Stability of Solid State Reaction Fronts

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We analyze the stability of a planar solid-solid interface at which a chemical reaction occurs. Examples include oxidation, nitridation, or silicide formation. Using a continuum model, including a general formula for the stress dependence of the reaction rate, we show that stress effects can render a planar interface dynamically unstable with respect to perturbations of intermediate wavelength. [S0031-9007(98)07122-1]

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Many important reactions occur at solid-solid interfaces, and require one of the reacting species to diffuse to the interface through one of the solids. The oxidation of silicon, a complex process vital to the fabrication and function of silicon devices, is the best known example; but the oxidation of metals, nitridation of silicon, and silicide formation fall into the same general category. Since the original and reacted materials typically have different lattice constants, the reaction generates stress, which in turn alters the reaction rate. In nonplanar geometries, where the stress is nonuniform, the resulting structure can be drastically affected [1–3]. There is a longstanding effort to understand these stress effects on morphology in Si oxidation and in other systems [1–6].

It is well known that, in the case of epitaxial growth of a solid at a free surface, stress causes a morphological instability in an initially planar surface [7]. In this paper, we show that the stress at a solid-solid reaction front can similarly lead to an instability [8].

The instability here, however, differs in two important respects from that occurring in epitaxial growth. First, the instability in epitaxial growth is driven by the thermodynamics, always acting to lower the energy of the system. In contrast, the reaction instability is essentially dynamical in nature. It results from the effect of stress on the *reaction rate* rather than on energetics. Stress may either stabilize or destabilize the planar reaction front, even though the energy is always lowered by long-wavelength deviations from planarity. Second, a free surface under stress is always unstable at long wavelengths and stable at short wavelengths. In contrast, solid-solid reaction fronts are stabilized at long and short wavelengths by diffusion and interface-tension effects, respectively. An instability can therefore occur only at intermediate wavelengths.

The system we study is illustrated schematically in Fig. 1. For simplicity, we use the language of oxidation to describe it. However, the model we now discuss is quite general, and applies equally well to the other reactions mentioned above. In oxidation, the surface layer of a solid (typically metal or semiconductor) is in contact with a reservoir of oxidant, such as O_2 gas. The surface oxidizes, producing a thin solid film of oxide, as shown in Fig. 1. The oxidant must diffuse through the film to the film-substrate interface in order for further oxidation and film growth to occur.

Typically there is some volume change upon oxidation, which produces stress [1]. This in turn affects the oxidation and diffusion rates. In some materials, such as SiO_2, viscous flow of the oxide film or other inelastic processes can relieve these stresses, in whole or in part. Deal and Grove [9] proposed a simple model for the oxidation of planar substrates at high temperatures, where viscous flow is so rapid that stress relaxation can be treated as instantaneous. Their model has become the standard framework within which many subsequent oxidation problems involving curved geometries [1] have been analyzed.

Here we address the opposite regime, where the system is purely elastic and there is no viscous flow. This case is important for oxidation and other reactions at lower temperatures. As device structures shrink toward the nanometer scale, and processing temperatures are correspondingly reduced, the stress-induced instability we describe may well become important in systems where it was previously irrelevant.

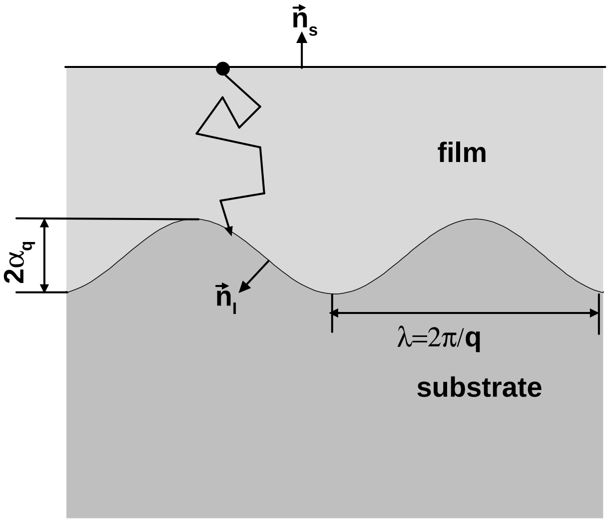

FIG. 1. An illustration of the geometry of the solid state reaction. The diffusion of the mobile reactant is represented by a random walk.

