Thermal Stability of Strained Nanowires

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Stranski-Krastanow strained islands undergo a shape anisotropy transition as they grow in size, finally evolving toward nanowires. This effect has been explained until now via simple energetic models that neglect thermodynamics. We investigate theoretically the stability of strained nanowires under thermal fluctuations of the long side. We find phase transitions from nanowires back to nanoislands as the temperature is increased and as the height of the nanostructure is raised or lowered, and we predict regions of phase coexistence. Our results are general, but explain recent data on the growth of erbium silicide on a vicinal Si surface.

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The investigation of two-dimensional nanoislands has provided fundamental understanding of the mechanism of epitaxial growth. Instabilities in heterostructure growth are exploited to form self-organized nanodots and nanowires that are of much smaller size than similar nanostructures realized on lithographically prepatterned substrates [1,2]. Typically, competition of plastic and elastic relaxation processes in strained epitaxial layers drives their formation [3,4]. In Stranski-Krastanow growth [3,5], where interactions between adatoms and of adatoms with the surface are comparable, both dislocated or single crystalline islands can grow after the initial wetting layer has reached a critical thickness. Formation of single crystalline rather than dislocated islands depends on the material, the amplitude of the lattice misfit, and the possible interplay of the Asaro-Tiller-Grinfield instability [6,7]. It can be controlled in many ways, e.g., by undulations and/or patterning in the surface layers of the substrate [8] or by tuning areal island densities and temperature [9].

It has been predicted and observed experimentally that dislocation free islands in early stages of growth can undergo a shape anisotropy transition as their size becomes critical [10–12]. Eventually their growth becomes quasi-one-dimensional, and they form perfect nano-objects with well defined height and width, that is, nanowires. Previous theoretical treatments have been based on simple energetic models of the island or wire that include competition between strain relief and surface energy. Although useful, these models completely neglect thermal fluctuations which are important in such quasi-one-dimensional systems because high entropic gains of the (thermodynamically extensive) long sides can lead to various instabilities.

Our objective is thus to introduce thermal effects in the theory within the context of a statistical mechanical model. We find that above a critical temperature the wire does indeed become unstable, and this temperature depends on the threshold of the plastic relaxation of the film. Moreover, we find that the wires become unstable as the deposition continues at constant temperature. We explain the observations of a recent set of experiments on the growth of erbium silicide nanostructures on the vicinal Si(001) surface that was studied at different postannealing temperatures and coverages [13–15].

We first review the Tersoff and Tromp model of the shape transition [10] on which more detailed studies have been based [11,12]. By considering both surface energy and strain relaxation, Ref. [10] arrives at the following expression for the energy for unit area of a rectangular island of dimensions L, X:

$$\frac{\epsilon}{\epsilon_o} = -\frac{d}{X}\ln\frac{Xe}{d} - \frac{d}{L}\ln\frac{Le}{d}; \tag{1}$$

the parameters d, ϵ_o depend upon surface energy and strain. The surface density of energy in (1) is minimized by a square island of size $X = L = d$ and energy $d^2\epsilon_o$. Yet, depending on the growth condition, islands can grow metastably larger than the optimal size d^2. Minimizing at fixed area $A = XL$, Tersoff and Tromp obtained a critical area, $A_c = (ed)^2$, below which symmetric shapes, or $X = L = \sqrt{A}$, are energetically favorable and above which a symmetry breaking occurs. That is, as the surface A increases beyond the critical value, one of the lateral sizes, say X, shrinks down from ed, asymptotically approaching the equilibrium value d. The other side keeps growing eventually linearly as $L \sim A/d$.

This asymptotic behavior can be deduced by taking the limit for large L in (1) and thus obtaining the surface energy for lateral growth

$$V(x) = -\epsilon_o\frac{d}{x}\ln\frac{xe}{d}. \tag{2}$$

The constraint on the area is not required anymore, and the optimal lateral size is obtained via minimization of (2) as $x = d$. [We will from now on use lowercase x to denote the finite edge, and upper case L for the long edge—“long” as in the thermodynamic limit (Fig. 1).]

