Ginzburg-Landau Theory of Spiral Surface Growth

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A description of the spiral crystal growth of thin films in terms of a Ginzburg-Landau–like continuum field equation is proposed. The phase of the complex order parameter is identified with the local height of the growing surface and the absolute value represents the density of crystalline phase. This theory describes the helicoidal configuration from the growth of a screw dislocation core, as well as spontaneous nucleation of new dislocation pairs. [S0031-9007(98)05394-0]

Spiral waves arising in diverse physical, chemical, and biological systems are now one of the paradigms of nonequilibrium dynamical phenomena [1]. Examples include the Belousov-Zhabotinsky reaction, concentration waves in colonies of aggregating amoeba, waves in cardiac tissue, crystal growth, liquid crystal patterns, nonlinear optics, and many others. The above seemingly unrelated phenomena share a common feature: they often allow for a description within the framework of two component reaction-diffusion-type systems, for which spiral solutions are generic.

Spiral ridges are ubiquitous in surface crystal growth. Where a dislocation meets the surface its line tension produces a depression in the surface and considerably enhances the growth rate. If the Burgers vector of the dislocation has a component normal to the surface, a step runs from the point of emergence. As the crystal grows the steps wind up into spirals. Numerous observations of growth have revealed spirals associated with a dislocation emerging at their centers (dislocations slip out of the crystal after growth is completed leaving behind a slip trace). It has long been appreciated that dislocations have a large influence on the growth and equilibrium morphology of the crystals: Faraday [2] was the first to describe the importance of surface imperfections for crystal growth. Yet, despite even early observations qualitatively confirming Frank's original [3] theory and despite numerous efforts (mostly Monte Carlo simulations) [4] to analyze the problem, a consistent continuum theory of spiral surface growth is still absent.

A resurgence of interest in spiral growth has occurred in connection with fabrication of high-temperature superconducting films. Scanning tunnel microscopy (STM) images of yttrium oxide films (YBCO) [5,6] revealed that over a wide range of experimental conditions (temperature, growth rate, lattice mismatch with the substrate), the growing surface of the crystals develops spiral ridges. Typical patterns, observed in the growth process of thin YBCO films, are shown in Fig. 1. Strikingly, the density of growing spirals was found not to be directly related to the density of screw dislocation emerging from the substrate on which the film was grown: typically, the density of spirals substantially exceeds the density of substrate screw dislocations [7,8], suggesting that the spirals *nucleate spontaneously* in the process of growth. This observation is in conflict with past theory of surface growth, where the dislocations are treated in the framework of quasilinear elasticity, and spontaneous spiral nucleation is prohibited. Although a simple equation yielding rotating spirals in the presence of a screw dislocation had already been known in growth theory (the overdamped sine-Gordon equation, or solid-on-solid model; see, e.g., [9,10]), it has serious limitations related to the oversimplified treatment of the core region where the spiral initiates. The experiments suggest that spiral patterns are spontaneous solutions even in the absence of substrate screw dislocations as nucleation centers.

Here we propose a quantitative description of spiral surface growth in terms of a Ginzburg-Landau continuum evolution equation for the crystal surface. We show that this model supports spontaneous creation of spiral patterns even in the absence of substrate screw dislocations.
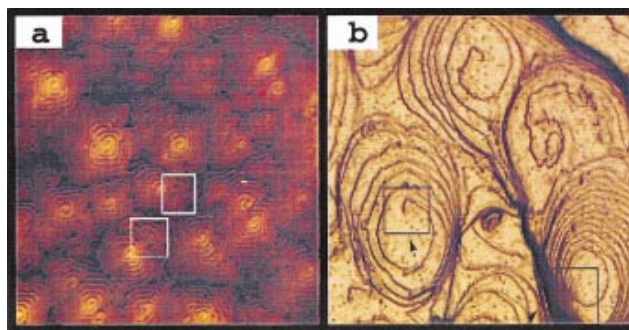

FIG. 1(color). STM images of YBCO thin film surface. (a) Low-resolution image of growing spirals; (b) high-resolution image of off-center screw dislocations. Courtesy of M. Hawley (Los Alamos National Laboratory).