Consider the geometry of Fig. 1, where the substrate-film interface is a plane modulated by a small sinusoidal perturbation with amplitude α_q and wavelength $\lambda = 2\pi/q$. Our task is to evaluate the interface velocity, and determine whether the deviation from planarity grows with time. If, for some q, α_q grows as the reaction proceeds, the planar interface is unstable.

The velocity $\vec{v}$ of a point $\vec{x}_I$ on the reaction front is

$$\vec{v}(\vec{x}_I) = R(\vec{x}_I)\rho_f^{-1}\hat{n}_I = [c(\vec{x}_I)k_1 - \rho_c k_2]\rho_f^{-1}\hat{n}_I\,. \quad (1)$$

Here R is the number of oxidant molecules per unit area that reacts at the interface per unit time to form oxide, n_I is the local unit normal to the interface (Fig. 1), ρ_f is the density of bound oxidant molecules in the oxide, $c(\vec{x})$ is the concentration of diffusing oxidant molecules in the film, k_1 and k_2 are the respective rate constants for the forward and reverse reactions (oxidation and reduction) at the interface, and ρ_c is the density of sites through which the oxidant can diffuse in the film. Any crystalline anisotropy is neglected for simplicity. The Fourier component of this velocity with wave number q gives directly the rate of change of α_q, and hence determines the stability of a planar interface.

With the current density $\vec{j}$ of diffusing oxidant molecules given by $\vec{j} = -D\vec{\nabla}c$, $c(\vec{x}, t)$ satisfies the diffusion equation $\partial c/\partial t = D\nabla^2 c$, where D is the oxidant diffusion constant. Typically, the diffusion is rapid enough to maintain a quasi-steady-state concentration [9], so c obeys simply

$$\nabla^2 c = 0\,. \quad (2)$$

The boundary condition on this equation at the interface comes from the requirement that all oxidant molecules flowing into the interface react with the substrate to produce oxide. This can be written as

$$\hat{n}_I \cdot \vec{j}[\vec{x}_I] = R(\vec{x}_I) = c(\vec{x}_I)k_1 - \rho_c k_2\,. \quad (3)$$

At the upper surface, the normal oxidant current equals the rate at which oxidant is incorporated into the upper surface of the film from the reservoir [9]:

$$\vec{j}(\vec{x}_S) = -h[c^* - c(\vec{x}_S)]\hat{n}_S\,. \quad (4)$$

Here h is a rate constant (Henry's constant), $\vec{x}_S$ is a point on the upper surface, c^* $[\geq c(\vec{x}_S)]$ is the concentration of oxidant in the oxide film in equilibrium with the reservoir, and n_S is the unit normal to the upper surface.

The solution of Eq. (2), subject to the boundary conditions (3) and (4), is complicated by the fact that the rate constants k_1 and k_2 depend on the local stress. The stress dependence has been discussed from a phenomenological perspective by several authors in the context of silicon oxidation [1]. Here we apply a recent more complete treatment [10], which we now briefly sketch. The reaction proceeds from an initial state of free energy F_1 to a final state of free energy F_2 through a transition state (the saddle point of the energy surface) with free energy F_t. The local reaction rates can then be written as

$$k_i = k_0 e^{-\beta(F_t - F_i)}, \quad (5)$$

where $\beta \equiv 1/k_B T$, k_B is Boltzmann's constant, $i = 1$ or 2 , and k_0 is a rate constant reflecting the microscopic "attempt frequency." F_1, F_t, and F_2 represent free energies coarse grained over distances large compared to atomic dimensions but small compared to other dimensions of the system. In general, F_1, F_t, and F_2 depend on the stresses and interface curvature throughout the system. Note that we are concerned with free-energy *changes* $F_i - F_t$ associated with a reaction event, and these depend only on the *local* stress and curvature.

We are considering stability with respect to an infinitesimal perturbation from planarity, so we expand the stress and reaction rate to the lowest order in α_q. Then, $F_i = \bar{F}_i + \delta F_i$, for $i = 1, t, 2$. Here $\bar{F}_i$ is the (local) free energy for the planar interface, including stress effects, and δF_i is the change due to the curvature and to the extra stress produced by the sinusoidal corrugation. Since δF is $O(\alpha_q/\lambda)$, we can take $\delta F \ll k_B T$, so $k_i \approx \bar{k}_i[1 - \beta(\delta F_t - \delta F_i)]$, with $i = 1, 2$ and $\bar{k}_i = k_0 e^{-\beta(\bar{F}_t - \bar{F}_i)}$. The reaction rate is then

$$R(\vec{x}_I) \approx \bar{R}(\vec{x}_I) + \beta c(\vec{x}_I)\bar{k}_1(\delta F_t - \delta F_1) - \beta\rho_c\bar{k}_2(\delta F_t - \delta F_2)\,, \quad (6)$$

where $\bar{R}(\vec{x}_I) = [c(\vec{x}_I)\bar{k}_1 - \rho_c\bar{k}_2]$ is the rate for the flat interface.

