DETERMINATION OF CONDITIONS FOR DEVELOPMENT AND GROWTH OF A METASTABLE DIAMOND PHASE OF CARBON AND ABSENCE OF STABLE GRAPHITE PHASE

L. O. Meleshko

UDC 636.425

Conditions for development and growth of just a metastable diamond phase of carbon and complete absence of graphite are determined. Based on the results obtained, a method for development of single-crystal diamond films not involving chemical etching of graphite is proposed.

In several works [1, 2], it is stated that simultaneous growth of crystalline nuclei of both metastable diamond and stable graphite takes place in carbon deposition from the gas phase. The phenomenon of development and growth of variously modified crystals is inherent not just in carbon. It is detected in almost half the elements of the Periodic Table. In order to explain this phenomenon, Ostwald formulated the "step rule" [3], according to which in cases where a series of transformations from a less stable to a more stable state is possible, usually the closest (with respect to the energy difference) more stable system is formed, but not the most stable one.

In [4, 5], the kinetics of development and growth of various nuclei of polymorphic betol (β-naphthyl salicylate, $C_{17}H_{12}O_3$) was investigated. It was found that nucleation of three different crystal modifications takes place simultaneously in this compound under identical conditions. For each kind of nuclei, the linear crystallization rate, probability of nucleation, and total conversion rate for various degrees of supercooling of the melt were investigated. Experiments have shown that curves of the temperature dependences of the nucleation and growth rates are different for each type of nuclei. Upon investigation of the crystallization kinetics, it was found that in cases where the conversion process is due to one type of nucleus, it is rather satisfactorily described by an S-shaped curve. Upon appearance of different modifications in the melt, the S-curve acquires a more complicated character. It was found that under these conditions, a less stable modification transforms into a more stable one. These regularities of structure development in nucleation and growth of crystals of different modifications have a general character. They can be used for explanation of the possibility of simultaneous development and growth of diamond and graphite crystals in carbon deposition from the gas phase. However, as opposed to betol, a substantial delay takes place in the polymorphic diamond-to-graphite transition as a result of the high activation barrier inherent in covalently bonded crystals.

In carbon deposition from the gas phase, hydrocarbon pyrolysis $C_nH_k \rightarrow C_{sol} + H_2$ takes place in two different ways [2]:

$$C_nH_k \rightarrow C_{diamond} + H_2 ; \quad C_nH_k \rightarrow C_{graphite} + H_2 .$$
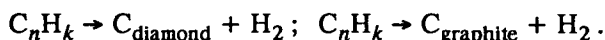
In the case where methane CH_4 is used for diamond synthesis, a chemical reaction of decomposition is used:

$$CH_4 \rightleftarrows C_{diamond} + 2H_2 ; \quad CH_4 \rightleftarrows C_{graphite} + 2H_2 .$$
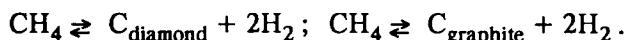
In this case, dissolution of graphite can take place simultaneously according to the reaction
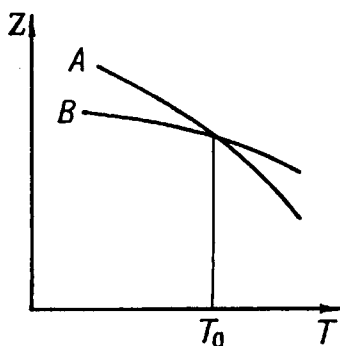
$$C_{graphite} + 2H_2 \rightarrow CH_4 .$$
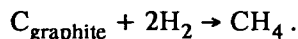
Fig. 1. Dependences of the thermodynamic potentials Z of vapor (A) and solid
(B) phases on the temperature T.

Gould [6] has proposed the following mechanism of the reaction of carbon atoms with graphite: an impinging H atom, upon interacting with two surface-chemisorbed H atoms, forms a complex that, upon interacting with another H atom, forms a CH_4 molecule that desorbs subsequently. As a result, gasification of graphite takes place in the presence of a high concentration of hydrogen in the gas phase, whereas diamond is virtually not gasified up to 1000°C [7]. Thus, using the atomic hydrogen, one can completely inhibit the reaction $CH_4 \rightarrow C_{graphite} + 2H_2$ and obtain the deposition in the form of just the diamond modification of carbon. This method is widely used in practice for growth of diamond films at temperatures below 1000°C. Above this temperature, graphite growth dominates over its etching, and therefore, the method of chemical etching is unsuitable under these conditions. Moreover, in this case diamond is also etched by atomic hydrogen, which reduces its growth rate. In this connection, the need for a search for an alternative approach to solving this problem emerges. It cannot be excluded that the existence region of a diamond single crystal is situated on the structure existence diagram in the region corresponding to temperatures above 1000°C, for which no experimental investigations have been carried out so far. In the present work, a novel approach to this problem is proposed that makes it possible to produce single-crystal diamond films with total exclusion of graphite without employing chemical etching. The approach is based on the concept that, under conditions of equilibrium with respect to graphite, supersaturation with respect to diamond takes place, upon which nucleation and growth of just diamond crystals are possible.

