MODELING OF EQUILIBRIUM FORMS OF LIQUID DROPS IN GRAPHOEPITAXY FROM SOLUTIONS

Yu. V. Apanovich and V. I. Klykov

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The first successful experiment on graphoepitaxy was growth from solution [1]. Subsequent works concentrated mainly on obtaining semiconductor films, primary silicon films. Graphoepitaxy from solutions has now been set aside, though it has a number of undoubted advantages:

- it is a convenient model object: by studying growth from low-temperature solutions it is possible to study processes in high-temperature solutions in a melt, the direct observation of which is difficult;

- it is of applied value, since many important materials can be grown by this method under controlled conditions; and

- it can be used as an intermediate stage for multistepped graphoepitaxy.

It is shown in [2] that in graphoepitaxy from solutions onto a pattern in the form of a two-dimensional lattice, evolution of the shape of the evaporating drops, which affects the azimuthal orientation of the growing crystals, occurs. It is clear that in order to develop a controlled graphoepitaxy process it is necessary to understand in detail all characteristic features of this phenomenon and its relationship to technological factors. For this reason in this work we modeled the evolution of the shape of a liquid drop by means of a computational experiment.

1. Mathematical Model. We shall study a square cell, containing the evaporating drop of solution. The cell is formed on a flat substrate by protuberances, whose profile in the transverse cross section has the form of a Gaussian curve (Fig. 1). The protuberances are arranged so that gaps, which facilitate the tangential growth of a single-crystalline layer, appear between their faces. We place the origin of a Cartesian coordinate system at the center of the cell in such a manner that the z axis is perpendicular to the surface of the plate. Since the cell is square, by exploiting its symmetry we shall study the problem of finding the equilibrium shape of a drop in the region Ω_1 constituting one-eighth of the cell. The region Ω_1 is an isosceles right triangle OAB (Fig. 1).

Let Ω be the projection of the region occupied by the drop in Ω_1 on the xy plane, while γ is the projection of the line of contact of the three phases. The surface of the protuberance and of the cell in Ω_1 is defined by the equation

$$z=\Phi(x,y),\ \Phi(x,y)=\begin{cases}A\exp\left[-\dfrac{(y-0.5)^2}{B^2}\right], & 0\leqslant x\leqslant 0.35,\ 0\leqslant y\leqslant\\ \leqslant 0.5,\ y\geqslant x,\\ A\exp\left[-\dfrac{(y-0.5)^2+(x-0.35)^2}{B^2}\right], & 0.35\leqslant x\leqslant\\ \leqslant 0.5,\ 0\leqslant y\leqslant 0.5,\ y\geqslant x.\end{cases} \tag{1.1}$$

The parameters A and B enable selecting the form of the surface which is closest to that used in experiments. We shall assume that there is no convective motion of the liquid, evaporation occurs slowly, and the drop passes sequentially through a series of equilibrium shapes corresponding to different volumes of the liquid.

According to [3], for the liquid to be in equilibrium it is necessary and sufficient that on the line of three-phase contact the Dupres–Young condition be satisfied, while on the free surface Laplace's equation of capillarity is satisfied:

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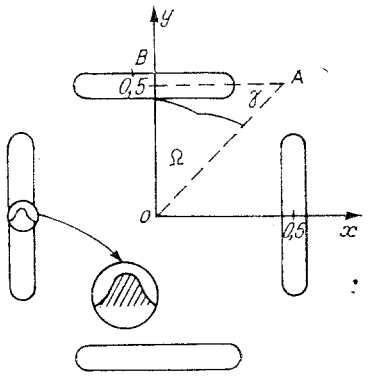

Fig. 1

$$p_0 - p = \sigma_{lv}(k_1 + k_2), \tag{1.2}$$

where p is the pressure in the drop, p_0 is the vapor pressure, $\sigma_{\ell V}$ is the coefficient of surface tension at the liquid–vapor boundary; and k_1 and k_2 are the curvatures of the principal normal sections.

The length of the side of the square cell L = 22 μm is taken as the characteristic size in the problem. For drops of aqueous solutions of salts, having a size L, Bond's number is Bo = 10^{-4}-10^{-5}. Therefore, gravity can be neglected and it may be assumed that the form of the drop and the position of the line of three-phase contact are determined solely by capillary forces. Therefore, the pressure p in the volume of the drop is constant, and then Eq. (1.2) reduces to

$$k_1 + k_2 = -C, \tag{1.3}$$

where the constant $C = (p - p_0)/\sigma_{\ell V}$ depends on the volume of the drop.

