

Homogeneous formation of a diamond in the gaseous phase

D. V. Fedoseev, B. V. Deryagin, A. V. Lavrent'ev, and I. G. Varshavskaya
Institute of Physical Chemistry, USSR Academy of Sciences

(Submitted 27 March 1980)

Pis'ma Zh. Eksp. Teor. Fiz. **32**, No. 1, 7-9 (5 July 1980)

The possibility of producing diamond and other metastable types of carbon in the gaseous phase at low pressures is shown. Experiments in which a laser beam excited liquid hydrocarbons were performed.

PACS numbers: 61.55.Dc, 42.60. — v

The possibility of growing diamonds from the gaseous phase as a result of heterogeneous crystallization has been demonstrated. Diamond films have been obtained by chemical crystallization¹ and condensation of the ion and atomic beams on a cooled substrate.^{2,3} A homogeneous nucleation of a diamond or of other metastable types of carbon in the gaseous or vapor phase can occur in principle.

Unfortunately, the theoretical calculation of nucleation at large supersaturations is extremely complicated, whereas at large supersaturations the probability for the formation of metastable phases and structures increases.⁴ We shall analyze qualitatively the variation of the homogeneous nucleation rate on the basis of the original Folmer-Weber equation.⁵ We note that the use of the more exact expressions obtained by Zel'dovich and Deryagin⁷ leads to qualitatively similar results.

Let us represent the homogeneous nucleation rate J at a pressure P and temperature T as follows

$$J = \left[\frac{\alpha P^2}{(2\pi mkT)^{1/2} \sigma} \right] \frac{U}{kT} \exp\left(-\frac{U}{kT}\right), \quad (1)$$

where U is the work required to produce a homogeneous, critical nucleus, α is the condensation coefficient, and σ is the surface energy. We can easily see that Eq. (1) contains the dimensionless parameter U/kT . The first factor in Eq. 1, which depends weakly on the temperature, can be assumed to be a constant. We find from the extremum condition $dJ/d(U/kT) = 0$ that the nucleation rate has a maximum when

$$\left(\frac{U}{kT}\right)_{max} = 1 \quad (2)$$

Here this maximum is

$$J_{max} = \frac{\alpha P^2}{(2\pi mkT)^{1/2} \sigma} \exp(-1) \quad (3)$$

and for each possible phase it is inversely proportional to its surface energy. The remaining values in Eq. (3) are the same for all the phases.

Thus, it follows from Eqs. (2) and (3) that as the supersaturation increases the probability for the appearance of metastable phases in a given system increases, and the maximum of their nucleation rate occurs when the condition (2) is satisfied. This is a general conclusion which is valid for other systems in addition to the carbon system.

The possibility of diamond formation has been previously verified experimentally⁸ by condensing a pulsed discharge plasma in the vapors of organic liquids. However, because of the sputtering of graphite or metallic electrodes, it was impossible to eliminate the heterogeneous nucleation of a diamond. Therefore, we set up an experiment in which foreign particles were not introduced into the crystallization zone.

A drop of an organic liquid (octane, decane), after breaking away from a capillary, passed through the focused radiation beam of an LG-25 infrared laser. The radiation density in the beam was 2000 W/cm². After partial evaporation the drop broke down into fine droplets. The aerosol that formed was collected in a cell or directly on a substrate.

Electron-microscope studies showed that the condensation products had $\leq 1\text{-}\mu$ solid globular and faceted particles. We were able to establish by means of electron diffraction that carbyne and graphite are also produced (see Table I).

It must be noted that a diffraction from globular particles gives primarily an amorphous scattering pattern (halo), whereas the presence of reflections is characteristic of the faceted particles. Reflections characteristic of diamond and carbyne are often obtained from the same particle. This is attributable to a growth of two different phases on the same nucleus either simultaneously or sequentially.

The results described above help to explain the presence of traces of carbyne and the absence of graphite in the diamond-like films obtained from atomic beams.³ In fact, the nucleation rate of carbyne is higher than that of graphite for a condition

TABLE I. Analysis of electron diffraction patterns of carbon phases (interplanar spacings, Å).

1	2	3	4	5	Interpretation
4.20	—	—	—	—	carbyne
3.72	—	—	—	—	carbyne
2.06	—	2.07	2.05	halo	diamond
1.75	—	—	—	—	carbyne
1.46	1.47	—	—	—	carbyne
1.27	—	1.27	1.27	halo	diamond
1.06	—	1.06	1.07	—	diamond
—	1.01	—	—	—	carbyne
0.880	—	0.88	0.885	—	diamond

under which a diamond is produced. In addition, we can predict on the basis of the above discussion that the carbon phases, which has a maximum nucleation rate at a higher supersaturation than that of a diamond must have a high surface energy, according to Eq. (3), and hence a high microhardness.

A large number of metastable phases cannot be obtained by using the laser method. The use of plasma-chemical methods, which harden the solid particles very rapidly, is a better approach.

In conclusion, we note that the Folmer-Weber equation was obtained under the conditions of dual collisions. At high supersaturations the size of the critical nucleus of a new phase is commensurable with that of an atom. Therefore, we should again emphasize the qualitative nature of the theoretical analysis which most likely characterizes the formation probability of a given type of chemical bond.

¹B. V. Deryagin and D. V. Fedoseev, *Rost almaza i grafito iz gazovoi fazy* (Growing Diamond and Graphite from the Gaseous Phase), Nauka, Moscow, 1977.

²G. M. Golyanov and A. P. Demidov, French Pat. No. 2,157,957, 1973.

³N. N. Matyushenko, V. E. Strel'nitskiĭ, A. A. Romanov, and V. G. Golok, *Dokl. Akad. Nauk Ukr. SSR Ser. A*, 5, 459 (1976).

⁴J. Martin and R. Doherty, *Microstructure Stability of Metallic Systems* (Russ. Transl., Atomizdat, Moscow, 1978).

⁵D. Hires and G. Pound, *Evaporation and Condensation* (Russ. Transl., Metallurgiya, Moscow, 1966).

⁶Ya. B. Zel'dovich, *Zh. Eksp. Theor. Fiz* 12, 525 (1942).

⁷B. V. Deryagin, *Zh. Teor. Eksp. Khim.* 4, 471 (1973).

⁸D. V. Fedoseev, *Izv. Akad. Nauk SSSR Ser. Khim.* No. 9, 2157 (1979).