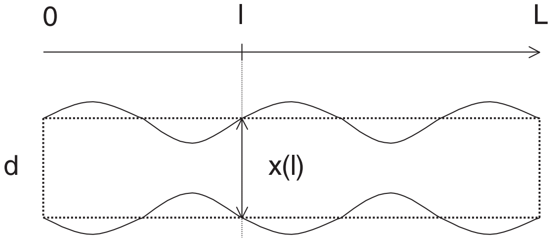

FIG. 1. The nanowire with lateral edges $x_1(l)$, $x_2(l)$ allowed to fluctuate in the coordinate l, $0 \leq l \leq L$; $x(l) = x_1(l) - x_2(l)$ is the relevant degree of freedom for our problem. The amplitude of fluctuations is largely exaggerated in the figure.

We will now explore the thermal stability of a long wire whose lateral size d minimizes the asymptotic energy in (2) under fluctuations of its long edges. We allow the lateral edges $x_1(l)$, $x_2(l)$ to fluctuate in the coordinate $0 \leq l \leq L$. The problem is simplified by the introduction of $x = x_1 - x_2$, $x_+ = x_1 + x_2$. The elastic energy of those fluctuations is thus simply $T = kx_1'^2 + kx_2'^2 = \frac{1}{2}kx'^2 + \frac{1}{2}kx_+'^2$. As the term in x_+ only contributes to equipartition, it can be disregarded. The partition function in the continuum limit is a Gaussian path integral over the allowed fluctuations

$$Z(\beta) = \int \prod_l [\mathrm{d}x(l)] e^{-\beta \int_0^L \mathrm{d}l[(k/2)x'^2(l) + dV(x(l))]}. \tag{3}$$

Incidentally, in the case of infinitely stiff boundaries, or $k \to \infty$, the path integral in (3) becomes restricted to straight lines $x(l) = x_o$, and one obtains for the size the Tersoff and Tromp's value d, minimum of V, plus thermal fluctuations that never diverge at finite temperature, and thus no phase transition.

Standard transformations [16,17] allow us to write (3) as the trace

$$Z(\beta) = \left(\frac{2\pi}{\beta k \lambda}\right)^{L\lambda} \mathrm{Tr}\left[\exp\left(-\frac{L}{d}\hat{H}_\beta\right)\right] \tag{4}$$

of the one-particle, temperature dependent Hamiltonian given by

$$\hat{H}_\beta = -\frac{d}{2\beta k}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \beta d^2 V(x). \tag{5}$$

The coefficient in front of the trace simply adds to the free energy the equipartitive contribution of free oscillators (λ is the linear density of oscillators $\lambda = K/k$, with K the microscopic spring constant). We thus only need to concern ourselves with the diagonalization of the (temperature dependent) effective Hamiltonian. In the limit of a long wire, or $L/d \to \infty$, the density operator in (4) projects on the lowest bound state—provided that $\hat{H}_\beta$ has one. One can reproduce the previous calculation for the partition function and demonstrate that the probability of a lateral size x is given by $p(x) = \lim_{J \to 0^+} |\psi_\beta^{0,J}(x)|^2$ where $\psi_\beta^{0,J}$ is the lowest bound state of the operator $\hat{H}_\beta + Jx$, where J is a chemical potential. (There is a bath of adatoms around the surface, and also a reservoir along the "infinite" L direction, so that we can safely assume $J = 0$. Yet one could try to envision different experimental situations when J might play a role and ensure stability at any temperature.) Clearly when $\hat{H}_\beta$ has no bound states—which might happen for β below a certain β_c—then $p(x)$ is flat, and we conclude that the elongated structure is not stable at that temperature. Thus the search for stability of long wires is reduced to the problem of existence of a bound state in a suitable one-particle Hamiltonian operator, a situation reminiscent of localization or delocalization of one-dimensional interfaces of the solid on solid model [18–20].