Following [3], we introduce the vector function $\mathbf{x} = \mathbf{x}(\xi, \eta)$, $0 \leq \xi \leq 1$, $0 \leq \eta \leq 1$, which transforms the region Ω into Ω*, which is a unit square in the coordinates ξ, η. We shall give the components $x = x(\xi, \eta)$ and $y = y(\xi, \eta)$ in the form

$$x = f\left(\frac{\pi}{4}\xi\right)\eta \sin\frac{\pi}{4}\xi,\ y = f\left(\frac{\pi}{4}\xi\right)\eta\cos\frac{\pi}{4}\xi,\ 0 \leqslant \xi \leqslant 1,\ 0 \leqslant \eta \leqslant 1. \tag{1.4}$$

Here we use the equation of the line γ in polar coordinates $r = f(\varphi)$, $0 \leq \varphi \leq \pi/4$ (the angle φ increases in the clockwise direction away from the y axis). The transformation (1.4) maps the line γ into the side of the square $0 \leq \xi \leq 1$, $\eta = 1$. We shall write Eq. (1.3) in the coordinates ξ, η in the form

$$\mathbf{n} \cdot \Delta_r \mathbf{x} = -C, \tag{1.5}$$

where

$$\Delta_r \mathbf{x} = \frac{1}{\sqrt{a}}\left[\frac{\partial}{\partial\xi}\left(\frac{a_{22}\partial\mathbf{x}}{\sqrt{a}\,\partial\xi} - \frac{a_{12}\partial\mathbf{x}}{\sqrt{a}\,\partial\eta}\right) + \frac{\partial}{\partial\eta}\left(-\frac{a_{12}\partial\mathbf{x}}{\sqrt{a}\,\partial\xi} + \frac{a_{11}\partial\mathbf{x}}{\sqrt{a}\,\partial\eta}\right)\right];$$

n is the vector normal to the surface of the drop; $\mathbf{n} = \frac{1}{\sqrt{a}}\left(\frac{\partial\mathbf{x}}{\partial\xi} \times \frac{\partial\mathbf{x}}{\partial\eta}\right)$; $a_{\alpha\beta} = \frac{\partial\mathbf{x}}{\partial u_\alpha} \cdot \frac{\partial\mathbf{x}}{\partial u_\beta}$ is the metric tensor; $\mathbf{x} = (x, y, z)$; $\alpha, \beta = 1,2$; $u_1 = \xi$; $u_2 = \eta$; $a = a_{11}a_{22} - a_{12}^2$.

We shall set the boundary conditions for (1.4) on the line $0 \leq \xi \leq 1$, $\eta = 1$ as follows:

The Dupres–Young condition

$$\frac{\mathbf{x}_\xi \times \mathbf{x}_\eta}{\sqrt{\mathbf{x}_\xi^2\mathbf{x}_\eta^2 - (\mathbf{x}_\xi \cdot \mathbf{x}_\eta)^2}} \cdot \mathbf{N} = \cos\alpha, \tag{1.6}$$

where N is the vector normal to the surface of the substrate at the points $x = x(\xi, 1)$, $y = y(\xi, 1)$, α is the angle of contact between the three phases, which we assume is constant and equal to 45°;

the contact condition

$$z(\xi, 1) = \Phi(x(\xi, 1), y(\xi, 1)), \quad 0 \leqslant \xi \leqslant 1. \tag{1.7}$$

On the remaining boundaries of Ω^* we impose the boundary conditions corresponding to the symmetry of the problem:

$$\begin{gathered} \partial z/\partial \xi = 0, \quad \xi = 0, \quad 0 \leqslant \eta \leqslant 1, \quad \partial z/\partial \xi = 0, \quad \xi = 1, \quad 0 \leqslant \eta \leqslant 1, \\ \partial z/\partial \eta = 0, \quad 0 \leqslant \xi \leqslant 1, \quad \eta = 0. \end{gathered} \tag{1.8}$$

Since it is necessary to find the equilibrium shape of the drop in the cell, the following condition must be added:

$$z \geqslant \Phi(x(\xi, \eta), y(\xi, \eta)), \; 0 \leqslant \xi \leqslant 1, \; 0 \leqslant \eta \leqslant 1. \tag{1.9}$$

Thus the equilibrium shape of the drop and its line of contact with the substrate will be determined by Eq. (1.5), the system of boundary conditions (1.6)-(1.8), and the condition (1.9). The question of the stability of this equilibrium form is not studied in this work.

