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NANOMATERIALS

COALESCENCE AND THE INITIAL STAGE OF FORMATION OF NANOFIBERS BY THE "VAPOR–LIQUID–SOLID" SCHEME

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It has been shown that the diffusion interaction of growing impurity clusters within catalytic nanodroplets determines the important geometric parameters of a nanofiber. The characteristic time of coalescence of the clusters has been found.

Keywords: *mathematical modeling, Kelvin effect, supersaturation, radii of curvature, cluster, solubility.*

Introduction. Such objects as nanofibers, nanotubes, and nanowires attract particular interest among the whole variety of nanomaterials [1]. Nanofibers are currently manufactured from many elements of the IVth-a group of the Periodic Table, including carbon, silicon, and germanium ([2–4] and references therein). To produce nanofibers from these materials one uses certain catalytic nanoparticles, the so-called nanodroplets. For example, catalytic nanoparticles of gold are used in the case of silicon nanofibers, whereas catalytic nanoparticles or nickel of iron are used for production of carbon nanofibers. It has turned out that the complex mechanism of "vapor–liquid–solid" phase transitions on the surface of a catalytic nanoparticle is always used when nanofibers are formed. In this mechanism, molecules in the gaseous phase supply chemically bound carbon (silicon, germanium) to the catalytic-nanoparticle surface. On it, we have molecular decay and carbon (silicon, germanium) atoms diffuse into the particle. A supersaturated solid solution of, e.g., carbon, is created within the catalytic nanoparticle by cooling.

We have been able to show that the process of nucleation in this supersaturated solution is the most advantageous thermodynamically at the phase boundary of the catalytic nanoparticle and the substrate [4]. It is noteworthy that the coefficient of surface tension of the substrate exerts a substantial influence on the nucleation rate of clusters. The characteristic radius of the formed critical clusters is of the order of 1 nm; the radius of nanodroplets is usually tens of nanometers. If the supersaturated state of the solid solution is held for some time, the clusters grow and begin to diffusively interact with each other. Part of the clusters in the nanodroplets coalesces and forms different associations [4] among which half-tori are of particular importance (Fig. 1). In the process of further growth, half-tori with a maximum radius of curvature provide the basis for nanofiber formation. The nanofiber leaves the nanoparticle in the process of growth so as to diminish the thermodynamic contribution of the arising deformations and grows, as is schematized in Fig. 2.

This work seeks to explain a number of experimental facts obtained in studying the physics of the process of nanofiber formation. In particular, of interest are the questions: why is the diameter of a nanofiber virtually equal to the diameter of a catalytic nanodroplet and why are nanofibers not formed from rather small nanodroplets [5]?

To answer these questions we numerically investigate the coalescence of clusters due to the Kelvin effect [6]. In particular, we illustrate our approach with calculations of diffusion processes for the coalescence of two half-tori within a catalytic nanodroplet. It seems evident that the investigated effects are not confined to the interaction of carbon clusters.

Mathematical Model. The Kelvin effect determines the equilibrium number density of the atoms n_{eq} above a curved phase-transition surface characterized by two principal radii of curvature R_1 and R_2 of two mutually perpendicular normal cross sections of the surface [6, 7]:

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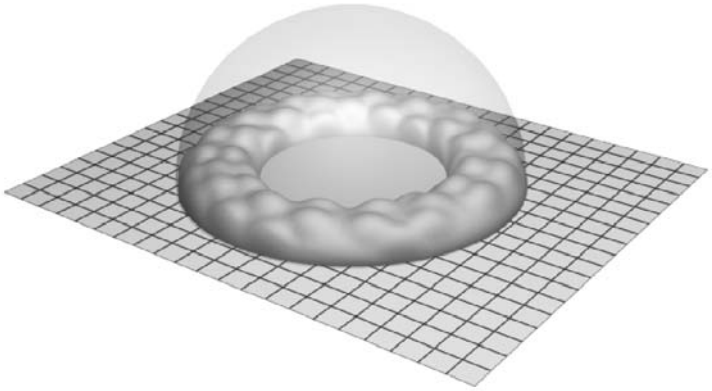

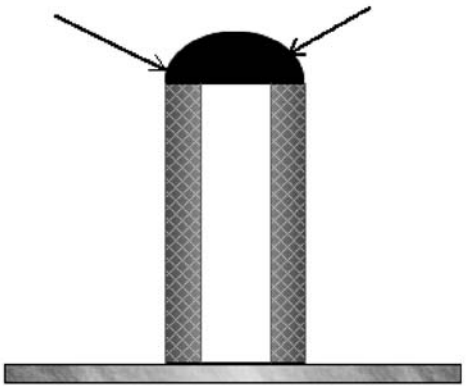

Fig. 1. Formation of a half-torus from hemispherical clusters within the catalytic nanodroplet.

