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V. P. Novikov and V. P. Dymont

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Synthesis of diamondlike films by an electrochemical method at atmospheric pressure and low temperature

V. P. Novikov[a] and V. P. Dymont
Academy of Sciences of Belarus, Institute of Solid State Physics and Semiconductors, Minsk 220072, Belarus

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A technique of carbon film synthesis based on an electrochemical process was developed. A solution of acetylene in liquid ammonia was employed as the electrolyte. Films were deposited at the metallic anode. Two types of films were produced. Films of type I are transparent and fragile, whereas those of type II are black and plastic. The films were investigated by the electron diffraction method and Raman spectroscopy. The electron diffraction data for type I films demonstrate the films' high degree of crystallinity. Values of lattice plane spacings agree with data on cubic diamond modifications. The Raman spectrum of type I films shows a line at 1334 cm^{-1} (full width at half-maximum equal to 15 cm^{-1}), inherent in that of diamond and an essentially amorphous carbon component. Spectra of the type II films do not feature the Raman peak of diamond. © *1997 American Institute of Physics.* [S0003-6951(97)02602-8]

The diamondlike carbon (DLC) films have unique properties that make them candidates for a number of applications. Among these are corrosion protective coatings of metals, wear-resistant coatings and use as optical and electronic components. As a rule, diamondlike carbon films are deposited using a variety of chemical vapor deposition techniques, as well as the ion-beam techniques, and laser processing.[1,2] We have succeeded in demonstrating a new method in which the metastable growth of DLC films occurs at atmospheric pressure and low substrate temperature. Our method is based on an electrochemical (galvanic) process.

A solution of acetylene in liquid ammonia was used as a starting electrolyte. The choice of such a system is based on the assumption that the acetylene dissociates in NH_3 by the scheme:

$$C_2H_2 \longrightarrow C_2H^- + H^+,$$

and the ions are discharged:

$$C_2H^- \xrightarrow{-2e^-} C_{2n}\cdot + H^+. \tag{1}$$

The acetylene was synthesized by calcium acetylide hydrolysis. The ammonia was obtained via distillation of NH_4OH. A Dewar vessel with a volume of 50 cm^3 was used as an electrochemical cell. This cell was filled up by the electrolyte. Plates of different metal foils (Ni, Co, Fe) 1–2 cm^2 in area were used as electrodes. The electrolysis voltage and current density were varied in the 2.0–5.0 V and $10^{-3}-10^{-5}$ A/cm^2 ranges, respectively. The deposition time ranged from 5 to 10 h. The thickness of films lay between 0.5 and 3 μm. Assuming that reaction (1) takes place, the estimated current efficiency of carbon was 40%+20%. The films were investigated by scanning electron microscopy, the electron diffraction method, and Raman spectroscopy.

Depending on the electrolysis conditions, two types of films were produced on the anode. Films of type I were transparent and fragile. They were smooth and homogeneous in thickness, as shown in Fig. 1. Their resistivity was 10^8-10^{10} Ω cm. The type II films were black and plastic. They had a platelike morphology of grains. Their resistivity was 10^2-10^4 Ω cm.

Both types of films were inert to heavy acids and alkalies and did not dissolve in organic solvents. The type of film produced depended on various factors, such as electrode material, its preliminary treatment, and the electrolysis voltage. Type II films were grown when the electrochemical etching of the electrode took place. Figure 2 presents typical transmission electron microscopy (TEM) diffraction micrographs of the annealed films. The electron diffraction pattern of type I films shows up as a system of narrow rings. This means there is a high degree of film crystallinity. Lattice plane spacings measured from diffraction patterns are given in Table I in comparison with the ASTM values for diamond. It is