2. Numerical Solution Procedure. The formulation of the problem given above does not contain explicitly as a parameter the volume of the drop $v = \int_{\Omega} (z - \Phi(x, y))dx\,dy$. Therefore, in this work the sequence of equilibrium shapes corresponding to different drop volumes is obtained from the solution of the boundary-value problem (1.5) for a set of nearly equal values of the constant C. From the solution obtained we calculate the volume of the drop corresponding to the fixed value of C. It should be noted that this correspondence may not be unique (see, for example, [3]). The problem for fixed C was solved in the following stages:

1) For the initial approximation the set of points (r_i, φ_i), $1 \leq i \leq n_\xi$, arranged uniformly over the angle $\varphi = \frac{\pi}{4}\xi$, $0 \leq \xi \leq 1$ was given; these points were obtained either from the solution already found with the closest value of C or lay on an arc of a circle with fixed radius; the number of points coincided with the number of nodes in the difference grid n_ξ in the variable ξ;

2) A difference grid corresponding to a uniform grid in Ω^* with the steps $h_\xi = 1/(n_\xi - 1)$ and $h_\eta = 1/(n_\eta - 1)$ was constructed in the region Ω at the points (r_i, φ_i), where $1 \leq i \leq n_\xi$; the coordinates of its nodes in the Cartesian system are given by

$$\left.\begin{aligned} x_{ij} &= r_j (j-1) h_\eta \sin\left[h_\xi (i-1)\frac{\pi}{4}\right], \\ y_{ij} &= r_j (j-1) h_\eta \cos\left[h_\xi (i-1)\frac{\pi}{4}\right] \end{aligned}\right\} 1 \leqslant i \leqslant n_\xi, \; 1 \leqslant j \leqslant n_\eta;$$

3) Using the values of the function z, found at the preceding iteration, we determine $n_x \Delta_r x$ and $n_y \Delta_r y$;

4) The difference equation approximating (1.5) with the boundary condition (1.7) was solved; the stages 3 and 4 were repeated until the fixed convergence criterion with respect to the function z was satisfied;

5) Using the function z obtained we calculated the values of the mismatch of the condition (1.6) at all points (r_i, φ_i), $1 \leq i \leq n_\xi$;

6) The line γ was displaced [i.e., the new coordinates (r_i, φ_i), $1 \leq i \leq n_\xi$) were determined] in such a way that the maximum modulus of the mismatch of (1.6) decreased; if this value became less than 10^{-3}, then the calculations were terminated, and otherwise the calculations continued with the new position of the line γ at the stages 2, ..., 6, etc.

In Ω^*, Eq. (1.5) was approximated by a conservative difference scheme with second-order approximation on a square (20 × 20 nodes) grid.

3. Results and Discussion. To compare the results of the modeling with experiment, we prepared on the surface of an amorphous substrated (fused quartz) with the help of photolithography and liquid etching a microrelief in the form of a line grating with a period of 22 μm. Since the rate of etching of the amorphous substrate is isotropic, there will be a

smooth transition from the surface of the substrate to the protuberances, forming the cell. If, furthermore, the etching is carried out in a special manner, for example until the photoresist is completely removed, then the tops of the protuberances will also be rounded. The profile of the protuberance in the transverse section can then be approximated by a Gaussian curve with the constants A and B, determining the height and width of the protuberance, respectively. The endfaces of the protuberances are formed by the surface of revolution of the Gaussian curve. On the whole, the surface of the microrelief in the coordinates x, y in the region Ω_1 can be approximated by the expression (1.1). The modeling was carried out for a substrate with a relief of two forms: a "flat" relief (A = B = 0.1) and a "steep" relief (A = 0.1, B = 0.03). The contact angle was set equal to 45°.

The results of the calculations are most conveniently displayed graphically in the form of contour lines z = const. Figures 2 and 3 show the square cell in the coordinates x, y, the contour of the drop, and the isolines of the free surface. Here the following circumstances should be kept in mind: the computational procedure has the peculiarity that the equilibrium forms of the drops were found with successively increasing volume of the drop, while in reality during evaporation the volume of the drops decreases. For this reason, in the experiment the evolution of the drops proceeds in a sequence opposite to that shown in Figs. 2 and 3.

"Flat" relief, i.e., in (1.1), A = B = 0.1, corresponding to the case of microrelief with very flat and smooth tracings of the protuberances. The sequence of equilibrium forms of the liquid for this case is shown in Fig. 2. With C = 5 (Fig. 2a) the volume of the drop is small, and the line of three-phase contact is a circle, passing along the practically flat bottom of the cell without touching its protuberances. The form of the drop coincides with good accuracy with the exact solution for a drop on the plane.

As the volume of the drop is increased, the line of contact approaches the protuberances, which distort its form. At C = 2 (Fig. 2b) it is evident that the lines z = const have the form of deformed squares, rotated by 45° relative to the cell. We shall call this orientation diagonal or twinned with respect to the cell.