Expanding δF to lowest order in the local strain and curvature gives

$$\delta F_t - \delta F_i = (\gamma_i\kappa + \sigma_i^n\delta\epsilon_{nn} + \sigma_i^p\delta\epsilon_{pp})\rho_f^{-1}. \quad (7)$$

Here γ_i is the curvature derivative of $F_t - F_i$, and acts as an effective interface tension; κ is the local curvature of the interface; $\delta\epsilon_{nn}$ and $\delta\epsilon_{pp}$ are the extra strains normal and parallel to the interface due to deviations from planarity; and σ_i^n and σ_i^p are coefficients ("activation stresses") reflecting the stress of the transition state relative to that of the initial or final state in the normal and parallel directions, respectively. (This neglects crystalline anisotropy [10].) Note that the expansion for $\delta F_t - \delta F_i$ can be written in terms of the strains $\delta\epsilon_{nn}$ and $\delta\epsilon_{pp}$ of either the film or the substrate, but the coefficients σ_i^n and σ_i^p assume different values in the two cases. Equivalently, one can write Eq. (7) as $\delta F_t - \delta F_i = (\gamma_i\kappa - \epsilon_i^n\delta\sigma_{nn} - \epsilon_i^p\delta\sigma_{pp})\rho_f^{-1}$, where $\delta\sigma_{nn}$ and $\delta\sigma_{pp}$ are the extra stresses resulting from deviations from planarity. The coefficients ϵ_i^n and ϵ_i^p are the normal and parallel "activation strains" [6,11], and are related to the activation stresses through the stress-strain relation, Eq. (8), yielding (for the film) $\sigma_1^{n,p} = -(\lambda^f + 2\mu^f)\epsilon_1^{n,p} - \lambda^f\epsilon_1^{n,p}$.

We evaluate the strains for the geometry of Fig. 1 using linear elastic theory [12]. The volume expansion accompanying oxidation gives rise to elastic displacements $\vec{u}(\vec{x})$ of the material at position $\vec{x}$. Taking both the substrate and oxide to be isotropic elastic media but with different elastic constants, one expresses the stress tensor $\overleftrightarrow{\sigma}$ in terms of $\vec{u}$ through the standard relation

$$\sigma_{ij}^{s,f} = \lambda^{s,f}(\vec{\nabla} \cdot \vec{u}^{s,f})\delta_{ij} + \mu^{s,f}(\partial u_i^{s,f}/\partial x_j + \partial u_j^{s,f}/\partial x_i) - 3K^{s,f}\eta^{s,f}\delta_{ij}\,. \tag{8}$$

Here η is the misfit strain parallel to the surface, with $\eta^s = 0$ and $\eta^f = \eta$ for the substrate (s) and film (f), respectively; $K^{s,f}$ are the bulk moduli, $K^{s,f} \equiv \lambda^{s,f} + 2\mu^{s,f}/3$; and $(\lambda^{s,f}, \mu^{s,f})$ are the Lamé coefficients. The above form of the stress tensor incorporates the requirement that the stress-free state for the substrate has zero displacement, $\vec{u}^s = 0$, while the stress-free state for the film is achieved through a uniform stretching or diagonal strain η in all three directions relative to the reference substrate; i.e., $u_i^f(\vec{x}) = \eta x_i$ for $i = x, y, z$.

This treatment assumes a fixed misfit at the interface, and would be exact for an interface between two crystals with a fixed epitaxial relationship, such as Si-$NiSi_2$. However, the case of greatest interest, Si-SiO_2, is more complex. The large volume increase upon oxidation is largely accommodated by expansion normal to the interface, with only a modest residual misfit stress. Since the microscopic oxidation processes that determine the residual stress are unknown, our assumption is reasonable but untested in the context of Si oxidation.