To solve the problem posed, we consider the mechanism of graphite and diamond sublimation consisting in detachment of certain atoms of the surface layer from their neighbors and their removal to the environment. The transition of the substance from the crystalline state to the gaseous one is possible within the entire temperature and pressure range within which coexistence of the solid and liquid phases occurs. The main kinetic characteristic of sublimation is its rate determined by the weight of the substance m_s evaporating per unit time interval, which depends on the intensity of the thermal molecular motion, i.e., on the temperature, and the rate of condensation of molecules, which depends on the vapor pressure. For each temperature a certain well-defined pressure exists at which the rates of transfer of molecules from the solid state into the vapor and back are equilibrated. Under these conditions, a dynamic equilibrium in which the number of molecules N_s sublimating during a given time interval from the solid state equals the number of molecules N_{con} condensing during the same time interval. In this case the numbers of molecules in the crystal and the gas phase are constant, and therefore, the resulting process rate equals zero. Vapor in equilibrium with the corresponding crystal is called saturated vapor.

A crystal and its vapor are qualitatively different phases. Both have corresponding dependences of the thermodynamic potential $Z(p, T)$. With increasing temperature (at p = const), the Z-isobars descend and become convex (Fig. 1). The crossing point of these two curves at T_0 (the equilibrium temperature) determines the condition of equilibrium of the two phases (vapor A and crystal B). It should be noted that the thermodynamic potential Z characterizes only a pure substance. In cases where the latter enters the composition of a multicomponent system, the equilibrium condition is determined by the chemical potential $\mu(p, T)$.

Crystallization is a process directed toward a more stable phase. At pT = const, the chemical potential μ is its driving force. When $\mu_A > \mu_B$, the phase transition from A to B takes place by means of crystalline nucleation
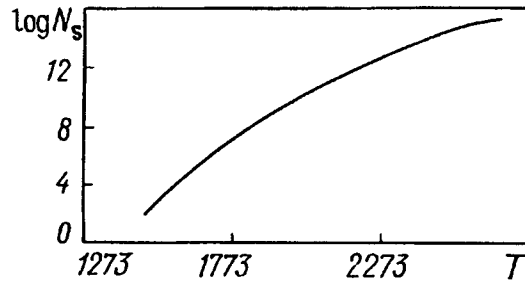
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Fig. 2. Dependence of the number of sublimated carbon atoms from bulk graphite on the absolute temperature T in coordinates of $\log N_s$ vs T.

and ensuing growth of nuclei. If $\mu_A < \mu_B$, nuclei of the new phase created as a result of a fluctuation are nonviable and will gradually disappear. When the stock phase is a gas [8],

$$\mu_A - \mu_B = kT \ln \frac{p}{p_0}, \tag{1}$$

where p is the pressure of the supersaturated vapor, and p_0 is the equilibrium vapor pressure. At $p = p_0$, $\ln (p/p_0) = 0$, and therefore $\mu_A = \mu_B$. In this state, corresponding to the equilibrium state, the driving force of the process vanishes, and crystal growth is impossible.

According to the kinetic theory of gases, the number of molecules N_c of a given species impinging on a surface of area Ω in the equilibrium with the vapor phase per unit time interval equals [9]

$$N_c = p\Omega/(2\pi m kT)^{1/2}, \tag{2}$$

where p is the vapor pressure at the temperature T, m is the mass of a molecule, and k is the Boltzmann constant. According to experimental data of van Laar, the equilibrium pressure of graphite vapor can be calculated by the formula

$$p = K \exp \left(- \frac{108498}{T} - 3 \ln T + 46.552\right) \ \text{Pa}, \tag{3}$$

where K_1 is a constant that depends on the choice of the system of units.

By solving Eqs. (2) and (3) simultaneously for the number N_s of carbon atoms sublimating from graphite, we obtain the following expression:

$$N_s = \frac{K}{\sqrt{m_s T}} \exp \left(- \frac{108498}{T} - 3 \ln T + 46.552\right), \tag{4}$$

where K is a constant. Results of calculations by Eq. (4) are presented in Fig. 2. It is evident that the graphite sublimation rate m_s ($m_s = m_0 N_s$, where m_0 is mass of a carbon atom) is small at temperatures below 1000°C, but increases substantially with increasing temperature above 1000°C.

It follows from the above data that in order to avoid formation of graphite in synthesis of diamond, one should provide conditions under which the condensation rate of carbon atoms would not exceed the sublimation rate. This can be achieved by maintaining the equilibrium saturation with respect to graphite. In this case supersaturation with respect to diamond takes place, since the diamond sublimation rate is extremely low (substantially lower than that of graphite). Under actual conditions, graphite nuclei appear on the substrate surface or faces of diamond crystals in the form of small formations, which are more reactive than large ones. Therefore, the number of particles sublimated will somewhat exceed that defined by Eq. (4). The temperature dependence of the sublimation rate with regard for the sizes of the nuclei can be determined both theoretically and experimentally.

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