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Control over the sp^2/sp^3 ratio by tuning plasma parameters of the Thermoionic Vacuum Arc

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ABSTRACT

Thermoionic Vacuum Arc (TVA) plasma was used for the deposition of pure, hydrogen-free DLC films. TVA is an original deposition method using a combination of anodic arc and electron gun system for the synthesis of thin films from solid precursors under vacuum of 10^{-6}Torr. It was found that, in order to tune amorphous carbon to have a specific sp^3 fraction, the following parameters are essential: filament current (I_f), arc current (I), applied voltage (V) and the distance to the substrate (d). A Philips CM 120 ST TEM system with a Resolution of 1.4 and a 1.4M magnification was used in this work. Other techniques were SAED (Selected Area Electron Diffraction) and FFT (Fast Fourier Transform). Also, the chemical composition of the films was studied with XPS, Mg; SG (W = 1252eV). The sp^3:sp^2 ratio found ranges between 20 and 50%, depending on the electrical parameters. Measured fringes could be indexed using cubic (diamond) structure of carbon, (ICSD 79-1467).

1. Introduction

Nanostructured carbon thin films have recently drawn attention owing to the improved properties of coated surfaces such as wear resistance, electrical properties, hardness, roughness, smoothness, low friction coefficients, chemical inertness [1–6]. Thanks to these properties, nanocrystalls open up possibilities for applications in nanoelectronics, novel optical devices, integrated digital circuits, biomedical applications, etc. [7–9].

Hydrogen-free carbon films have higher hardness than their non-hydrogenated counterparts, a lower IR absorbance due to the absence of absorbing C–H oscillations and they also have higher thermal stability, which is otherwise limited by the effluent hydrogen in a-C:H materials [10].

Presently there are three methods for obtaining nanostructured hydrogen-free carbon materials: Filtered Cathodic Vacuum Arc (FCVA) [11–13], Mass Selected Ion Beam (MSIB) [14] and Pulsed Laser Deposition (PLD) [15–17] Apart from these, combined techniques like Laser Arc are also used [18,19].

The best control of the synthesis of nanostructured materials can be achieved by *the use of energetic species* either by direct ion beam deposition or by bombardment of materials (ion beam-assisted methods). The Cathodic Vacuum Arc can only provide low energy ions (less than 10eV). Also, due to the high arc currents used in such arcs, unwanted macroparticles are generated, limiting the applicability of this method. On the other hand, most systems applying energetic species are characterized by a complex nature of precursor particles with a large distribution of energies [20]. This makes the controlled growth and study very difficult.

An original plasma-based technique providing high energy carbon ions (of hundreds eV) suitable for the deposition of pure non-hydrogenated DLC films is presented here. The technique is known as Thermoionic Vacuum Arc (TVA).

2. Experimental

The basic principle of the TVA method briefly consists in ignition of an arc plasma in the vapors of the anode material, here graphyte. A schematic overview of the experimental setup is given in Fig. 1. Carbon vapors are obtained by heating the material with fast thermo electrons generated by an externally heated filament and accelerated by the anode. A Wehnelt cylinder is used for focusing of the electron beam. The anode is biased with high voltage of 2–3keV. More details of the TVA technique are given in Refs. [21–24]. The experimental setup of the TVA source used in the current work offers higher plasma stability than the previous setups. This is due to the vertical symmetry of the cathode–anode configuration which allows perpendicular bombardment of the electron beam onto the anode surface.

The TVA plasma is localized above the anode, where the highest vapor pressure is obtained. The ions created in this plasma are accelerated towards the chamber walls (and subsequently towards the substrate) due to the potential difference between the plasma potential and the grounded walls. The energy of ions is directly