To compute the stresses, one must solve the elastic force-balance equation $\vec{\nabla} \cdot \overleftrightarrow{\sigma} = 0$ for both substrate and film, subject to the boundary conditions $\sigma \to 0$ as $z \to -\infty$ (in the substrate), $\overleftrightarrow{\sigma}^f \cdot \hat{n}_S = 0$ (force balance at the upper surface), $\vec{u}^s(\vec{x}_I) = \vec{u}^f(\vec{x}_I)$ (continuity of displacement at the interface), and $\overleftrightarrow{\sigma}^s \cdot \hat{n}_I = \overleftrightarrow{\sigma}^f \cdot \hat{n}_I$ (force balance across the oxide-substrate interface) [13].

For the planar interface ($\alpha_q = 0$), the displacement and stress must vanish in the substrate. For the film, only the z component of the displacement is nonzero: $u_z^f(z) = \epsilon_f z$, with $\epsilon_f = 3K^f\eta/(\lambda^f + 2\mu^f)$. The only nonvanishing components of $\overleftrightarrow{\sigma}^f$ are the diagonal ones parallel to the interface: $\sigma_{xx}^f = \sigma_{yy}^f = -2\mu^f\epsilon_f$.

For the planar film, the oxidant current must be uniform throughout the oxide. So, by solving Eq. (2) with the boundary conditions (3) and (4), one readily calculates the growth rate of the oxide thickness $l(t)$ from Eq. (1):

$$\frac{d}{dt}\, l(t) = \frac{(c^* - \rho_c\bar{k}_2/\bar{k}_1)/\rho_f}{1/\bar{k}_1 + 1/h + l(t)/D}\,. \tag{9}$$

This result is essentially identical to that of Deal and Grove [9], viz., $l(t)$ grows as t at short times and as $t^{1/2}$ at long times. Note that in practice $c^* > \bar{k}_2\rho_f/\bar{k}_1$, so $l(t)$ always increases with time.

For the modulated geometry of Fig. 1, the interface position is $z_I(x,t) = z_0(t) + \alpha_q(t)\cos(qx)$, $z_0(t)$ being its average position at time t. We calculate the curvature, displacements, and stresses to linear order in α_q/λ. With Eq. (7), one can then express $\delta F_t - \delta F_i$, and hence the oxidant flux $\vec{j}(\vec{x}_I)$ at the interface, in terms of α_q, λ, the oxide thickness l, and the parameters of the problem, such as γ_i and $\sigma_i^{p,n}$. One then solves $\nabla^2 c = 0$ in the oxide, to $O(\alpha_q/\lambda)$, subject to the boundary condition (4) at the upper surface and (3) at the interface. Knowing $c(\vec{x}_I)$, one uses Eq. (1) to determine the interface position $z_I(\vec{x}, t)$: $z_0(t)$ is given by the solution of the planar problem, and the amplitude, $\alpha_q(t)$, of the perturbation evolves according to

$$d\alpha_q/dt = \Omega_q\alpha_q\,, \tag{10}$$

where

$$\Omega_q = \rho_f^{-1}(-w_0 + w_1 q - w_2 q^2)\,. \tag{11}$$

The w_0, w_1, and w_2 terms, respectively, represent the effects of diffusion, stress, and interfacial tension.

The w_i can be written as

$$w_0 = \frac{\bar{k}_1}{D\rho_f}(C_0\bar{k}_1 - r_c\bar{k}_2)f_0(ql)\,, \tag{12}$$

$$w_1 = -\beta\epsilon_f[(C_0\bar{k}_1\sigma_1^n - r_c\bar{k}_2\sigma_2^n)f_1^n(ql) + (C_0\bar{k}_1\sigma_1^p - r_c\bar{k}_2\sigma_2^p)f_1^p(ql)]\,, \tag{13}$$

$$w_2 = \beta(C_0\bar{k}_1\gamma_1 + r_c\bar{k}_2\gamma_2)f_2(ql)\,. \tag{14}$$

Here

$$C_0 \equiv \frac{c^*\rho_f^{-1} + r_c\bar{k}_2/h + r_c\bar{k}_2 l/D}{(1 + \bar{k}_1/h + \bar{k}_1 l/D)}\,,$$

and $r_c \equiv \rho_c/\rho_f$ is of order unity. The quantities $f_0(ql)$, $f_1^n(ql)$, $f_1^p(ql)$, and $f_2(ql)$ are complicated dimensionless functions of ql and the various parameters. The dependence of these functions on ql is weak, and they are of order unity over the range of ql's of interest. For many reactions, including the oxidation of silicon, $\bar{k}_2$ is negligibly small. Thus the reverse reaction (decomposition of the oxide) doesn't occur in practice. In this case, formulas (12)–(14) simplify, since $\bar{k}_2$ can be set to 0.