We introduce a complex order parameter Ψ, the phase of which is associated with the local height h of the crystal and where $|\Psi|^2$ represents the local density ρ of crystalline phase (related to the stress field). Coupling of the height with the density field eliminates the nonphysical singularity at the spiral core.

Our equation modeling the surface growth is a two-dimensional complex Ginzburg-Landau equation with additional terms accounting for the crystalline anisotropy (e.g., YBCO is a cubic crystal), discreteness of the atomic lattice, and thermal noise. Our numerical simulations show that such an equation provides a good phenomenological description for the existing experimental observations. We find, in particular, that at low levels of thermal noise (low temperature), spirals indeed start to wind from screw dislocations already existing in the substrate. However, the loci of spiral centers (i.e., the dislocation cores) evolve by circling around verticals starting from substrate dislocations, thus forming helicoidal lines in the bulk of the growing crystals. This is consistent with the experimental observation of off-center spirals [Fig. 1(b)]. At higher temperatures new spirals nucleate at the periphery of the existing spirals. At even higher temperature, the original spirals are destroyed and the newly born spirals become decorrelated from the screw dislocations in the substrate.

In order to derive the growth equation of crystalline spirals grown in vapor phase epitaxy, we consider first the large deposition rate limit where the local growth rate (h_t) of a flat, unstressed interface is governed by the local supersaturation (α) of the adatom density [3] $h_t \sim \alpha$. In this case the supersaturation $\alpha \sim \Omega^{(\text{flat})}/D$, where $\Omega^{(\text{flat})}$ is the deposition rate, and D is the diffusion constant for the unstressed interface. The growth rate of a flat, unstressed interface is [11]

$$h_t = \omega^{(\text{flat})} \sim \alpha. \tag{1}$$

As the stress field and the curvature of the surface develop, the local supersaturation is modified [12]. The stress field (σ) affects the diffusion constant: $D = D_0(1 - a\sigma)$ (compressive stress increases D, while tensile stress decreases it; $a > 0$ is a material and temperature dependent coefficient) [13]. Since the stress changes the local lattice spacing, it is related to a local change in crystal density as $\sigma \sim 1 - \rho/\rho_0$, where ρ_0 is the equilibrium crystal density. Using the relations among α, D, σ, and ρ, in the linear approximation one obtains

$$h_t^{(\text{stress})} = \omega^{(\text{flat})}\frac{(1 - c\rho)}{(1 - c\rho_0)} = \omega(1 - c\rho), \tag{2}$$

where $\omega = \omega^{(\text{flat})}/(1 - c\rho_0)$, and $c > 0$ is a material constant characterizing a stress-induced correction to the supersaturation [14]. The local curvature of the interface also changes the local chemical potential μ. Again in the

linear approximation [15], one takes

$$\mu^{(\text{curv})} - \mu^{(\text{flat})} \sim -\Delta h. \tag{3}$$

The negative sign expresses the fact that positive curvature corresponds to an energetically favorable situation where more bonds appear as compared to the flat surface, and accordingly the energy decreases. Near the negatively curved interface the adatoms have less bonds and the energy increases. The shift in the chemical potential gives rise to the growth rate:

$$h_t^{(\text{curv})} \sim \mu^{(\text{flat})} - \mu^{(\text{curv})} = B\Delta h. \tag{4}$$

The constant B can be chosen $B = 1$ after appropriate scaling of the length, height, time, deposition rate ω, and density ρ. In the following we use these scaled quantities. Thus, one obtains $h_t^{(\text{curv})} = \Delta h$. Combining both the stress and the interface curvature effects, we obtain for the growth rate

$$h_t = h_t^{(\text{curv})} + h_t^{(\text{stress})} = \Delta h + \omega(1 - c\rho). \tag{5}$$

The height of the interface at a fixed point can vary not only because of deposition or desorption, but also because of convective mass transport:

$$h_t^{(\text{conv})} = -\nabla h \mathbf{v}, \tag{6}$$

where $\mathbf{v}$ is the local convective velocity, which can be evaluated from the balance of the stress-induced diffusive flux $\sim -\nabla\rho$ and the convective flow $\rho\mathbf{v}$: $\mathbf{v} = -\nabla\rho/\rho$.

