

Growth of polycrystalline diamond films from the gas phase

B. V. Deryagin, D. V. Fedoseev, V. P. Varnin, A. E. Gorodetskiĭ, A. P. Zakharov, and I. G. Teremetskaya

Institute of Physical Chemistry, USSR Academy of Sciences
(Submitted February 18, 1975)
Zh. Eksp. Teor. Fiz. **69**, 1250-1252 (October 1975)

On growth of the face of a diamond octahedron from the gas phase, a transition from epitaxially arranged crystal layers to polycrystalline layers with arbitrarily oriented crystallites is observed. This arrangement is subsequently replaced by polycrystalline textured layers with a texture axis [110] perpendicular to the plane of the backing.

PACS numbers: 68.50.+j

The very possibility of growth of diamond in its metastability region is usually associated with the orienting action of surface forces on the sample and on the properties of the new phase.^[1-3] Here it is assumed that the new diamond grown on a seed should follow the crystal structure of the surface layer of the seed crystal. For the case of moderate supersaturation this has been shown experimentally, for example, in ref. 4.

There are now reasons to suppose that the difficulties of obtaining diamond are due not so much to its metastability as to a number of chemical and physical properties of carbon, particularly its clearly expressed ability to form modifications with different types of binding corresponding to sp , sp^2 , and sp^3 hybridization of the electron orbits. In crystallization of carbon at large supersaturations and relatively low temperatures, each of these modifications arises with a definite probability and will possess an appreciable stability. The dominant type of binding depends on the conditions of crystallization; inclusions with other types of binding must be regarded as defects of the crystal structure.

We have studied the crystallization of diamond from the gas phase, activated by an electric discharge. This activation greatly increases the rate of deposition of carbon.^[5] The substrates in these experiments were twinned crystals of natural diamond with a well expressed (111) face with a length of edge along the $\langle 110 \rangle$ direction of about 3 mm.

To study the features of formation and growth of the carbon films we investigated their structure as the thickness of the deposited layer changed. The thickness of the samples could be changed by varying either the deposition time or the time of etching in KOH solution of the films obtained. The thickness of the films was determined in a MII-4 interference microscope or was evaluated indirectly by measuring the weight of the crystal. For thicknesses less than 0.05μ , the film thickness was measured by electron diffraction. The electron-diffraction technique has been described previously.^[4]

Analysis of the electron-diffraction pattern showed that in the initial stages of growth, for film thicknesses $0.05 \pm 0.1 \mu$, there is a very clearly observed tendency for suppression of epitaxial growth of the diamond phase and for appearance of diamond crystallites arbitrarily oriented with respect to the substrate. For a film thickness $0.1 \pm 0.5 \mu$ the upper layers of the film consists of polycrystalline diamond carbon with a crystallite size 50-200 Å. In the electron-diffraction patterns from these films, five to six diffraction lines are observed, including the (331) and (422) lines.

As a rule the peaks were displaced somewhat toward zero reflection angle, which resulted in an apparent increase of the interplanar distances in the films by 3-6% (see the table).

In the fourth column we have listed the extreme values of the interplanar distances obtained for different samples.

With further increase of the film thickness to 1-2 μ , depending on the growth conditions, we obtain either completely fine-grained crystalline films with arbitrary orientation of the individual grains or well textured films with a [110] texture axis perpendicular to the substrate. In some samples the texture axis precessed about the normal to the substrate along the generatrix of a cone with a vertex angle no more than 5-10°.

The transition from the (111) plane of the substrate to polycrystalline unoriented deposits occurred gradually as the film thickness was increased. At first, thin films of about 20-50 Å formed epitaxially placed crystalline layers of diamond, which were, however, strongly deformed. Then appeared crystallites rotated by 5-10° around the [111] direction, and only following them did diamond crystallites appear with arbitrary location. In the case of films with azimuthal texture about the [110] axis the latter arose only after formation of a polycrystalline unoriented layer.

It should be noted that simultaneously with the diamond structure in some experiments there arose a structure corresponding to pyrolytic graphite (pyrocarbon). However, the pyrocarbon which appeared did not suppress the growth of the diamond films. On the other hand, the growth of the pyrocarbon was suppressed by the growth of carbon with a diamond lattice. A feature of the electron-diffraction patterns obtained from the fine-grained crystalline diamond films was the smearing and displacement mentioned above of the diffraction lines in the direction of zero reflection angle. The cause of this shift of the lines is apparently relatively incomplete twinning in planes of the (111) type, which was observed

Interplanar distances and relative intensities of lines of polycrystalline diamond films

hkl	d , Å theory	I , relative units, theory	d , Å experiment	I , relative units, experiment
111	2.06	100	2.08-2.18	100
220	1.26	50	1.26-1.30	60
311	1.072	40	1.075-1.090	50
400	0.885	10	0.885-0.90	10
331	0.813	25	0.815-0.825	30
442	0.721	40	0.721-0.730	40

previously^[4] in obtaining epitaxial diamond films at pressures below atmospheric.

¹B. V. Deryagin and D. V. Fedoseev, *Uspekhi khimii* **39**, 1661 (1970) [Russian Chemical Reviews].

²J. C. Angus, H. A. Will, and W. S. Stanko, *J. Appl. Phys.* **39**, 2915 (1968).

³B. V. Deryagin and D. V. Fedoseev, *Sintez almaza iz gazovoĭ fazy* (The Synthesis of Diamond from the Gas Phase), *Znanie*, 1973.

⁴B. V. Deryagin, B. V. Spitsyn, A. E. Aleksenko, A. E. Gorodetskiĭ, A. P. Zakharov, and R. I. Nazarova, *Dokl. Akad. Nauk SSSR* **213**, 1059 (1973) [*Sov. Phys. Doklady* **18**, 822 (1973)].

⁵E. N. Eremin, *Elementy gazovoĭ elektrokhemii* (Elements of Gas Electrochemistry), Moscow State University, 1968.

Translated by Clark S. Robinson
137