Fig. 2. Sketch of the growth diagram of a nanofiber (arrows, molecular fluxes from the gaseous phase).

$$n_{\text{eq}} = n_0 \exp\left[\frac{\sigma v}{kT}(1/R_1 + 1/R_2)\right], \tag{1}$$

where n_0 is the equilibrium density of the impurity above the plane phase boundary, which is numerically equal to the solubility of the impurity in the material of the catalytic nanodroplet, σ is the coefficient of surface tension between carbon and the catalytic-nanodroplet material, k is the Boltzmann constant, T is the system's temperature, and v is the volume per atom in the condensed phase. For carbon, we have $v \approx 10^{-29}$ m^3. As follows from (1), the smaller the radii of curvature of the phase boundary, the higher the equilibrium density of the dissolved carbon. For a spherical cluster, the radii of curvature are equal to each other.

We assume that for the surface of a half-torus formally resulting from a cut of the torus by the substrate plane and that is in mechanical equilibrium with the substrate, two radii of curvature can be used: one is coincident with the radius of the ring (we denote it by R_1), and the second radius of curvature is coincident with the internal radius of the "tube" (we denote it by R_2). Thus, the radius R_1 plays the role of the averaged radius of curvature of the half-torus. It is larger than the minimum possible radius of curvature and smaller than the maximum possible radius of curvature of the half-torus. By virtue of the Kelvin effect, half-tori with a maximum possible averaged radius of curvature R_1 (which is nearly equal to the nanodroplet radius) have a minimum equilibrium value of number density of the dissolved impurity. It is natural that this circumstance ensures the most favorable conditions for growth of such a half-torus in a supersaturated solution. Growth of the half-torus is dependent on the supersaturation of the solid impurity solution.

The supersaturation of the solid solution S of the impurity (carbon) in the catalytic nanodroplet is equal to

$$S = n/n_0 . \tag{2}$$

When the supersaturation of the solid solution is fairly high, carbon clusters are formed at the phase boundary between the nanodroplet and the substrate. Once they have appeared, the average supersaturation within the nanodroplet diminishes, remaining nonuniform in the nanodroplet volume. The carbon stored in the nanodroplet is consumed with further growth of the clusters, being partially replenished by the fluxes from the gaseous phase.

The propagation of carbon in a nanodroplet containing two half-tori inside is described by the diffusion equation and corresponding boundary conditions. For simplicity, we consider the nanodroplet with cylindrical symmetry, for which the carbon-diffusion equation has the form

$$\frac{\partial n\,(r, z)}{\partial t} = \frac{D}{r}\frac{\partial}{\partial r}\left[r\frac{\partial n}{\partial r}\right] + D\frac{\partial^2 n}{\partial z^2}, \tag{3}$$

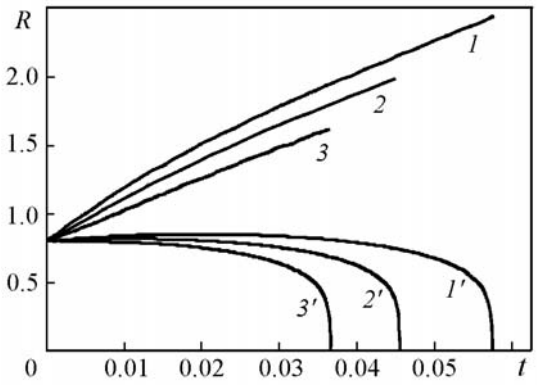

Fig. 3. Evolution of small radii of curvature of two half-tori within the nanodroplet (1, 2, and 3) for the half-torus with R_1 = 7.1 nm and 1′, 2′), and 3′) with R_1 = 3.1 nm): 1) S = 1.45, 2) 1.4, and 3) 1.35.

where the z axis is directed perpendicularly to the substrate and D is the diffusion coefficient of carbon.