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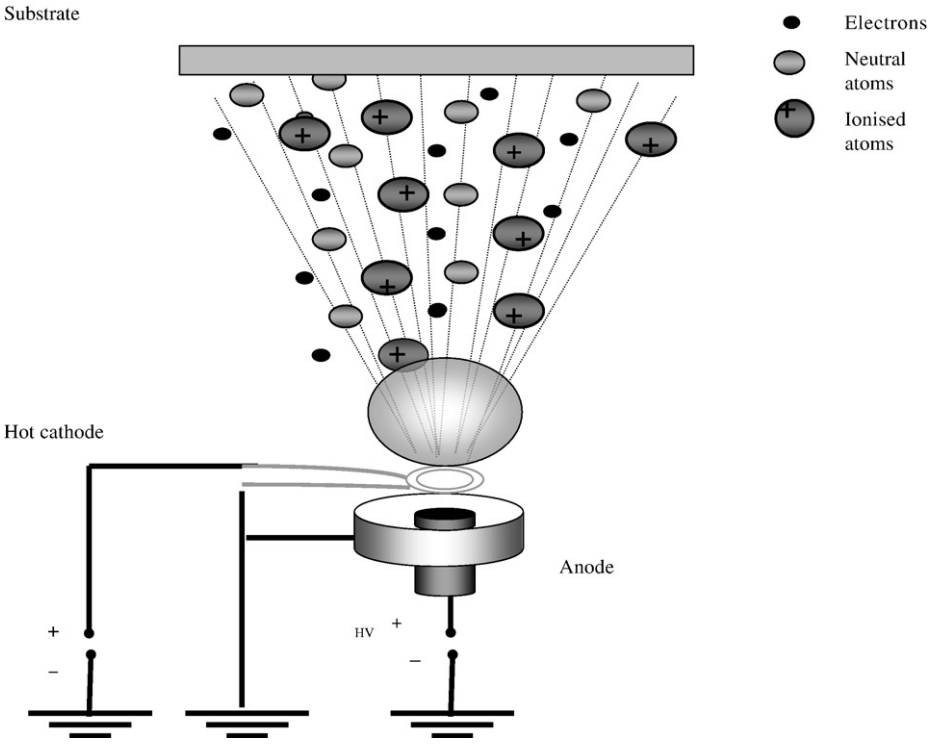

Fig. 1. Schematic diagram of the TVA system.

proportional to this potential difference. This is an important feature of the method, as ion energy can be relatively easily controlled by the plasma operating parameters (filament current (I_f), arc current (I), applied voltage (V) and the distance to the substrate (d). DLC of varying sp^3/sp^2 ratios was obtained by changing of deposition conditions. The sp^3 phase is responsible for the high mechanical properties and the sp^2 phase for the electron conductance properties of DLC films [25,26]. The influence of these plasma parameters on the preferential formation of sp^3 sites is analyzed here. Table 1 lists the experimental conditions used for the deposition of DLC.

The composite nature and the intrinsic non-homogeneity of the carbon nanostructured materials require the use of characterization methods with a very high resolution. One of the best characterization tools available is Transmission Electron Microscopy (TEM), preferably High-Resolution TEM (HRTEM). A Philips CM 120 ST TEM system of 120kV Max. HV with a resolution of 1.4 and 1.4M magnification was used in this work. Other techniques were SAED (Selected Area Electron Diffraction) and FFT (Fast Fourier Transform).

The chemical composition of the films was studied by XPS, Mg; SG (W = 1252eV). The C1s spectra were deconvoluted into three peaks: sp2, sp^3 and C–O.

3. Results and discussion

Current–voltage characteristics were automatically acquired using a computer controlled acquisition system. A typical current–voltage characteristic of the TVA plasma is presented in Fig. 2. The highlighted region represents the I–V range where the plasma characteristics can be tailored to obtain either high ion energies (A) or high ion densities (B).

X-ray Photoelectron Spectroscopy (XPS) was used to determine composition and sp^2 to sp^3 ratios in the outer layers of the film surface [27]. The wide scan in Fig. 3A) shows that the films obtained are pure, no contamination is present. Fig. 3B) shows the deconvoluted C1s peak with A peak — sp2 (284.9eV), B peak — sp3 (285.9eV), C peak — C–O (287.5eV). The results of the quantification of the deconvoluted XPS Carbon spectra of the samples studied are presented in Table 2. From all the spectra we can report that the sp^3:sp^2 ratio ranges between 20 and 50%, depending on the electrical parameters. A higher sp^3:sp^2 ratio was obtained at higher arc voltage.

