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Diamond-like nanostructured carbon film deposition using thermionic vacuum arc

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Abstract

Diamond-like nanostructured carbon films were deposited by a new type of vacuum arc technique, named thermionic vacuum arc (TVA) in a high-vacuum (10^{-6} mbar) chamber. This is our first report in an international journal on TVA use for nanostructured carbon film deposition. TVA technology has two main advantages: (1) the continuous bombardment of just depositing thin film by energetic carbon ions generated in carbon vapors plasma and (2) the ions energy can be fully controlled and changed at will even during deposition. The structures of the films have been characterized by high-resolution transmission electron microscopy, selected area electrons diffraction and fast Fourier transmission. The measured interatomic distances reveal a diamond-like nanostructure carbon film with an average grain size approximately 3–5 Å and a d-spacing of 0.286 nm, which corresponding to a rhomboedral lattice of diamond/carbon (ASTM 0015—pattern no 79-1473). The results demonstrate that the TVA is suitable for the preparation of diamond-like nanostructured coatings with high quality.

Keywords: Nanostructures; Diamond-like carbon; Ion bombardment; High-resolution electron microscopy

1. Introduction

Diamond-like carbon (DLC) films have drawn strong attention recently owing to their various distinguished properties, such as high hardness (3000–5000 kg mm^{-2}), low friction coefficients (0.1–0.2), chemical inertness, wear resistance (1.6×10^{-9} mm^3 (m N)$^{-1}$) and electrical properties [1–5].

The DLC materials with strong chemical bonding are defined by an arrangement of atom with a high sp^3/sp^2 ratio incorporated in amorphous structure. A mixture of sp^2 and sp^3 carbon sites will tend to segregate into sp^2 bonded graphitic structures embedded in a hard sp^3 bonded matrix [6].

Moreover, in the last years the scientific interest has been focused for growing DLC films of a few nanometers in size. Due to valuable electrical, nonlinear optical and mechanical properties, these DLC nanocrystals open up possibilities for different kinds of applications in nanoelectronics, novel optical devices, integrated digital circuits, etc. [7].

The properties of diamond-like nanostructures carbon may vary between those of diamond and graphite, depending on the deposition method and preparation conditions. Techniques using energetic carbon ions for preparing hydrogen free DLC films [8] are: mass selected ion beam [9], filtered cathodic arc [10–12], laser ablation [13], laser arc [14,15] and pulsed laser [16,17].

In this paper, diamond-like nanostructured carbon films were obtained using another hydrogen free technique for deposition, named: thermionic vacuum arc (TVA).

2. Experimental

The basic principle of the TVA method is described in Refs. [18,19] in detail. The experimental set-up used for DLC nanostructure deposition is represented in Fig. 1.

The electrode arrangement consists of a heated cathode surrounded by a Wehnelt cylinder, that concentrates high voltage accelerated electrons from the cathode on

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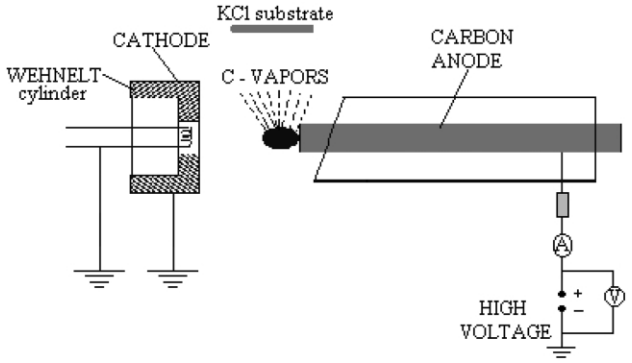

Fig. 1. Schematic view of the electrodes arrangement for carbon plasma generation (directly heated cathode).

the anode material—a carbon rod. The electrodes are mounted inside a large vacuum vessel. Continuously evaporating anode material ensures in the interelectrodic space a steady state carbon vapor density. At further increase of the applied high voltage a discharge ignites in pure carbon vapors and a stable operation of TVA is established. The applied high voltage during arc running in pure carbon vapors was 1.1 kV.

