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A NEW POSSIBILITY OF BUILDING UP THIN DIAMOND FILMS IN PRECIPITATION OF CARBON FROM THE GASEOUS PHASE

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A new method for building up thin diamond films is suggested based on the difference in the rates of sublimation of graphite and diamond. It is recommended that this method be used for producing diamond films at temperatures above ~1000°C without application of a chemical etching agent.

It has been found by now that in precipitation of carbon from the gaseous phase, crystal nuclei of both metastable diamond and stable graphite appear and grow simultaneously. In order to get rid of the graphite and produce a pure diamond film, use is usually made of atomic hydrogen, which at temperatures above 100°C etches well graphite and other forms of nondiamond carbon and has little effect on diamond [1]. Here the hydrogen concentration needed for total suppression of the reaction $C_nH_k \rightarrow C_{\text{graph}} + H_2$ is usually rather high. In [2], for example, it is reported that in building up polycrystalline diamond films on silicon substrates a mixture of 3% CH_4 + 97% H was used. However, certain negative factors are inherent in the method of chemical etching. In particular, at such a high concentration (97% H) hydrogen, sorbed on the surfaces of diamond crystals, blocks the faces and fronts of growth, preventing electron condensation of carbon atoms and establishment of their bonds through the orbitals of excited states, thus favoring a decrease in crystal growth. Along with this, hydrogen atoms are captured and incorporated into the diamond lattice, as a result of which specific disruptions of homogeneity occur. Moreover, at temperatures above ~1000°C growth of graphite predominates over its etching. Thus, thin diamond films produced at present, just like natural ones and synthetic diamonds, contain different imperfections of the crystal structure, impurites, and inhomogeneities that exert a negative influence on the mechanical, electrophysical, optical, and physicochemical properties of the crystals. Therefore, synthesis of structurally perfect homogeneous single-crystal diamond films that possess the best reproducible properties is one of the most important problems of modern materials science. Devices, machines, and mechanisms manufactured based on these films will be characterized by extremely high properties that still have no analogs in modern practice. However, synthesis of these films involves certain difficulties that no one has yet succeeded in overcoming within the framework of existing concepts and methods applied.

Taking into account the huge need and promising prospects for employing these films in the national economy, we selected another way of solving this problem that is based on the difference in the sublimation rates of graphite and diamond. It is known that the sublimation rate of diamond is very small and is not determined, whereas for graphite it is rather high and increases sharply as the temperature increases above ~1000°C.

According to the general principles of statistical mechanics, the fluctuation energy of thermal vibrations, which is determined by the quantity kT (k is the Boltzmann constant) is the operating factor of separation of particles from a crystal surface. At low temperatures the process of separation of particles from their neighbors (sublimation, evaporation) virtually does not occur, while at high temperatures it usually proceeds at a high rate. Therefore, at low temperatures it is necessary to use chemical etching, whereas at high temperatures, when the sublimation rate is high, chemical etching is not needed.

When a crystal grows, its sublimation occurs simultaneously. Under conditions of saturation of the gaseous phase, the number of additions of particles to sites of growth is equal to the number of separations. In

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this case a dynamic equilibrium occurs, in which the number of particles in the crystal and the gaseous phase is constant and, consequently, the resultant rate of the process is equal to zero. Under conditions of supersaturation, the number of additions of particles predominates over the number of separations, as a result of which crystal growth is observed. If the supersaturation is low, then favorable conditions can appear for the transition of the atoms to an ordered arrangement and formation of a perfect crystal lattice. In the case of high supersaturations, order may not be observed in the atomic arrangement, and the structural perfection of the film will deteriorate correspondingly if here the mechanism of crystal growth is constant.

