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FORMATION OF CONICAL STRUCTURES DURING THE GROWTH OF NANOFIBERS IN A GLOW DISCHARGE PLASMA

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A theoretical model of the growth of conical carbon structures, when employing the "vapor–liquid–solid body" mechanism in a glow discharge plasma, is suggested. It is shown that the radius of a catalytic nanoparticle influences the cone apex angle.

In [1], experimental data on the appearance of conical structures during the growth of carbon nanofibers in a glow discharge plasma are discussed qualitatively. The conical structures attract great interest of research workers [2 and bibliography therein], since they can be used as emitters in optoelectronics. In [1], a physical idea on the nature of the formation of conical structures is also suggested. The idea behind it is that the carbon vapors formed in the process of plasma decomposition of hydrocarbons easily settle on freshly grown nanofibers. Thus, a major outcome of [1] is that the carbon cones obtained have an internal structure.

Here we present a theoretical description of this process, using a mathematical model (developed in [3]) of the growth of carbon nanofibers via the complex "vapor–liquid–solid body" mechanism. In Fig. 1, the physical picture of the formation and growth of conical structures is shown.

Mathematical Model. The rate of growth of a nanofiber along the length L is governed by the equation [3]

$$\frac{dL}{dt} = D(T)\,\frac{Sn_{\text{eq}}}{Rn_{\text{s}}}\,, \tag{1}$$

where $D(T)$ is the coefficient of diffusion of carbon in the material of a catalytic nanoparticle of radius R and substrate temperature T; $n_{\text{eq}}(T)$ is the numerical density of the carbon molecules corresponding to the equilibrium solubility of carbon in the catalyst material; S is the supersaturation of a solid solution; n_{s} is the numerical density of carbon molecules in a nanofiber. The expression for the rate of growth of tubular nanofibers was also obtained in [3].

We note that nanoparticles from nickel, iron, or their alloys are usually used as catalytic nanoparticles. If the specific flux of molecules J that carry carbon from a gas phase (plasma) exceeds the value $D(T)n_{\text{eq}}/R$, growth of the catalytic nanoparticle surface with amorphous carbon begins. The composition of the flux J depends on the plasma composition and discharge conditions [4]. Further we assume that the nanofiber temperature coincides with the substrate temperature [5].

It is important to emphasize that for experimental conditions at atmospheric pressure the process of deposition of carbon atoms on a nanofiber first proceeds in a free-molecular regime, since the nanofiber diameter is approximately equal to the diameter of the catalytic nanoparticle [3]. Thus, even at an atmospheric-pressure discharge [4] the Khudsen number $\text{Kn} = \lambda/R >> 1$.

According to [1], a cone is formed when carbon is deposited from a plasma onto the nanofiber surface. Indeed, it can easily be shown that in a free-molecular regime the equation for the change in the cone radius $R(z)$ at the height z has the form

$$\frac{dR(z)}{dt} = \begin{cases} 0\,, & \text{if } z > L\,; \\ \dfrac{P_{\text{c}}}{n_{\text{a}}\sqrt{2\pi mkT_{\text{p}}}}\,, & \text{if } z < L\,, \end{cases} \tag{2}$$

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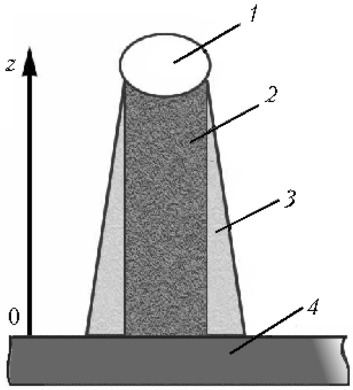

Fig. 1. Structure of the conical formation on a nanofiber: 1) catalytic nanoparticle; 2) carbon nanoparticle; 3) amorphous carbon; 4) substrate.

where n_a is the numerical density of carbon atoms in the amorphous layer; P_c is the partial pressure of carbon atoms in a discharge; as a rule, this value is determined by special calculations or measurements.

It follows from Eqs. (1) and (2) that at the given height z the cone radius increases linearly in time. We note that in Eq. (2) we neglect carbon evaporation from the nanofiber, since usually the nanofiber temperature is equal approximately to $(600–800)^{o}$C and it is determined by the temperature of the substrate. At such a temperature the pressure of the saturated carbon vapors is extremely small.