The cathode is a filament made from tungsten wire of 1.5 mm diameter. The intensity of the heating current of the filament is approximately 100 A. The anode was used as a carbon rod with $\Phi = 10$ mm and a length of 10 mm. The interelectrodic distance was maintained approximately 4 mm.

The thin films of carbon have been deposited on KCl substrates with a deposition rate of 3 Å s^{-1}.

The cathode and the vacuum chamber are on the ground, so the carbon plasma has a potential against the chamber wall equal with the cathode potential fall, which accelerates the ions towards the vacuum vessel

Fig. 3. Electron diffraction pattern.

wall. This means that on the substrate arrive not only the evaporated neutral atoms but also incident energetic ions. More than 10 years extensive measurements on TVA in metal vapors permitted us to establish the following properties of TVA.

–energy of ions (directed energy not random energy) is proportional with arc voltage drop
–arc voltage drop (i.e. the energy of ions) depends for a constant arc current on interelectrodic distance and on cathode (filament) temperature, these parameters being easily changeable even during operation.

The great advantage of TVA method is that the energy of ions can be fully controlled by TVA voltage drop and changed at will even during deposition, achieving even more than 400 eV. This potential is roughly equal to 40% from the TVA potential drop. Specially designed device with retarding potential for ions has been used

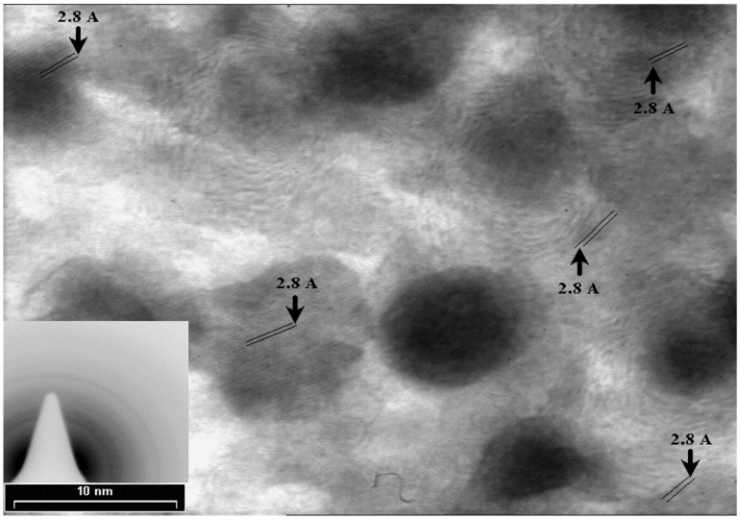

Fig. 2. HRTEM image and SAED (inset).

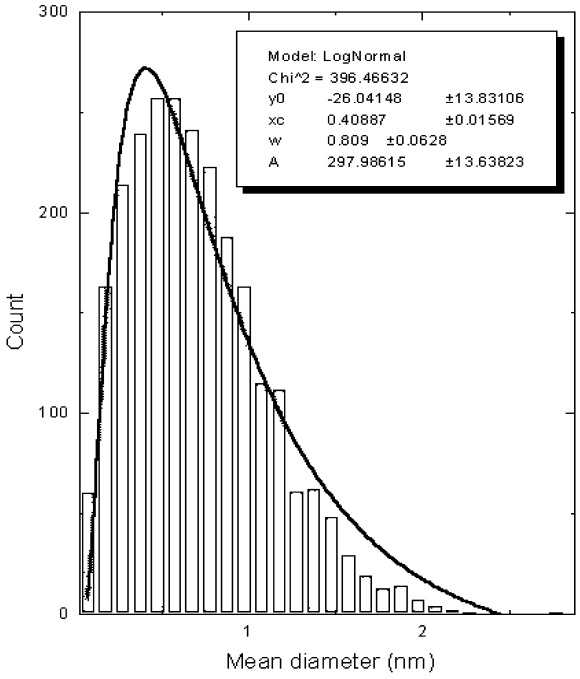

Fig. 4. Grain size distribution.

for energy measurements. At this stage (carbon TVA studies) we do not measure the ion/neutrals ratio for incident particles on sample. We reported such measurements earlier in the case of metal vapor TVA.