Formation of a single-crystal film begins from the appearance of nuclei of a new phase and their subsequent growth. At the same time, independently of the initial form of the nuclei under rather long and stable conditions the form of the crystal becomes stationary and determinable by the synthesis parameters [3]. According to [4], nuclei of the same size can have different forms. However, in the initial stage until the ratio of the surface of the nucleus to its volume is expressed by a considerable magnitude, the spherical form is most probable, since of all known facetings of this volume this form possesses the lowest free energy. When a nucleus appears on a solid substrate, the condition of minimum free energy is satisfied by a spherical segment that is similar to a dome-shaped droplet. As the size of the nucleus increases, the ratio of its surface to its volume decreases and the form factor can be predominant over the surface factor. As a result, a polyhedron is formed whose form is determined by Wolfe's law. In solving the problem posed, we restricted ourselves to a spherical form, that is the most favorable in the initial stage. The introduction of other forms does not change substantially the calculation results [4].

When a dome-shaped crystal nucleus B appears in the vapor phase A, the total thermodynamic potential Z of the vapor-crystal system changes by [5]

$$\Delta Z = \left[\frac{\pi r^3}{3 v_B}(\mu_B - \mu_A) + \pi r^2 \sigma\right](2 - 3\cos v + \cos^3 v)\,. \tag{1}$$

In the case of a supersaturated vapor the chemical-potential difference is expressed by the formula [4]

$$\mu_A - \mu_B = kT \ln\left(\frac{p_r}{p_\infty}\right). \tag{2}$$

For a supercooled vapor in relation to the condensation temperature T_0 we obtain the following expression [4]:

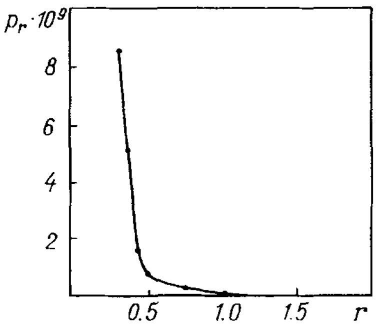
$$\mu_A - \mu_B = \int_T^{T_0} \frac{q}{T}\,dT \approx \frac{q}{T_0}(T_0 - T)\,. \tag{3}$$

Finding the maximum of expression (1) relative to r with account for Eq. (2), we obtain

$$\ln\frac{p_r}{p_\infty} = \frac{2\sigma v_B}{rkT}\,. \tag{4}$$

This equation is fulfilled at a pressure p_r different from p_∞. The limiting cases where $r = r_{\min}$ and $r = r_{\max}$ are of practical interest. The minimum nucleus radius $r_{\min}$ cannot be smaller than the mean distance between neighboring particles [4], while the maximum $r_{\max} = r_\infty$ corresponds to an infinitely large crystal. Calculations show that the extremely small nucleus of radius $r_{\min}$ contains just a few molecules [6]. Although for objects of such small sizes a macroscopic theory is not rigorously applicable, we can use it to evaluate the limiting value of the sublimation rate of graphite. From the experimental data of Van Laar [7] we obtain the following formula [8] for the equilibrium pressure of the vapor over a graphite macrocrystal:

$$p_\infty = K_1 \exp\left(-\frac{A}{T} - B\ln T + C\right), \tag{5}$$



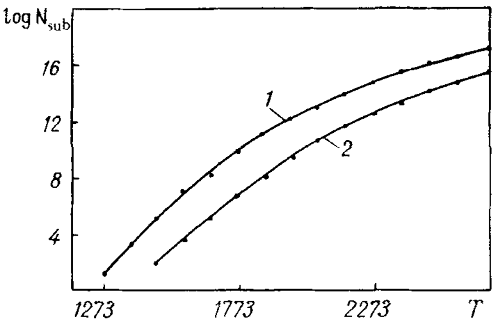


Fig. 1. Curve of the elasticity of the saturated carbon vapor over a dome-shaped nucleus of graphite as a function of its size. p_r, Pa; r, nm.