A large number of crystalline inclusions inside the amorphous Carbon film *with diamond spherical grain* were observed by BFTEM (Bright Field Transmission Electron Microscopy) image at 65,000× working magnification 200nm spot size.(Fig. 4). BFTEM image (145kx

Table 1
Experimental conditions for the deposition of DLC by TVA

Sample	I_f [A]	I_{arc} [mA]	U_{arc} [V]	d [cm]
C1	50	1500	1300	30
C2	50	1720	800	30
C3	45	3000	3400	31
C4	53	3000	970	35
C5	45	2000	1270	35
C6	53	2000	1800	35

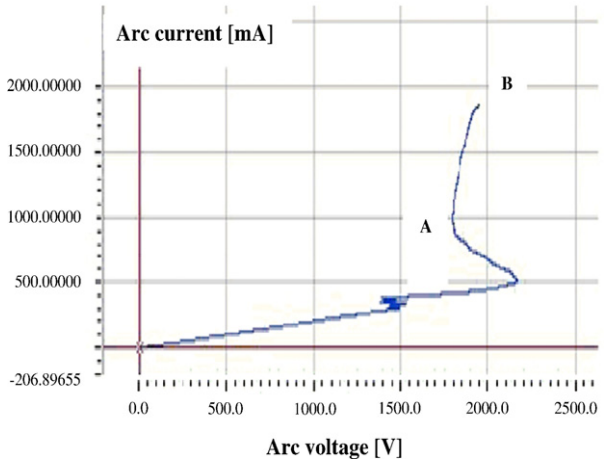

Fig. 2. Current–voltage characteristic of the TVA plasma.

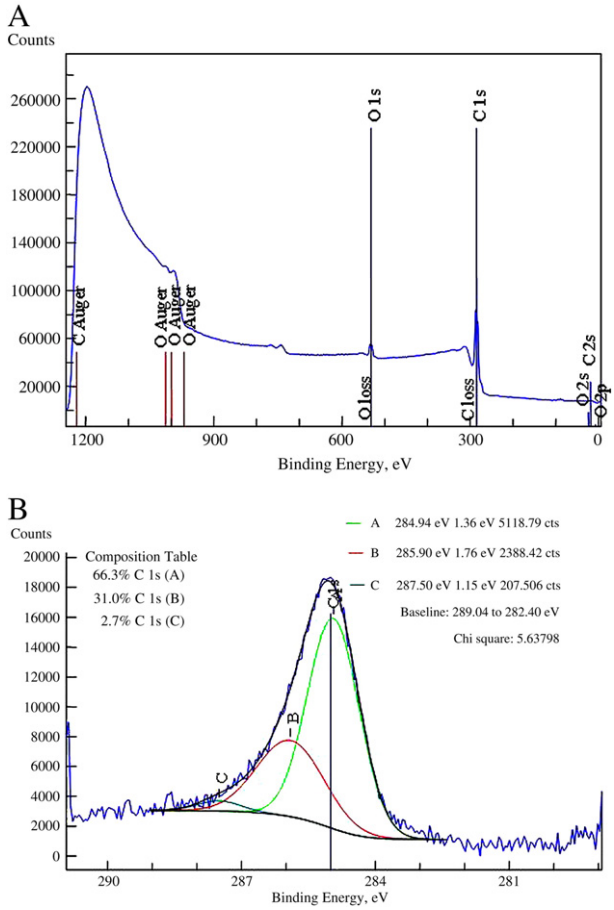

Fig. 3. A) XPS wide scan spectra for a typical Carbon thin films deposited by TVA; B) Deconvolution of the C1s peak (A peak — sp2, B peak — sp3, C peak — C–O).

working magnification) shaded correction and median filtered. Automated algorithm was carried out on separated grains. The values of particles were counted and measured using Analysis software. Morphology was determined from BFTEM image.

We calculate the mean diameters assuming a log-normal distribution (see Eq. (1)) of experimental data. The mean value of measured diameters from BFTEM images is 4.(1) nm.

$$y = y_0 + A\exp\left(\frac{\ln^2(x/x_c)}{2w^2}\right) \quad (1)$$

It is interesting to note that the inclusions have perfectly round shapes of about 5nm diameter (Fig. 4B). The histogram from the Fig. 4A confirms the maximum frequency of appearance for 5nm diameter, in agreement with the HRTEM image.

Measured fringes could be indexed using cubic (diamond) structure of carbon, with lattice constant a = 0.356nm, space group Fd3m, ICSD 79-1467.

According to the SAED diffraction pattern (given in Fig. 5) using a 420mm camera length and 200nm spot size, these shapes are made of diamond — structured nanoparticles having the diamond specific orientations (220) and (111).