On the other side, the discharge is ignited in high vacuum conditions (10^{-6} mbar) and the growing of the film is produced only with own carbon atoms. This is why the deposited film has high purity, without droplets (like in other types of arcs), a good adherence and a roughness being of the order of 5 nm or less. SEM images obtained at the Essen University using 10^4 magnification have shown no droplets in the deposited carbon film.

High-resolution transmission electron microscopy (HRTEM) was performed on a Philips CM 120 ST (120 kV) TEM having a point resolution of 1.4 Å and a magnification of 1.2 M.

3. Results and discussion

HRTEM images and diffraction patterns have been obtained in the films grown on the KCl substrates after they were floated off in water. The structure of the deposited film using TVA is shown in Fig. 2.

In this image, several regions with the contrast of fringes are embedded in the contrast of the amorphous material. In the inset is presented selected aria diffraction pattern (SAED).

Electron diffraction performed on the carbon nanostructures indicated the presence of the well-defined rings, with a d-spacing of 0.28 nm corresponding to a rhomboedral lattice of diamond/carbon. These data are according to ASTM 0015 (American Society of Testing Materials) Pattern no 79-1473 (Fig. 3).

The grain size distribution (Fig. 4) has shown an average grain size approximately 2–4 nm, which correspond to diamond-like nanostructure films [20].

More precision measurements have been made with fast Fourier transmission (FFT) on HRTEM image (Fig. 5). This technique eliminates some information from

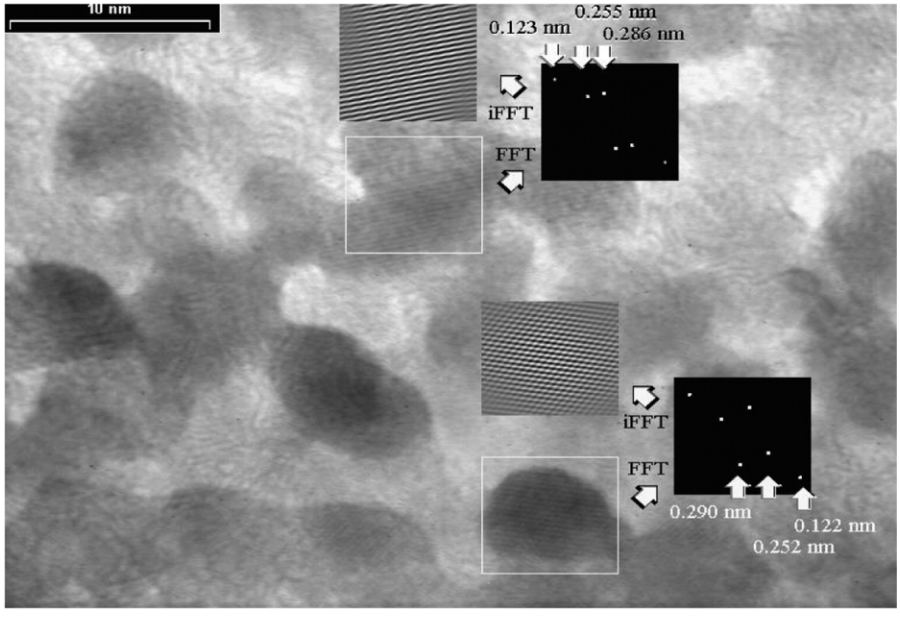

Fig. 5. Images filtered with blobs type filters in FFT space.

initial image and kept the periodical information, like lattice plane fringe.

As we can see in Fig. 5, the d-spacing were 0.286 and 0.290 nm, very close by 0.288300 nm (ASTM pattern).

4. Conclusions

DLC film was obtained using TVA technique.

The TVA is a suitable method for the deposition of carbon film in spite of the high point for evaporation of carbon (3700 K).

The structure of the film has been investigated by HRTEM, SAED and FFT and the results have shown the d-spacing corresponding to 0.288 nm given by ASTM-0015 for rhomboedrical lattice. Of course, the optimization in the deposition conditions, however, must be necessary to obtain the high quality of DLC films. Some other mechanical testing of the film is needed for reporting the direction of application of this quite new method for deposition.

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