The twinning orientation of the surface of the drop, which remains weakly convex, persists with C = 1 and C = 0.6 (Fig. 2c, d). Calculations for C < 0.6 could not be performed. This is apparently linked to the fact that for fixed A, B, and α = 45° configurations with a convex surface cannot be realized.

"Steep" relief (A = 0.1, B = 0.03). In this case, the sequence of equilibrium shapes corresponding to the increase in the volume of the liquid at first repeats the sequence studied above (Fig. 2a-d). Then, when the volume of the liquid v > 0.0415, a transition occurs in a jumplike manner into the next equilibrium position (Fig. 3). The sign of the constant C changes (C = −0.6), the surface of the liquid becomes convex, and the line of phase contact becomes strongly bent at the angles of the cell. The lines z = const form at the center of the drop a rounded square, oriented parallel to the cell.

Further increase in the volume at first gives rise to a more parallel orientation of the top of the drop (Fig. 3b), but then the surface of the drop straightens out and becomes almost flat (C = 0), while the lines z = const form a figure with an intermediate shape (Fig. 3c), which then transforms into a square with the diagonal orientation (Fig. 3d). The surface of the liquid in this case is convex. This form of the surface of the drop remains right up to values C = 0.5 and volume v = 0.110. For v > 0.110 the liquid probably completely covers the microrelief, forming a continuous layer.

The results of the numerical experiment are in agreement with the direct observations of evaporating drops. Figures 4 and 5 show drops of the solution of aluminopotassium alums; the pictures were obtained using an interference light filter (λ = 0.574 μm). The diagonal (Fig. 4) and parallel (Fig. 5) orientation of the tops of the drops can be seen.

The evolution of the shape of the drops enables following the change in the symmetry of the capillary force field, determining the orientation of the centers of crystallization. The origin of the twinning orientation of the KCl crystal (Fig. 6), observed in hydroepitaxy from solution together with the parallel orientation, can now be understood.

The results of the calculations show that the replacement of twinning orientation of the tops of the drops by parallel orientation is determined by the change in the volume of the drop and the form of the lines on the substrate and that the parallel orientation should apparently not be observed on a "shallow" and "flat" microrelief. This result must be checked

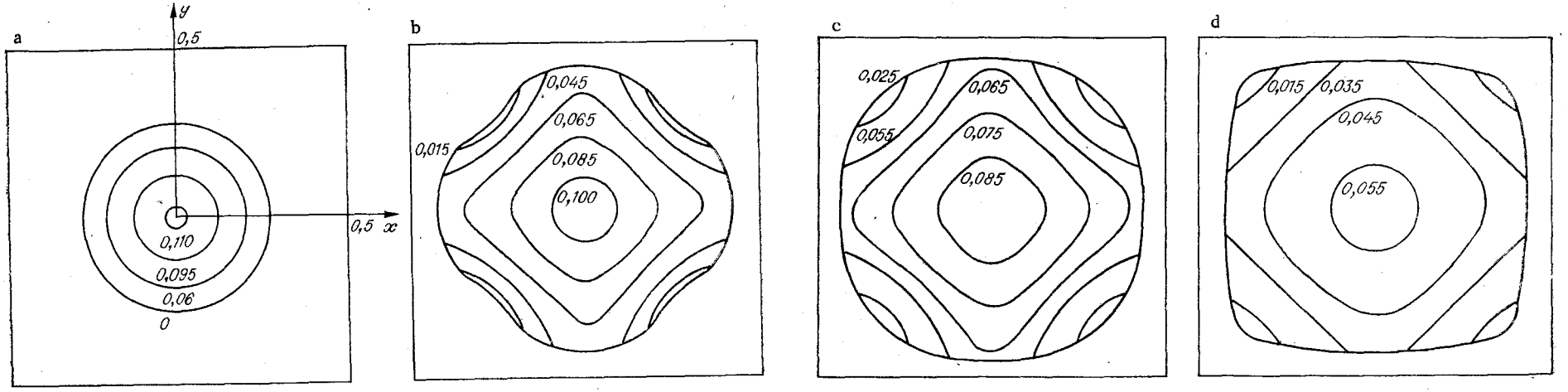
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Fig. 2

