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THERMIONIV VACUUM ARC – NEW TECHNIQUE FOR HIGH PURITY CARBON THIN FILM DEPOSITION

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New technology for carbon film deposition is presented. The carbon film is condensing from carbon plasma generated by a thermionic vacuum arc with carbon anode. Carbon film is bombarded during deposition by energetic carbon ions at fixed energy. High purity, hydrogen free and nanostructured layers are obtained the characteristic size of structures being in the order of few nanometers.

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1 Introduction

Presently there is a great interest in amorphous carbon (a-C) films that contain significant fractions of sp^3 bonding. This bonding gives such diamond-like carbon (DLC) structures with useful properties such as wear resistance, adhesion, electrical conductivity, hardness, and stress and oxidation resistance. A DLC material, whose properties resemble, but do not duplicate those of diamond, is a random covalent network of sp^2 – bonded "graphitic" carbon structures interconnected by sp^3 "diamond-like" linkages with no long-range crystalline order [1, 2].

DLC can be prepared by a variety of vapor deposition techniques. A common feature is growing from beams containing a significant fraction of medium-energy ions (20–500eV). In this paper a new technology, namely Thermionic Vacuum Arc, is described for carbon layer deposition.

2 Method

Thermionic Vacuum Arc (TVA) is an externally heated cathode arc which can be established in high vacuum condition, in vapors of the anode material, continuously generated due to the incoming power P given by the relation $P = U_{anode} * I_{anode}$ where U_{anode} is the anode potential

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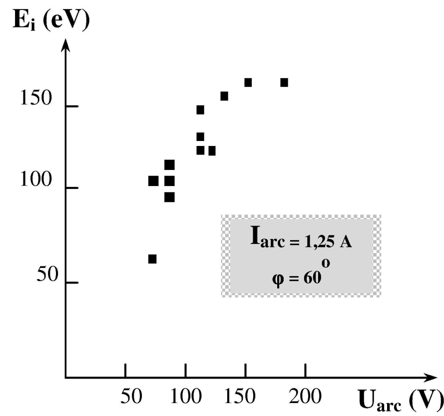

Fig. 1. Correlation of measured maximum ion energies and the arc voltage drop $U_{\rm arc}$ where f defines the angle between the imaginary lines perpendicular to the anode and the axis of the cathode.

fall and I_{anode} is the arc current [3–6]. The arc is ignited between a heated cathode provided with a whenelt cylinder and the anode which is a crucible containing the material to be evaporated.

Because this system can heat any material at increased temperature, it is one of the most adequate technologies for carbon evaporation. In this case, instead of crucible containing the material to be evaporated, a carbon rod is used directly. Moreover, the discharge can be ignited in high vacuum condition, ensuring high purity and deposition of hydrogen free carbon layer.

This new type of arc offers the unique opportunity to generate energetic ions, with a controlled value of the directed energy, which are bombarding the condensing thin film on the substrate. The ions are just those (the substrate bombarding ions are generated just from the atoms of the depositing material, no gas being present in the vacuum chamber during the process) of the depositing atoms on substrate.

The directed energy of ions is related to the cathode fall. Indeed because cathode is at ground potential, the plasma against the wall of the vacuum vessel is at a potential equal to the cathode fall. Consequently, a potential difference equal to the cathode fall will accelerate the ions towards the walls of the vacuum vessel up to energy of 500 eV, for characteristical anode currents of 1 A.

Simple means are available to control the value of the ions energy like anode-cathode distance, relative position of electrodes, cathode heating current, etc. Even during deposition, the value of the cathode fall can be changed in a range of some hundred volts.

Such behaviour is easy to understand. Indeed, for a constant thermionic arc current, if the temperature of the cathode (namely cathode heating current) is decreased, in order to maintain the same arc current, the potential drop over the arc must be increased, which has a consequence the increase of the potential drop at the cathode. Similar explanations are valid for the effect of other mentioned parameters. Experimental measurements on the ion energy distribution have shown that between the directed energy of ions (away from plasma source) and the arc potential drop is nearly a linear relation we can see in Fig. 1. It gives an easy control of the value of ions energy through arc voltage drop. The ion density depends on the arc current. For 1.8 A arc current, the ion density is 5% from the neutral carbon density atoms. However, due to the

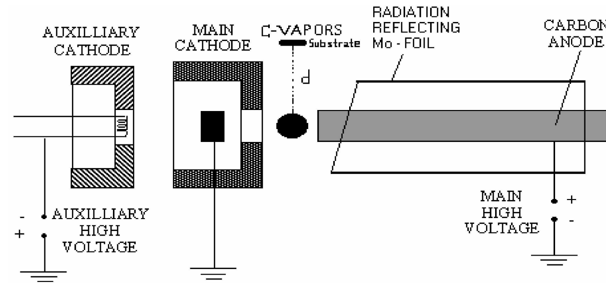

Fig. 2. Schematic view of the electrodes arrangement for carbon plasma generation (indirectly heated cathode).

electric field between plasma source and vacuum vessel wall, the ions are much faster collected than neutral atoms.

Two experimental arrangements for carbon evaporation have been used. In Fig. 2 the experimental arrangement of Thermionic Vacuum Arc with indirectly heated cathode (by electron bombardment) in order to increase the cathode life–time which was reacting with carbon vapor generating tungsten carbide and diminishing the cathode lifetime is shown schematically.

In this figure, d is the distance between the substrate and the point where is ignited the arc-discharge ($d = 80$ mm). The substrate is at ground potential, mounted on a stainless steel plate of 1 mm thickness, in the direction indicaated by discontinuous line. The heat transfer to substrate from plasma was mainly by radiation. The temperature on the substrate level was around 200–250°C, the heating being due to radiation. The real position of carbon rod was slightly turned by 10–15° with respect to the horizontal line.