Table 2
The percentage of sp^3 reported for the carbon samples deposited by TVA

Sample	C1	C2	C3	C4	C5	C6
sp^3:sp^2	31.9	21.9	46.8	27.4	31.9	27

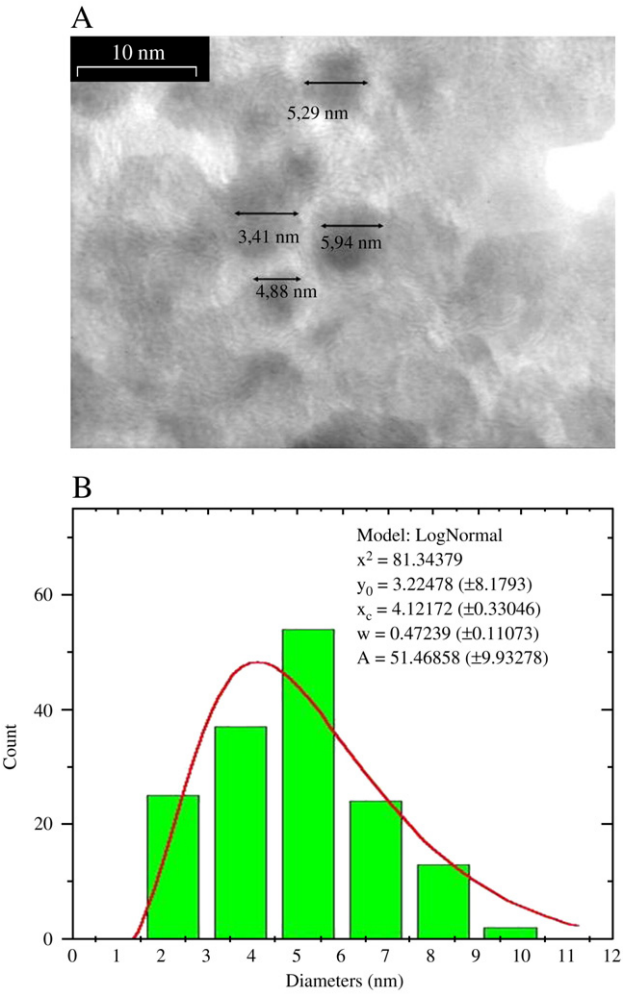

Fig. 4. HRTEM images of a Carbon film obtained by TVA at 10nm scale (A) and Grain size distribution (B).

There is a clear evidence of diamond structure formation embedded in amorphous carbon in all samples. the greater the applied voltage, the greater the diameter of the grains, with a mean diameter in the range between 3 and 7nm.

4. Conclusions

The original plasma deposition method, Thermoionic Vacuum Arc (TVA), is an interesting candidate for obtaining hydrogen-free carbon thin films at a nanometric scale, with a controlled final percentage of

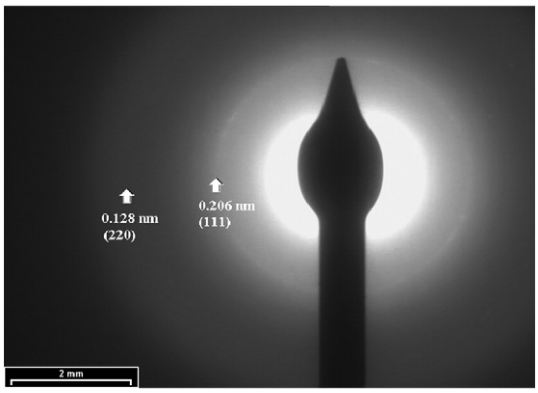

Fig. 5. SAED image of the Carbon thin film obtained by TVA method.

sp^3 content, depending on plasma operating parameters. It was found that the sp^3:sp^2 ratio is higher at higher applied voltage, when the plasma potential and consequently the Carbon ion energy is higher. Due to the fact that the TVA plasma source runs under vacuum conditions, the ions emerging from the core of the plasma do not undergo collisions on their way to the substrate. This fact is very important, as the ion energy can be fully controlled via the arc voltage.

As no buffer gas or catalyst is needed for the TVA plasma ignition, the films obtained are hydrogen-free and pure.

The present work demonstrated that the Thermoionic Vacuum Arc method can be used to obtain Diamond crystallites embedded in an amorphous carbon matrix of cubic diamond structure with lattice constant a = 0.356nm, space group Fd3m, ICSD 79-1467.

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