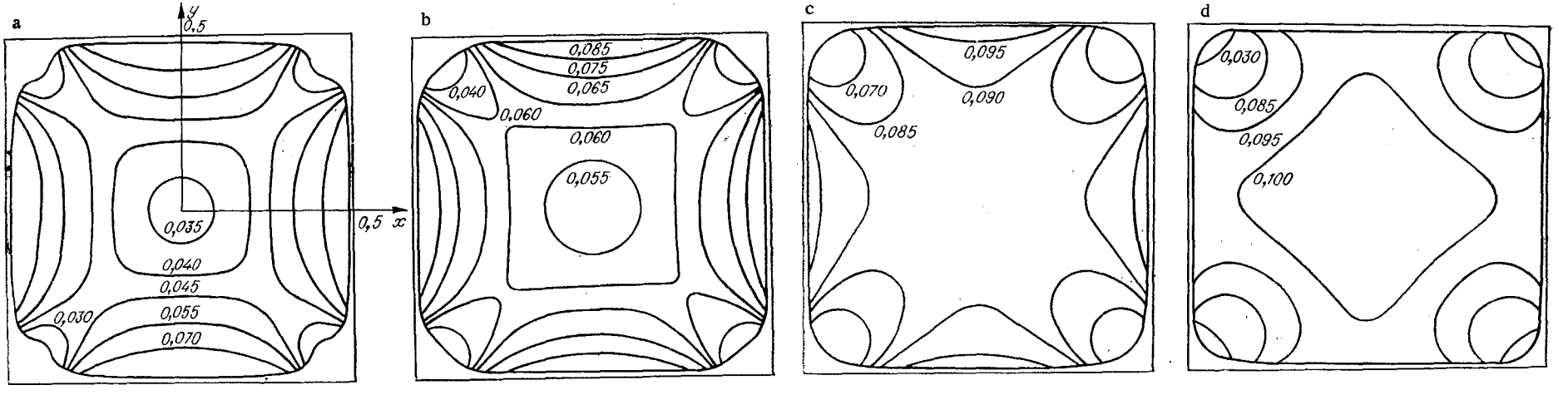
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Fig. 3

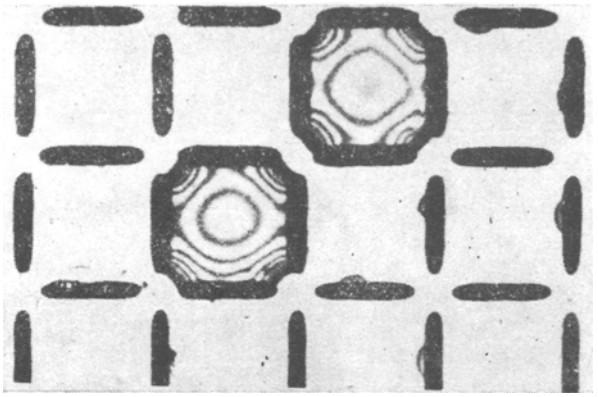

Fig. 4

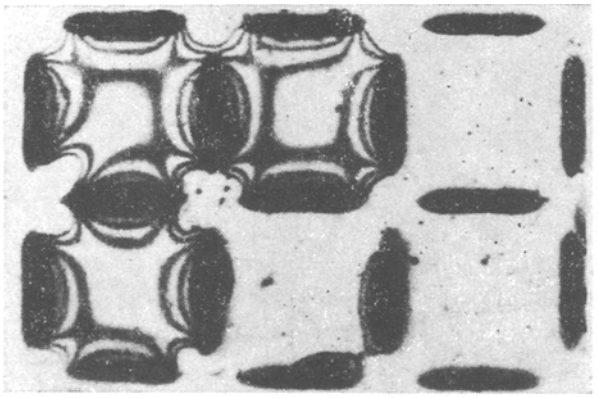

Fig. 5

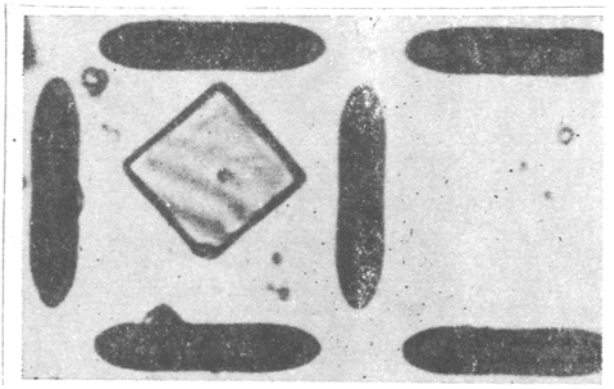

Fig. 6

experimentally. Both parallel and twinning orientations of crystals growing from solutions can exist on a deep and steep relief.

The characteristics of the evolution of symmetrical figures and surfaces of liquid drops described above are also characteristic of triangular and hexagonal lattices, though for the latter they are not very distinct.

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