As can be shown, the equation for the change in the radius of curvature R_2, which allows for the diffusion character of dissolved-impurity transfer, has the form

$$\frac{\partial R_2}{\partial t} = \frac{Dm\,[n - n_{\text{eq}}\,(R_2)]}{R_2 \rho}\,, \tag{4}$$

where m is the mass of the carbon atom and ρ is the mass density of the cluster (for numerical calculations; it can be assumed, with a high degree of accuracy, to be equal to the density of a macroscopic material). In this work, we disregard the possible change in the second radius of curvature R_1.

The boundary conditions to Eq. (2), which reflect the physics of the problem, can be represented as follows: there is no mass exchange on the interface between the nanodroplet and the substrate; therefore, we have

$$\nabla n\,(r, 0) = 0\,; \tag{5}$$

on the remaining nanodroplet surface, a constant supersaturation of carbon is maintained; therefore, we have

$$S = \text{const}\,. \tag{6}$$

Calculation Results. The evolution of the fields of number density of carbon within the nanodroplet and above the two half-tori, which results from solution of the three-dimensional diffusion equation (3), will be presented in a later and expanded work. Here we restrict our consideration to investigation of coalescence effects.

Figure 3 shows results of calculations of the evolution of small radii of curvature R_2 for three different supersaturations S on the exterior surface of the nanodroplet. We assume that they are equal for both half-tori at the initial instant of time. We recall that the radius R_1 actually determines the position of the half-torus on the substrate within the catalytic nanodroplet (see Fig. 1).

From the data of Fig. 3, it is clear that half-tori with a lower value of the effective radius of curvature are dissolved after a fairly short time. In complete agreement with the numerical calculations, this time can be evaluated as $\sim R^2/D$, where R is the nanodroplet radius. Half-tori with a higher value of R_1 grow virtually linearly; the higher the supersaturation of the solid solution at the boundary, the higher the growth rate. The lower the supersaturation at the nanodroplet boundary, the faster the process of dissolution of the half-torus.

As our calculations have shown, when the carbon supersaturation is fairly high, first both half-tori grow. As they grow, the supersaturation diminishes and the influence of coalescence begins to manifest itself: the half-torus with a smaller R_1 begins to dissolve.

Conclusions. For a deeper understanding of the complex "vapor–liquid–solid" mechanism of producing nanofibers we have carried out mathematical modeling of the diffusion interaction of two half-tori within the catalytic nano-

droplet. It has been shown for the first time that, under the conditions of slight supersaturation of the solid solution of carbon (silicon, germanium), half-tori with a maximum possible averaged radius of curvature R_1 grow, whereas other half-tori are dissolved. The characteristic dissolution time is of the order of the diffusion time for the entire catalytic nanodroplet. Thus, the experimental fact that the external radius of a nanofiber is virtually coincident with the radius of a catalytic nanodroplet is physically explained as a consequence of the coalescence effect.

The formation of half-tori on the substrate is associated with the growth of impurity clusters formed after the process of nucleation of the dissolved impurity and with their partial coalescence. It is natural that all clusters and their groups, even those that have not formed half-tori, are prone to the coalescence effect.

Also, the use of expression (1) makes it possible to understand that the creation of a supersaturated solid impurity solution in a relatively small catalytic nanodroplet (of the order of several nanometers) does not lead to a substantial growth of clusters. By virtue of the Kelvin effect, clusters are virtually in equilibrium with the solid solution; the supersaturation of the solution is very low and the growth of the clusters is very slow. As a result, a macroscopic consequence of their growth. i.e., a nanofiber, does not appear.

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NOTATION

D, diffusion coefficient of the impurity, m^2/sec; *k*, Boltzmann constant; *m*, mass of the impurity atom, kg; *n*, number density of the impurity, $atom/m^3$; *R*, radius, nm; *S*, supersaturation; *T*, temperature, K; *t*, time, sec; *v*, volume per atom, m^3; ρ, mass density of the nanofiber material, kg/m^3; σ, coefficient of surface tension, J/m^2. Subscripts: 1, larger radius of curvature; 2, smaller radius of curvature; 0, equilibrium solubility in the macroscopic material; eq, equilibrium.

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