The explicit q dependence of the last two terms in Eq. (11) results from the strains ($\delta\epsilon_{nn}$ and $\delta\epsilon_{pp}$) and the curvature (κ) behaving like q and q^2, respectively. Thus the smoothing influence of the oxidant diffusion term (i.e., w_0) dominates and maintains stability (i.e., keeps $\Omega_q < 0$) at small q [14]. This is the inverse of diffusion-limited *growth*, where the role of diffusion is destabilizing, as in the Mullins-Sekerka instability. The interface tension (i.e., w_2) term prevents perturbations of very small wavelengths from growing, stabilizing the planar interface at large q.

Planar growth is unstable, i.e., $\Omega_q > 0$, when $w_1 > 0$ and $\Delta = w_1^2 - 4w_0w_2 > 0$, the instability occurrs only over the range of wavelengths $q_- < q < q_+$, where

$$q_\pm = (w_1 \pm \sqrt{w_1^2 - 4w_0w_2})/2w_2\,.$$

This is illustrated in Fig. 2.

To illustrate that the instability may occur under realistic conditions and at relevant wavelengths, we consider Si oxidation, simplifying the problem with the usual assumption that $\bar{k}_2$ is negligibly small. We must first estimate the

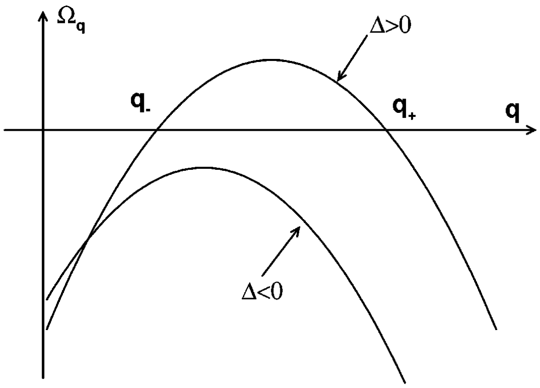

FIG. 2. An illustration of the stability calculation results. Notice that the interface is always stable ($\Omega_q < 0$) in both the small and large q limit, and only become unstable ($\Omega_q > 0$) in the intermediate range $q_- < q < q_+$ when $\Delta > 0$.

parameters σ_1^n and σ_1^p, but a crude, order-of-magnitude estimate suffices for the current illustration. Because oxidation is accompanied by expansion, the oxidation reaction should proceed more readily when the existing material near the interface has been dilated, i.e., when $\delta\epsilon_{nn}$ and $\delta\epsilon_{pp}$ are positive. In other words, one expects both coefficients σ_1^n and σ_1^p to be negative. Our elastic theory calculation shows, however, that $f_1^n(ql) < 0$ and $f_1^p(ql) > 0$ [with $f_1^n(ql) + f_1^p(ql) > 0$], so the sign of w_1 is determined by the relative magnitudes of σ_1^n and σ_1^p. Thus the instability presumably will not occur for all values of parameters.

It can, however, occur for reasonable parameter values. Assume, e.g., that σ_1^n and σ_1^p are comparable, and can be crudely estimated as $-2\mu_f\epsilon'$; here ϵ' is an effective strain which is taken to be of order one, $\epsilon' \sim 1$, consistent with the large, order-unity volume change accompanying oxidation. This choice makes $w_1 > 0$. For the other parameters, we use rough numbers for wet oxidation in silicon [9]. Taking $l(t) \ll D/\bar{k}_1$ (the most favorable limit for the occurrence of the instability), $c^* \sim 3 \times 10^9$ cm^{-3}, $\bar{k}_1 \sim 5 \times 10^{-5}$ cm/sec, $D \sim 10^{-9}$cm^2/sec, $\rho_f \sim 10^{22}$ cm^{-3}, $w_2 \sim 10^9$ cm^{-1} sec^{-1} , and $\beta\mu^f \sim 1.6 \times 10^{24}$ cm^{-3} at about 900 °C, we find that the inequality $w_1 > 2\sqrt{w_0 w_2}$, and hence the instability, holds for all ϵ_f greater than about 2×10^{-4}, which can indeed be achieved for modest values of misfit strain η. For the numbers above, we find, roughly, $q_- \sim 2 \times 10^4$ cm^{-1}, and $q_+ \sim 5 \times 10^7$ cm^{-1} for $\epsilon_f = 0.01$. This implies an instability for wavelengths between roughly 1 nm and 3 μm.