Last, we must take into account that the crystal growth is a stepwise process due to the discreteness of the crystal lattice. The conventional approach (see, e.g., [15]) is to modulate the growth rate by adding a periodic potential term $\gamma f(\rho)\sin(h)$ to the equation of motion, where a_0 is the lattice spacing, and $f(\rho)$ is some function which vanishes at $\rho = 0$, since there is no discreteness (crystal structure) for small density. The particular form of this function is not relevant since far from the core the density approaches its constant equilibrium value. For simplicity we take $f(\rho) \sim \sqrt{\rho}$. Bringing all the above contributions together we arrive at the following equation:

$$\partial_t h = \Delta h + \nabla h \nabla \rho/\rho + \omega - \omega c\rho - \gamma\sqrt{\rho}\sin h. \tag{7}$$

If we associate the interface height with the phase of the complex order parameter $\psi = R\exp[ih]$, $\rho = R^2$, we can write the self-consistent growth equation

$$\partial_t \psi = \Delta\psi + [1 + i\omega - (1 + i\omega c)|\psi|^2]\psi$$
$$+ \gamma|\psi|^2 + \eta, \tag{8}$$

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where ω is the material deposition rate, η is a random (thermal) noise, and γ is the parameter characterizing the discrete nature of the growth process on the atomic scale. The term $i\omega c|\psi|^2\psi$ accounts for the stress-induced correction to supersaturation and the thermal noise is modeled by the δ-correlated Langevin noise term $\eta(x, y, t) = \eta_r + i\eta_i$, $\langle\eta(x, y, t)\eta(x', y', t')\rangle = 2T\delta(x - x')\delta(y - y')\delta(t - t')$, where T has the meaning of temperature.

Equation (8) is our main relation. One can immediately obtain from Eq. (8) the equation for $R = |\psi|^2$, expressing the density evolution (for $T = 0$):

$$\partial_t R = R - R^3 + \Delta R - (\nabla h)^2 R + \gamma R^2 \cos h. \quad (9)$$

Although Eq. (9) incorporates local dynamics in the growth process (long-range interaction can arise through the stress field), it turns out that it is sufficient to describe the *principal phenomenology* of our problem: formation, rotation, and nucleation of spirals.

Far from the core, the density ρ becomes slaved to h (omitting slowly varying terms $\partial_t R, \Delta R$):

$$R^2 \approx 1 + \gamma R \cos h. \quad (10)$$

Assuming $c, \gamma \ll 1$, and substituting R from Eq. (10) into Eq. (7) we arrive at the first order sine-Gordon equation with some corrections:

$$\partial_t h \approx \Delta h - \gamma \sin h + \omega. \quad (11)$$

This has been used in earlier considerations to describe a wide range of phenomena, including roughening transitions and spiral growth [9,10,15,16]. The drawback of this reduced equation is that although it produces (appropriate initial conditions are necessary to introduce screw dislocations) spiral growth possessing the correct rotating symmetry [9,10], it fails to correctly describe the core region where the spiral initiates. This has two important consequences: (a) a spiral core remains pinned to its initial location [17] and (b) Eq. (11) does not yield *spontaneous* spiral nucleation. We show that Eq. (8) consistently describes these phenomena.

We performed numerical simulations of Eq. (8) using an implicit Crank-Nicholson method with no-flux boundary conditions. The number of grid points was typically 200×200. Selected results are presented in Figs. 2 and 3. The stable spiral solution to Eq. (8) is shown in Fig. 2(a). The spiral was initiated from an initial condition containing 2π topological charge (circulation) at the defect's core. In order to model square in-plane crystalline anisotropy we have added to the equation the term $-\nu(\partial_x^4 + \partial_y^4)$. As we can see from the picture, the spiral assumes a "ziggurat" shape, resembling the STM images of Ref. [5]. Notably, the spiral core meanders around the center of the spiral's rotation. The reason for this meandering is the effect of discreteness on the growth process, characterized by the term $\gamma|\psi|^2$. This term breaks transla-
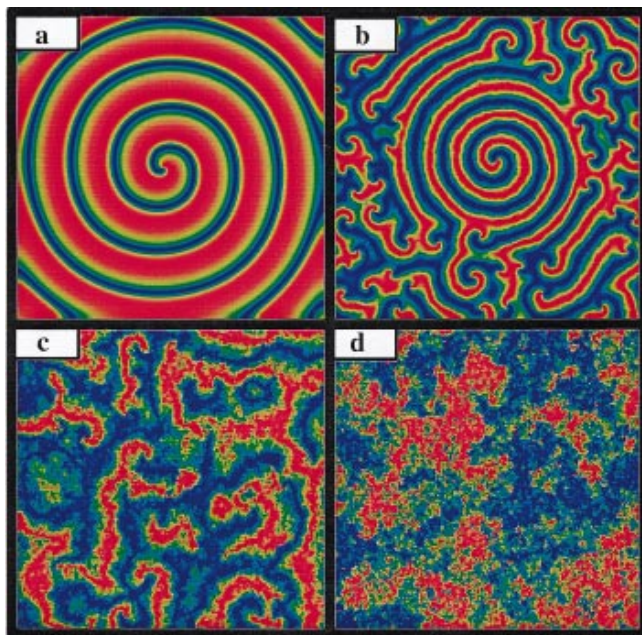