The angle α between the lateral side of the cone and its height is determined from the equation obtainable from simple geometric considerations:

$$\tan\alpha = \frac{R\,(P_c n_s - 1)}{n_a D\,(T)\,S n_{eq}\,(T)\,\sqrt{2\pi m k T_p}}\,. \tag{3}$$

It is seen that the larger the radius of the nanoparticle, the larger the cone angle formed by amorphous carbon near the nanofiber. At a constant partial pressure of carbon in a gaseous phase the cone apex angle decreases strongly on increase in the substrate temperature, since the diffusion coefficient $D(T)$ and solubility $n_{liq}(T)$ increase exponentially with temperature. It may quite be that this fact associated with the substrate temperature makes the cases of experimental observation of conical structures rare. It is obvious that carbon cone-like structures must result at low enough substrate temperatures [1, 2, 4]. When the partial pressure of carbon is increased, then to observe cones with the same angle the substrate temperature must also increase.

Experimental values of the angle α lie in the range $5–15^{o}$C [1, 6]. Numerical estimation according to (3) shows that for a nickel nanoparticles with R = 10 nm at the temperature $T = 700^{o}$C such angles are formed if the partial pressure of a pure carbon is equal to 0.2 Pa. As noted above, the partial pressure of a pure carbon among the products of decomposing hydrocarbons depends on the general pressure in a gas mixture, its composition, and on the power of plasma source. Application of atomic hydrogen obtainable on supply of molecular hydrogen or ammonia into a plasma allows one to realize the process also at higher partial pressures of carbon. In this case, a portion of carbon from the nanofiber surface is entrained by hydrogen [1], i.e., the cone apex angle decreases.

If in the course of an experiment an appreciable amount of closely spaced nanofibers is formed, then due to the jam effect the cone angle will change in motion from the periphery to the center of the massive of conical structures.

At a high partial pressure of carbon vapors the cone radius will increase rapidly approximately to the value equal to the free path length after which, as is well known, the rate of growth decreases sharply already in the regime of a continuous medium. As a result, the nanofiber near the substrate is coated practically by a cylindrical layer of amorphous carbon, and the conical part will be observed only near a catalytic nanoparticle. An experimental observation of this transition to a cylindrical layer is presented in [7].

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NOTATION

D, diffusion coefficient of carbon in a catalytic particle, m^2/sec; *k*, Boltzmann constant; Kn, Knudsen number; *L*, cone height; *m*, mass of carbon atoms, kg; *n*, numerical density, m^{-3}; *P*, pressure, Pa; *R*, radius of a catalytic particle, m; *S*, supersaturation of a solid solution, m; *t*, time, sec; *T*, temperature, K; *z*, height; α, cone apex angle; λ, mean free path of a carbon atom, m. Subscripts: a, amorphous; c, carbon; eq, equilibrium; p, plasma; s, solid.

REFERENCES

1. K. L. Klein, A. V. Melechko, T. E. McKnight, et al., Surface characterization and functionalization of carbon nanofibers, *J. Appl. Phys.*, **103** (061301) (2008).
2. K. Ostrikov and A. B. Murphy, Plasma-aided nanofabrication: where is the cutting edge? *J. Phys. D: Appl. Phys.*, **40**, 2223–2241 (2007).
3. F. N. Borovik and S. P. Fisenko, Kinetics of the formation and growth of nanofibers following the "vapor–liquid–solid body" scheme, *Pis'ma Zh. Tekh. Fiz.*, **33**, No. 4, 27–32 (2007).
4. S. A. Zhdanok, S. V. Gorbatov, A. A. Mikhailov, et al., Low-temperature plasma-chemical synthesis of carbon nanotubes on nickel patterns obtained by the photocatalytic-lithography method, *Inzh.-Fiz. Zh.*, **81**, No. 2, 203–205 (2008).
5. F. N. Borovik, S. P. Fisenko, and S. I. Kas'kova, Thermodynamics and transfer processes in nanowhisker formation on a substrate, in: V. E. Borisenko, S. V. Gaponenko, and V. S. Gurin (Eds.), *Physics, Chemistry and Application of Nanostructures*, World Scientific, Singapore (2007), pp. 451–454.
6. V. I. Merkulov, A. V. Melechko, M. A. Guillorn, et al., Sharpening of carbon nanocone tips during plasma-enhanced chemical vapor growth, *Chem. Phys. Lett.*, **350**, 381–385 (2001).
7. N. A. Kiselev, A. V. Krestinin, J. L. Hatchinson, et al., Extreme length carbon nanofilament with single-walled nanotube cores grown by pyrolysis of methane or acetylene, *Carbon*, **44**, 2289–2300 (2006).