Fig. 2. Dependence of the number of carbon atoms sublimated from a dome-shaped graphite nucleus containing the minimum possible number of particles ($r = r_{min}$, curve 1) and from volumetric graphite ($r = \infty$, curve 2) on the absolute temperature T. T, K.

where A = 108,498; B = 3; C = 46.552. For the number N_{sub} of atoms sublimated from unit surface of the graphite macrocrystal per unit time, we obtain [8]

$$N_{sub} = \frac{K}{\sqrt{m_{sub}T}} \exp\left(-\frac{A}{T} - B \ln T + C\right). \tag{6}$$

Solving Eqs. (4) and (6) simultaneously, we have

$$N_{sub}(T, r) = K\left[\exp\left(-\frac{A}{T} - B \ln T + C\right) \exp\left(\frac{2\sigma v_B}{rkT}\right)\right]. \tag{7}$$

Results of calculations carried out by formulas (4) and (7) are presented in Figs. 1 and 2. From Fig. 1 it is seen that the pressure of the saturated vapor over a nucleus of spherical form depends substantially on its radius r, namely, the smaller the value of r, the more the vapor pressure over it exceeds the pressure over a plane surface. Figure 2 shows dependences of the number N_{sub} of carbon atoms sublimated from a dome-shaped nucleus of radius $r = r_{min}$ that contains the minimum possible number of particles $N = 8$ (curve 1) and a macrocrystal ($r = \infty$, curve 2) on the absolute temperature T. It is seen that the sublimation rate m_{sub} ($m_{sub} = m_0 N_{sub}$) of the dome-shaped nucleus is considerably higher than that from the plane surface of the macrocrystal. In both cases for graphite the rate increases sharply with the temperature T, whereas for diamond under similar conditions it is negligibly low and is not determined. This difference in the sublimation rates of the graphite and diamond was used for the development of a new method for building up homogeneous single-crystal diamond films that requires no chemical etching. For practical implementation of the method suggested, we must first determine the supersaturation in relation to diamond that, in conformity with the structural diagram, provides growth of a perfect single crystal. Then from curve 1 (Fig. 2) or by formula (7) we must find the number N_{sub} of atoms sublimated from graphite, which must be equal to (or somewhat greater than) the given number of condensing atoms N_{con}. This equality $N_{sub} = N_{con}$ is possible only at a certain temperature that can be found from curve 1 (Fig. 2) or by formula (7). When these conditions are met, nucleation and growth of just the diamond modification of carbon in the total absence of graphite is possible, since equilibrium saturation in relation to graphite is supersaturation in relation to diamond.

The method suggested can be used in practice both in an open reactor and in a closed vessel. In the first variant, equilibrium saturation in relation to graphite can be maintained due to an external source by filling with a hydrocarbon, for example, methane CH_4. In this case, in hydrocarbon decomposition hydrogen will be liberated, which, however, along with the useful property of the etching agent has certain negative factors not allowing synthesis of a structurally perfect homogeneous single crystal. In a closed vessel, diamond can be synthesized by recrystallization of graphite. Here equilibrium saturation in relation to the graphite and, consequently, the corresponding supersaturation in relation to diamond can be controlled by changing the temperature. This method makes it possible to synthesize, depending on the requirements, single, poly-, or amorphous structures of extremely high quality. In both variants, diamond should be synthesized within the limits of approximately 1300–2000 K, since at higher temperatures the risk of a polymorphic transition of diamond to graphite in the crystal volume arises.

The present method does not require chemical etching of graphite, but if necessary the two methods can be used simultaneously.

NOTATION

Z, thermodynamic potential of the system; r, radius of curvature of the nucleus; ϑ, angle of contact; σ, surface tension at the crystal-vapor boundary; v_B, volume for one particle of phase B; μ_A and μ_B, chemical potentials of phases A and B, respectively; p_r, pressure of the saturated vapor over a nucleus of radius r; p_∞, equilibrium vapor pressure over a plane surface at $r = \infty$; T_0, temperature of vapor condensation; q, heat of the transition $A \rightarrow B$ per molecule; $r_{\min}$, minimum admissible radius of a nucleus; $r_{\max} = r_\infty$, maximum nucleus radius; K_1, constant depending on the choice of the system of units; K, constant; N, number of atoms in a nucleus of a new phase; T, absolute temperature; m_{sub}, sublimation rate; m_0, carbon atom mass.

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