FIG. 2(color). Color-coded images of the surface height h, obtained from solution of Eq. (8). (a) Square-shaped spiral, $\gamma = 0.27$, $\omega = 0.8$, $c = 0.4$, $\nu = 2$, $T = 0$; (b) low-temperature nucleation of new spirals, $\gamma = 0.002$, $\omega = 3$, $c = 0.47$, $\nu = 0$, $T = 0.0000937$; (c) higher temperature nucleation of spirals $T = 0.0008437$; (d) rough growth $T = 0.0019$.

tion invariance in the direction of the surface growth and causes periodic forcing of the spiral core. Since, in the framework of Eq. (8), the mobility of the spiral is finite, this forcing causes finite periodic rotation of the spiral core. In the small γ limit the radius of the meandering is of the order γ and can be calculated analytically starting from the exact spiral solution.

We have found that the rotation frequency of the spiral and the surface growth rate decrease upon increasing the parameter γ. The dependence of the spiral frequency on γ is shown on Fig. 3. The spiral loses its stability and vanishes at some critical value of $\gamma = \gamma_c$. This value is slightly below the threshold γ_p for the pinning (or locking) of the growing surface due to the discreteness of the growth process. γ_p can be calculated from Eq. (8) and the condition for the existence of the stable equilibrium $\psi = $ const. This gives $\gamma_p^2 = 2\sqrt{(\omega^2 + 1)(\omega^2 c^2 + 1)} - 2 - 2\omega^2 c$, which is very close to the spiral stability limit. In principle, according to Eq. (11), spiral growth is possible even for $\gamma > \gamma_p$. However, in the framework of Eq. (8) we have found that the spiral tip contracts and eventually leaves the system. Persistence of spirals in Eq. (11) even for $\gamma > \gamma_p$ can be formally attributed to the pinning of the spiral core by *immobile* screw dislocation in the substrate.

Now we consider the effect of thermal noise. The spiral survives a small-amplitude noise perturbation. The main effect of the noise is diffusive motion of the core.
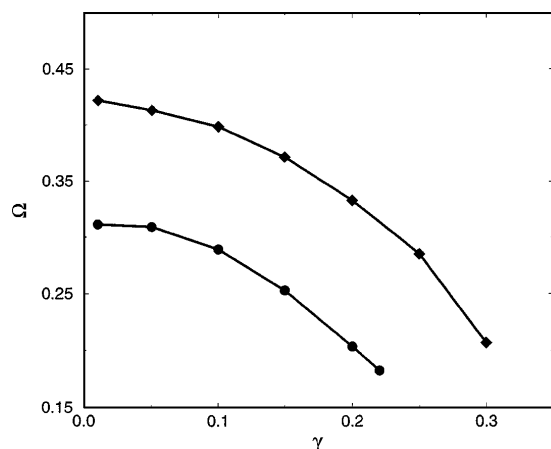
FIG. 3. The growth rate as a function of γ for two different values of c, $c = 0.5$ (diamonds) and $c = 0.625$ (heavy bullets) for $T = \eta = 0$.

