an amorphous structure, the interplanar distance identified using FFT is 0.265 nm, and we can assume the existence of an organization with neighbors at this distance. In conclusion, we can discuss the existence of an amorphous phase SiC.

In the case of sample S4 we have identified three different areas. In the first area, there are interference fringes that can be associated with the cubic structure of SiC (d_{200} ~ 0211 nm). In the second area there ordering at close range, the peak is located between the values of 0.207 and 0.255 nm. In the third area, distances between 0.213 nm and 0.383 nm distributed. Associate the two with SiC amorphous and amorphous zone 3 with C. In conclusion, in this case we obtain a no uniformly film in the structural point of view, with the amorphous structure, with valuable small crystalline inclusions of the order of 2-4 nm.

XPS analysis

X-ray Photoelectron Spectrosopy (XPS) - analysis was used to determine the chemical states of the elements present on the surface and, after quantitative analysis, to find the element and the chemical state relative concentrations as well. After scanning survey XPS spectra, the high-resolution photoelectron spectra of the most prominent XPS transitions (C^{1s}, O^{1s} and Si^{2p}) were recorded for the samples S5 (400 nm C-Si film on 200 nm C film on Si substrate at 200 °C), S6 (400 nm C-Si film on 200 nm C film on Si substrate at 400 °C) and S7(400 nm C-Si film in 200 nm C film on Si substrate at 600 °C).

It is appropriate to note here that all the calculations were performed assuming that the samples were homogeneous within the XPS detected volume. We have to emphasize that the errors in our quantitative analysis (relative concentrations) were estimated in the range of ± 10 %, while the accuracy for Binding Energies (BEs) assignments was ± 0.2 eV.

The superimposed CPS survey spectra is shown in Figure 4 and the deconvoluted C^{1s} XPS spectrum and deconvoluted Si^{2p} XPS spectrum in Figure 5 and Figure 6 respectively. The Table 1, Table 2 and Table 3 reveal the elements relative concentrations, carbon chemical state relative concentrations and silicon chemical state relative concentrations respectively.

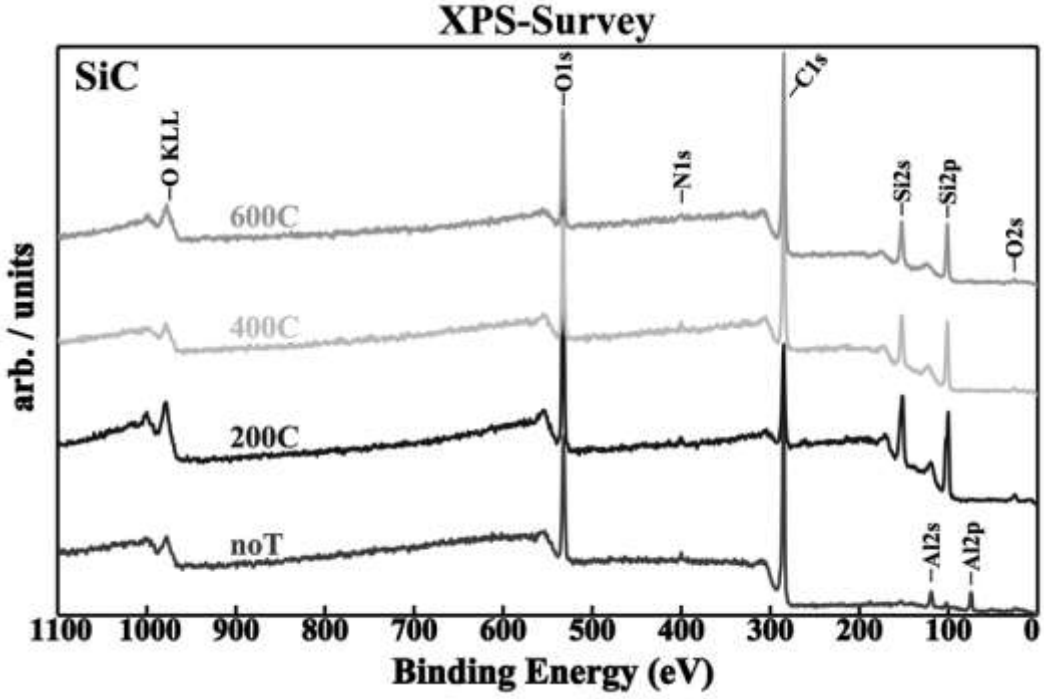

Fig. 4. The superimposed XPS-Survey spectra.