Also, in order to reduce heat losses from the anode by radiation, molybdenum cylindrical reflector was mounted at anode.

Tab. 1. Working parameters of TVA with indirectly heated cathode deposition duration: 180 s.

Rod diameter (mm)	Auxiliary discharge		Main discharge		Voltage drop over discharge space (V)
	Voltage (V)	Current (A)	Voltage applied (V)	Arc current (A)	
4	2 000	0.2	1 700	1.8	400
3	2 000	0.2	2 000	2.5	240

In Table 1 the working parameters of thermionic vacuum arc for a number of deposition experiments of carbon films using small cathode carbon rod distance (a few mm) are given. The thickness of the deposited carbon films on Si wafers of the order of 100–200 nm. During the experiments, a simple solution has been found both for cathode and anode. We used a thick filament wire with 1.5 mm diameter from thoriated tungsten cathode and a short length carbon

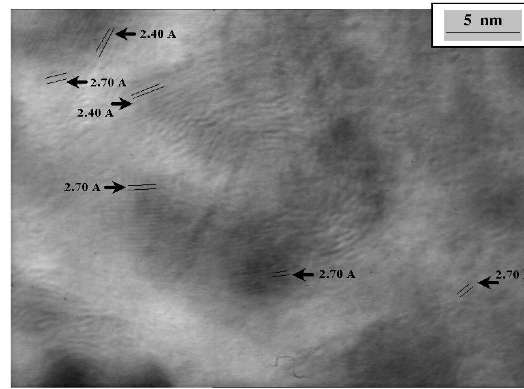

Fig. 3. HRTEM: Crystals surrounding by partial graphitised carbon on the amorphous carbon film.

rod supported by a refractory metal wire (tungsten) with a diameter of 1.5–2 mm anode. Other technological improvements are described below.

3 Experimental results and discussions

The main parameters were the cathode filament — thoriated tungsten wire of 1.5 mm diameter three times wound and heated by a current of 100 A; final vacuum during deposition was 10^{-6} mbar; applied high voltage during arc running in pure carbon was 1100 V; interelectrodic distance (cathode-anode) was 4 mm; sizes of the carbon anode (mounted on a $\Phi = 1.5$ mm tungsten wire) are $\Phi = 10$ mm, $h = 10$ mm; deposition time 300 s; deposition rate 3 Å/s; final thickness of the deposited pure carbon thin film 90 nm.

During the arc running and C thin film deposition, the anode was continuously rotating with 6 rpm and also the cathode-anode distance was adjusted each time when the arc current was decreasing by more than 10%. This way, a continuous working of the TVA was ensured.

The deposited C films were studied using TEM electronic microscopy with a magnification of 1.4 M and a resolution of 1.4 Å. The samples of deposited carbon films (deposited on NaCl or KCl monocrystals solved in water before TEM examination) show nanostructured films. The size of cylindrical structure has a diameter of 2.40–2.70 nm and a length of only 0-20 Å sustaining the nanostructured thin films as shown in Fig. 3. Preliminary Raman spectra confirmed the existence of sp^3 bounds beside sp^2 ones.

The TEM image of grains is shown in Fig. 4. The statistical function presented in Table 2 indicates a mean diameter of grain size about 6.52 nm. The grains with 5.5 nm diameter (see Fig. 5) have the maximum frequency of appearance. The electron diffraction diagrams show the existence of crystalline structure in the deposited thin films using TVA technique.

The new system of deposition is peculiarly adequate for hydrogen free, high quality-smooth and compact - carbon film deposition. The TVA easily ensures high energy needed to evaporate pure carbon.

Thermionic Vacuum Arc can be used successfully for hydrogen-free carbon film deposition, ensuring good qualities and high purity. Nanostructured carbon films with low roughness can

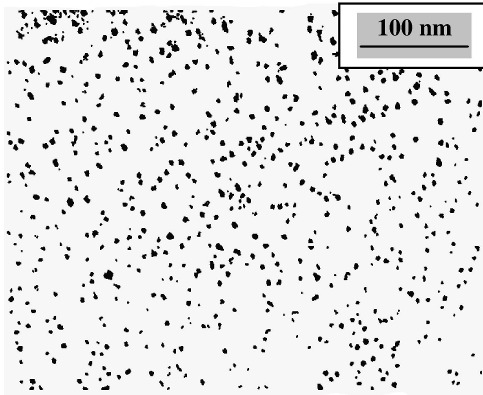

Fig. 4. TEM image of grains.

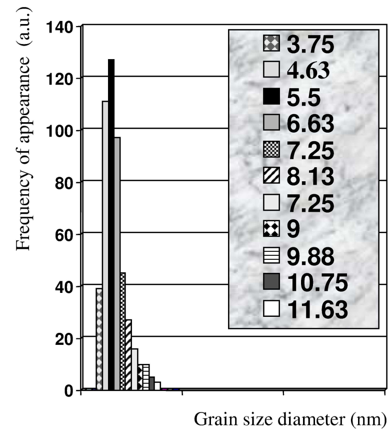

Fig. 5. Grain size distribution graph. In caption: diameter of the grain (nm).

Statistical Function	Diameter Mean
Base Unit	nm
Mean	6.52
Minimum	3.88
Maximum	15.09
Standard Deviation	1.77

Tab. 2. Statistical function of grains.

be obtained quite easily. Further developments will be related mainly to the improvement of the TVA stability at the transition from electron bombardment heating of carbon rod to the TVA arc plasma ignition and running. We present here just the first results on characteristics of carbon film obtained using TVA.

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