Equation (10) shows that the characteristic time τ_I over which the instability develops is set by $1/\Omega_{q_{\max}} = 4w_2\rho_f/(w_1^2 - 4w_0w_1)$, where $q_{\max} \equiv (q_+ + q_-)/2$ is the wave number for which α_q grows most rapidly. For the sample parameters above, one finds that $\tau_I \sim 1$ sec. This time scale is short compared with typical processing times, or with the other characteristic time $\tau_X = D\rho_f/2c^*\bar{k}_1^2 \sim 10^4$ sec, which is roughly the time when the motion of the planar interface crosses over from t to $t^{1/2}$ behavior.

Finally, we note that there is some intriguing experimental evidence of roughness in Si-SiO$_2$ interfaces for thin oxide layers [15] at 900 °C. However, because of the poorly understood complexities of real Si oxidation, with a volume expansion of order unity but a far smaller residual misfit, our results should be viewed as indicative of the type of behavior that may occur, rather than as quantitatively applicable.

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[1] See, e.g., D.-B. Kao, J. P. McVittie, W. D. Nix, and K. C. Saraswat, IEEE Trans. Electron Devices **35**, 25 (1988).

[2] H. I. Liu *et al.*, Appl. Phys. Lett. **64**, 1383 (1994); J. Vac. Sci. Technol. B **11**, 2532 (1993); P. Avouris, T. Hertel, and R. Martel (to be published); C. H. Hsueh and A. G. Evans, J. Appl. Phys. **54**, 6672 (1983).

[3] E. P. EerNisse, Appl. Phys. Lett. **35**, 8 (1979); R. B. Marcus and T. T. Sheng, J. Electrochem. Soc. **32**, 1278 (1982).

[4] W. C. Johnson, J. Appl. Phys. **68**, 1252 (1990).

[5] C. H. Chiu and L. B. Freund, Mater. Res. Soc. Symp. Proc. **436**, 517 (1997).

[6] W. Barvosa-Carter and M. J. Aziz, Phys. Rev. Lett. **81**, 1445 (1998).

[7] R. J. Asaro and W. A. Tiller, Metall. Trans. A, Phys. Metall. Mater. Sci. **3**, 1789 (1972); M. A. Grinfeld, Sov. Phys. Dokl. **31**, 831 (1986); D. J. Srolovitz, Acta Metall. **37**, 621 (1989); B. J. Spencer, P. W. Voorhees, and S. H. Davis, Phys. Rev. Lett. **67**, 3696 (1991); J. Appl Phys. **73**, 4955 (1993).

[8] Related stress-induced instabilities at reaction fronts have been independently analyzed in Refs. [5] and [6]. Reference [5] is a preliminary report with limited detail, but apparently uses a very different model for the effect of stress on the reaction rate. Reference [6] focuses on the stress dependence of the reaction rate, analyzing a case where no diffusion is required for the reaction.

[9] B. E. Deal and A. S. Grove, J. Appl. Phys. **36**, 3770 (1965).

[10] J. Tersoff, Y. Tu, and G. Grinstein, Appl. Phys. Lett. (to be published).

[11] See, e.g., W. Barvosa-Carter and M. J. Aziz, Mater. Res. Soc. Symp. Proc. **441**, 75 (1997); M. J. Aziz, P. C. Sabin, and G.-Q. Lu, Phys. Rev. B **44**, 9812 (1991); V. J. Fratello, J. F. Hays, and D. Turnbull, J. Appl. Phys. **51**, 4718 (1980); M. J. Aziz, S. Circone, and C. B. Agee, Nature (London) **390**, 596 (1997).

[12] See, e.g., L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon Press, Oxford, 1986).

[13] In principle, there is also an interface stress, which contributes a force at a nonplanar interface, but this term is typically negligible and is therefore omitted here.

[14] See C. Wagner, J. Electrochem. Soc. **103**, 571 (1956).

[15] A. H. Carim and R. Sinclair, J. Electrochem. Soc. **134**, 741 (1987).