The diffusion coefficient D_s, in first order, is proportional to the variance of the noise T: $D_s = \zeta T$. For $\gamma \rightarrow 0$ the coefficient ζ can be calculated analytically as a function of c [18]. Even for very weak noise there is a probability for creation of a pair of defects. However, at low temperature these defects tend to annihilate each other.

For higher temperature the random fluctuations can split the newly born defect pairs at a distance of the order of the spiral wavelength, since the diffusion of the spiral increases with temperature. Therefore, we can expect spontaneous nucleation of spiral pairs and persistence of well-defined spirals. This phenomenon is reminiscent of the topological Kosterlitz-Thouless transition. Our numerical simulations confirm this conclusion. In Fig. 2(b) we show a multispiral state formed from a single spiral under the influence of thermal fluctuations. The fluctuations cause the wave fronts emitted by the spiral to break and newly born defects are formed on the periphery of the original spiral. Some defects eventually grow, and others annihilate. As a result, new spirals nucleate spontaneously. This observation may explain the experimental observation [5,7] that the number of spirals on the surface may significantly exceed the number of screw dislocations in the substrate. We have found that the spirals in this regime diffuse and may eventually die, but that they retain their identity for many rotation periods.

For even higher temperature we have found that the spirals can still be distinguished in the growth process [Fig. 2(c)]. However, the individual spirals can be traced only 1–2 periods of rotation before they annihilate. At sufficiently high temperature [Fig. 2(d)] we observed the transition to rough growth, with no spirals surviving.

In conclusion, we have proposed a description of spiral surface growth in terms of a system of equations for the surface height and the crystalline density, which can be written as a Ginzburg-Landau equation for the corresponding order parameter. We have shown that this equation describes, in a natural way, the essential phenomenology of the growth process: core meandering of the growing spirals, spontaneous nucleation and separation of defects, and the transition to rough growth [5,7]. The parameters of the equation can be identified from comparison with existing experimental data and molecular dynamics simulations of the growth process. We also speculate that, under specific conditions, spontaneous nucleation of spirals may result in faster growth and anomalous roughening. Future studies will also address the interaction and pinning of the spiral core by substrate dislocations.

[1] M. Cross and P. C. Hohenberg, Rev. Mod. Phys. **65**, 851 (1993).
[2] M. Faraday, Philos. Trans. R. Soc. Exp. Res. Electr. **164**, 656 (1834).
[3] F. C. Frank, Disc. Faraday Soc. **5**, 48 (1949); **5**, 67 (1949); Adv. Phys. **1**, 91 (1952).
[4] G. H. Gilmer and P. Bennema, J. Appl. Phys. **43**, 1347 (1972); H. Müller-Krumbhaar, T. W. Burkhardt, and D. M. Kroll, J. Cryst. Growth **38**, 13 (1977); R.-F. Xiao, I. D. Alexander, and F. Rosenberger, J. Cryst. Growth **109**, 43 (1991); P. Bennema, J. Cryst. Growth **69**, 182 (1984).
[5] M. Hawley et al., Science **251**, 1537 (1991).
[6] J. Mannhart et al., Z. Phys. B **86**, 177 (1992).
[7] M. Hawley (private communication).
[8] G. Springholz, A. Y. Ueta, N. Frank, and G. Bauer, Appl. Phys. Lett. **69**, 2822 (1996).
[9] I. Aranson, M. Gitterman, and B. Shapiro, Phys. Rev. B **52**, 12 878 (1995).
[10] F. Falo et al., Phys. Rev. B **43**, 8081 (1991).
[11] H. Hertz, Ann. Phys. (Leipzig) **17**, 193 (1882); M. Knudsen, Ann. Phys. (Leipzig) **47**, 697 (1915).
[12] J. Tersoff, M. D. Johnson, and B. G. Orr, Phys. Rev. Lett. **78**, 282 (1997).
[13] M. Schroeder and D. E. Wolf, Surf. Sci. **375**, 129 (1997).
[14] A rough estimate for the coefficient c gives the value $c \sim 1$ (for details, see [13]).
[15] A.-L. Barabási and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, 1995).
[16] S. T. Chui and J. D. Weeks, Phys. Rev. Lett. **40**, 733 (1978).
[17] The free-energy functional corresponding to Eq. (11) diverges at the spiral's core.
[18] I. Aranson, H. Chate, and L.-H. Tang (to be published).