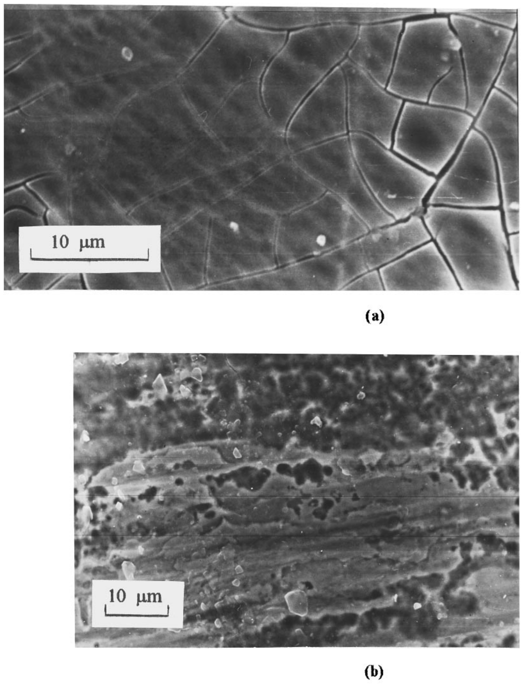

FIG. 1. Scanning electron micrographs of carbon films: (a) type I films and (b) type II films.

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[a] Electronic mail: ifttpanb%iftt.basnet.minsk.by@demos

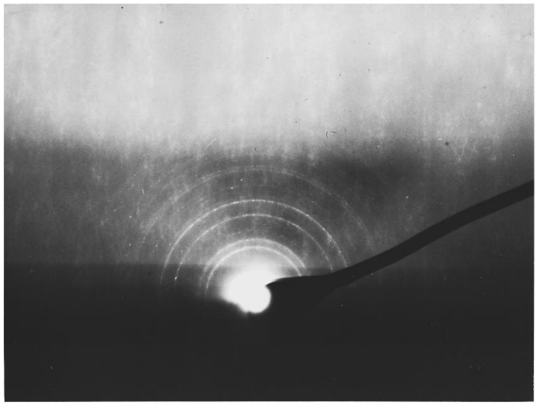

FIG. 2. Electron diffraction pattern of type I films.

shown that values of d for type I film coincide with those for diamond. It is particularly remarkable that reflexes, forbidden for diamond, were observed as well. The films of type II have no crystalline structure.

Raman spectra of the type I films had a diamond peak at 1334 cm^{-1} (full width at half-maximum is equal to 15 cm^{-1}) and an essentially amorphous carbon component. The spectra also showed the presence of a Raman peak at 1309 cm^{-1} [Fig. 3(a)]. As yet, the origin of this peak has not been determined. Spectra of the type II films do not feature a Raman peak of diamond. The broad spectra band with maximum in the neighborhood of 1580 cm^{-1}may be attributed to amorphous carbon [Fig. 3(b)].

Electrochemical oxidation of the acetylene ion on the anode,

$$n(\mathrm{C{\equiv}CH^-}) \xrightarrow{-\mathrm{ne}^-} \mathrm{C}_{2n}\mathrm{H}_n\,,$$

creates hydrogenated carbon with a hydrogen content of the order of 33.3 at %. It is well known that carbon hydrogenated to an equally high degree can exist only in the amorphous state. The formation of a highly crystalline diamond-like deposit is the indirect evidence of low hydrogen content. It is suggested that the following schemes of the carbon dehydrogenation take place:

(1) dehydrogenation of the growing film by an electrochemical anode process:

$$\underset{\text{chem. sorb.}}{\text{—C}{\equiv}\text{C—H}} \xrightarrow{\;-e^-\;} \underset{\text{chem. sorb.}}{\text{— C}{\equiv}\text{C}\cdot} + \mathrm{H}^+(\text{solv.}).$$

TABLE I.The lattice plane spacing values for electrolytical carbon film and cubic diamond.

Film		Diamond (a=0.3566 nm)	
Intensity	d (nm)	d (nm)	$h^2+k^2+l^2$
vs	0.240	0.251	2
s	0.201	0.206	3
w	0.174	0.178	4
s	0.141	0.143	6
s	0.121	0.126	8
vw	0.117	0.118	9
w	0.104	0.107	12
w	0.092	0.095	14
w	0.089	0.089	16
w	0.082	0.081	19