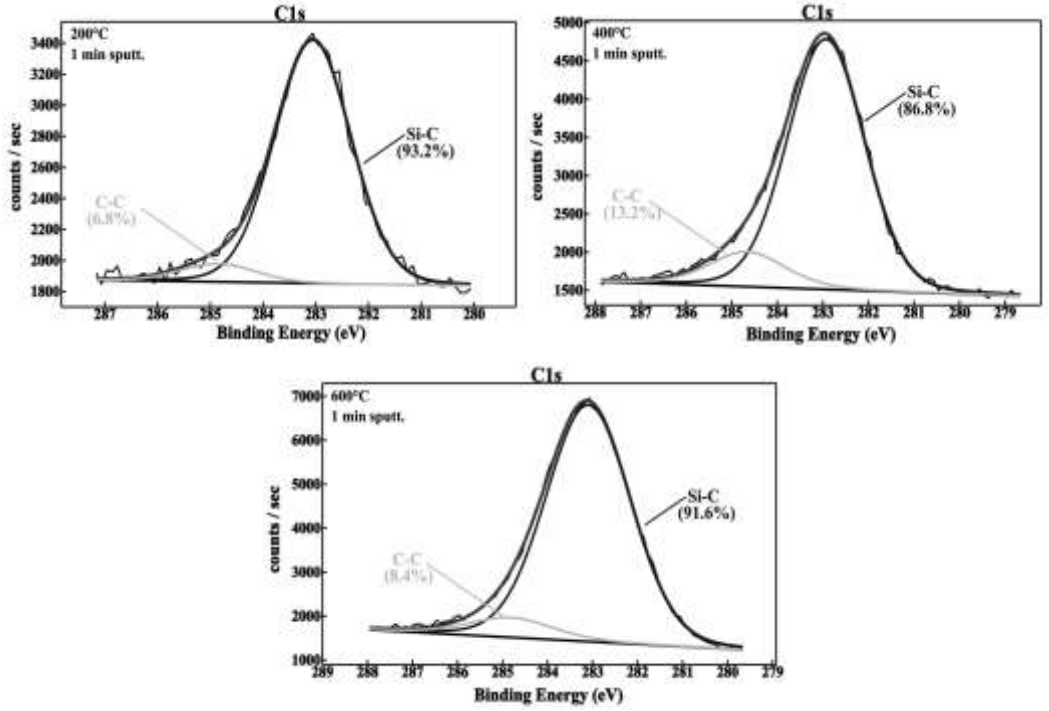

Fig. 5. The deconvoluted C1s XPS spectrum after 1 min sputt.

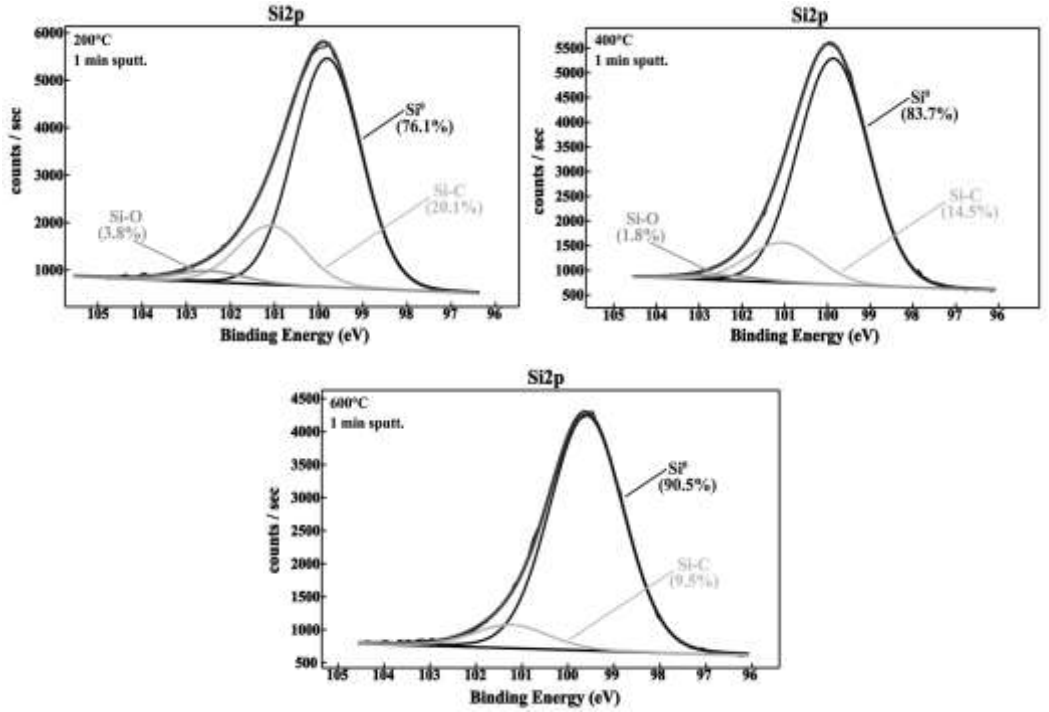

Fig. 6. The deconvoluted Si2p XPS spectrum after 1 min sputt.

Table 1. Element relative concentrations (at%)

200 °C	23.5	11.2	65.3
C/Si	26.5	-	73.5
400 °C	46.0	6.8	47.2
C/Si	49.4	-	50.6
600 °C	68.0	3.8	28.2
C/Si	70.7	-	29.3

Table 2. Carbon chemical state relative concentrations (at%)

Sample	**Carbon chemical state relative concentrations (%)/ Binding energy (eV)**			
	Si-C	**C-C**	**C-O**	**C=O**
200 °C as received	15.5 283.1	64.8 284.8	13.5 286.4	6.2 288.3
1 min sputt.	93.2 283.1	6.8 284.9	-	-
400 °C as received	20.2 282.7	66.3 284.5	11.1 286.3	2.4 287.7
1 min sputt.	86.8 282.9	13.2 284.7	-	-
600 °C as received	20.1 282.9	62.1 284.4	14.0 286.1	3.8 288.0
1 min sputt.	91.6 283.1	8.4 284.8	-	-

Table 3. Silicon chemical state relative concentrations (at%)

Sample	**Silicon chemical state relative concentrations (%)/ Binding energy (eV)**			
	Si^0	**Si-C**	**Si-O**	**Si^{4+}**
200 °C as received	48.9 99.7	14.8 101.2	22.2 102.4	14.1 103.4
1 min sputt.	76.1 99.8	20.1 101.1	3.8 102.5	-
400 °C as received	58.4 100.0	27.2 101.2	14.4 102.6	-
1 min sputt.	83.7 99.9	14.5 101.1	1.8 102.5	-
600 °C as received	64.4 100.0	24.0 101.3	11.6 102.6	-
1 min sputt.	90.5 99.6	9.5 101.3	-	-

From the survey spectra, deconvoluted spectra and from Tables result: The amount of carbon is increasing with increase of deposition temperature after Ar Ion etching accompanied by the decrease of oxygen and silicon amounts. It can be noticed a decrease of the carbon relative concentrations after etching showing a small amount of unavoidable contamination on top of the surface; The silicon relative concentrations are decreasing with temperature before and after etching The Si-C contribution decreases with increase of deposition temperature; The Si^0 feature is increasing from 48.9% at 200 °C to 64.4% at 600 °C on top of the surface, respectively from 76.1% at 200 °C to 90.5% at 600 °C in sub-surface region (after 1 min sputt. the analysis depth ~ 11.5 nm); The Si-C contribution is increasing from 14.8% at 200 °C to 24.0 at 600 °C on top of the surface, accompanied by a decrease in the sub-surface region, from 20.1% at 200 °C to 9.5% at 600 °C; Si4+ (SiO_2) are present only on the top of the surface for 200 °C thermal treated sample due to surface contamination; The amount of Si-O bond is diminishing both for as received and after sputtering in good agreement with element relative concentrations, which display a lower amount.

Conclusions

To obtain Si-C composite films was proposed Thermionic Vacuum Arc (TVA) method characterized by high voltage (0.3-4 kV) and low current (0.1-4 A) discharge ignited in pure vapors with possibility to control the ion energy using acceleration or deceleration potential drop on the substrate during the deposition by means of a DC bias supply.

Silicon carbon films obtained without bias at 600 °C and 1000 °C substrate temperatures, i.e. sample S1 and sample S2 respectively, consist by four successive C-Si films on 200 nm carbon film on Si substrate. In the case of sample S1 we observe a beginning of crystallization, FFT representation showing that there is organization at around 0.300 nm. Instead, in the case of sample S2 can be identified using FFT, SiC crystallites. SiC crystal is oriented in the [02$\underline{2}$] direction, measured interplanar distances are 0.259 nm and 0.229nm with Miller indices (111) and (200) determined assuming the SiC cubic structure (F4-3m). We can conclude that increase of the substrate temperature determine the increase of the crystallization rate of the structure.

To characterize the influence of the acceleration potential drop on the structural properties of Si-C thin films was used two samples S3 and S4, both consisting by 400 nm Si-C film on the 200 nm C film on Si substrate and glass substrate, respectively, DC bias being -400 V and -1000 V, and 200 °C substrate temperature in both case.

HRTEM images reveal an amorphous structure in the case of sample S3, interplanar distance being 0.265 nm, instead in the case of sample S4 we observed

valuable small crystalline inclusions of the order of 2-4 nm, associated with cubic structure of SiC (interplanar distances d_{200} ~ 0211 nm).

XPS analysis was performed on the samples S5 (400 nm C-Si film on 200 nm C film on Si substrate at 200 °C), S6 (400 nm C-Si film on 200 nm C film on Si substrate at 400 °C) and S7 (400 nm C-Si film in 200 nm C film on Si substrate at 600 °C) in all cases using a -600 V bias. Survey spectra and deconvolution spectra reveal the fact that the amount of carbon is decreasing with increase of deposition temperature after Ar ion etching accompanied by the decrease of oxygen and silicon amounts. The Si-C contribution is increasing from 14.8% at 200 °C to 24% at 600 °C on top of the surface, accompanied by decrease in the subs-surface region, from 20.1% at 200 °C to 9.5% at 600 °C.

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