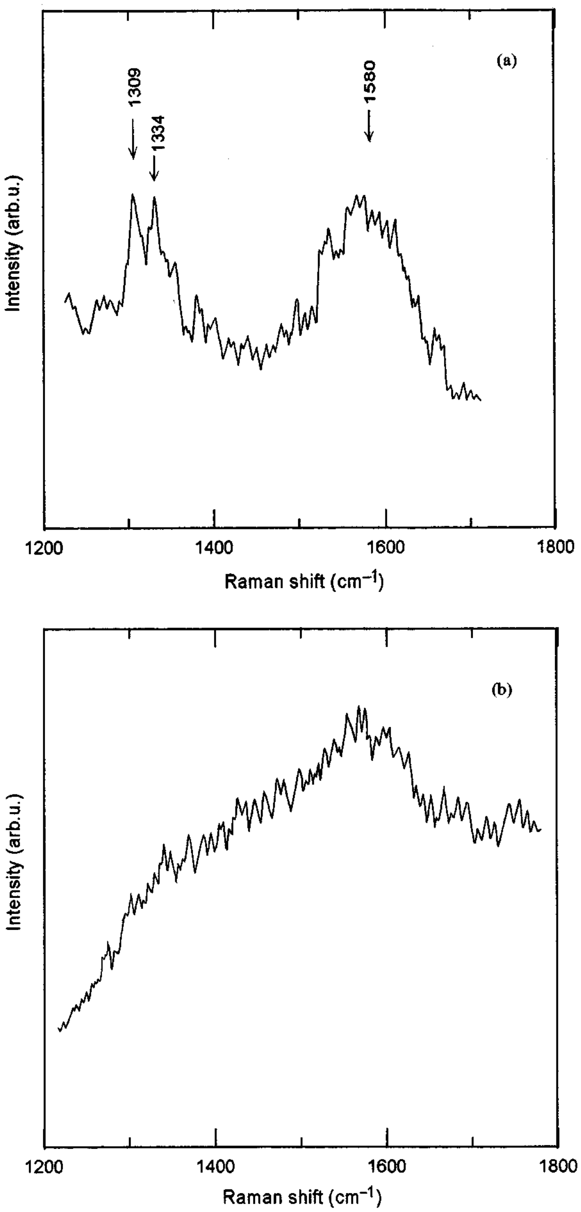

FIG. 3. Raman spectra of carbon films: (a) type I films and (b) type II films.

(2) Dehydrogenation of the film by another ion, for example,

$$\mathrm{NH_2^-} \xrightarrow{\;-e^-\;} \mathrm{NH_2}\cdot;$$

$$\underset{\text{chem. sorb.}}{\text{—C}{\equiv}\text{CH}}+\mathrm{NH_2} \longrightarrow \underset{\text{chem. sorb}}{\text{—C}{\equiv}\text{C}\cdot} + \mathrm{NH_3}.$$

(3) Catalytic dehydrogenation by metal cations:

$$\mathrm{Me}^0 \xrightarrow{-2e^-} \mathrm{Me}^{+2};$$

$$\mathrm{Me}^{+2}+n(\mathrm{C{\equiv}CH^-}) \longrightarrow \mathrm{Me(C{\equiv}C)}_n^{2-n} + n\mathrm{H}^+\ (\text{solv.});$$

$$\mathrm{Me(C{\equiv}C)}_n^{2-n} \xrightarrow{-(2-n)e^-} \mathrm{Me}^{+2}+\mathrm{C}_{2n}\,.$$

It is clear that scheme (3) refers to formation of type II films. Of great importance is the problem of primary growth of diamondlike films under metastable conditions that are more thermodynamically advantageous for growth of the graphite phase. In our case the nonequilibrium nature of electrolysis has to be taken into account. According to Ostwald's step rules, the formation of phases in nonequilibrium conditions begins with the least stable phase. There are, however, some favorable conditions for the growth of the diamondlike phase in this experiment:

(1) the possibility of hydrogen and nitrogen capture by the growing film that stabilizes the sp^3 configuration of carbon;[4]

(2) the low temperature of the synthesis that closely approaches the thermodynamic potential of the diamond and graphite phases.

We have thus shown that diamondlike films can be created by an electrochemical method at atmospheric pressure and low substrate temperature. This method has a number of potential advantages over other methods, as for instance, plasmochemical ones. Among these are (1) simplicity of apparatus, energy saving, and material saving; (2) simplicity of film doping and film modification; (3) favorable conditions for growing new metastable forms of carbon because of the low temperature and the fact that the process is not in equilibrium.

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