Before exploring this transition, one can immediately show a relationship between the critical exponent of $\bar{x} = \int x|\psi_\beta^0(x)|^2 \mathrm{d}x \sim t^{-\beta}$ and that of the specific heat $C \sim t^{-\alpha}$ when $t = (T - T_c)/T_c \to 0^-$. Indeed, from (4) we have for the free energy $F \simeq TLE_\beta^0/d$, where E_β^0 is the energy of the lowest bound state, while for $T \sim T_c^-$ one has $E_\beta^0 \sim d(2\beta k)^{-1}\bar{x}^{-2}$, since it is the exponential tail of the bound state around infinity that dictates $\bar{x}$. Thus $f \sim t^{2\beta}$, or $\alpha = 2(1 - \beta)$. We show at the end that $\beta = 1$.

The potential in (2) converges to zero slower than $1/x$ at infinity, while at zero it goes to infinity slower than the centrifugal energy; thus H_β, for any value of coupling constant (i.e., any temperature), has at least as many bound states (excluding S waves) as the hydrogen atom: infinite. Such a cursory look might convince the reader that nanowire formation should always be stable with respect to thermal fluctuations. In fact it is the long-range behavior of the potential that commands possible instability, but (2) is clearly unphysical for large x; simple intuition suggests that for large islands, energy density must be constant, as plastic relaxation of the elastic strain becomes unavoidable when the islands grow in size. Relaxation via dislocations has been observed experimentally in nanoislands and has already found to promote many complex phenomena [21], only recently explored via simplified approaches [22,23]. Fortunately our scenario is simpler: islands grow in a single crystalline manner until they reach a threshold size in which dislocations appear. Once dislocations start to form, they can coalesce, move, and make other dislocations more likely. It is thus both reasonable and simple to introduce an *ad hoc* plastic limit x_p beyond which the energy of the island simply grows linear with size.

We substitute the potential in (2), $V \to V_p$, with $V_p(x) = V(x)$ when $x < x_p$ and $V_p(x) = V(x_p) = V_p$ for $x > x_p$. $V_p(x)$ is now a well for $x > 0$ (Fig. 2) and thus might or might not admit a bound state, depending on the value of β. The Schrödinger problem for the potential in (2) has not been solved yet, nevertheless the critical temperature corresponding to the disappearance of the lower bound eigenstate can be obtained via a WKB approximation, which works well when T_c is not too large [24]:

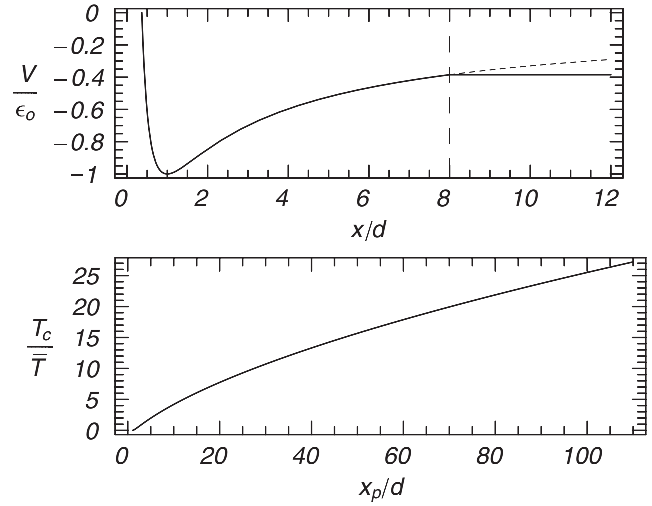

FIG. 2. Top: the potential of (2) (dashed line) with plastic limit set at $x_p = 8d$ (solid line). Bottom: behavior of T_c (in units of $\bar{T} = \pi^{-1}\sqrt{2^3 k \epsilon_o d^3}$) as a function of the plastic limit x_p.

$$T_c = \frac{2^{3/2}}{\pi}\sqrt{k\epsilon_o d^3}\, g\left(\frac{x_p}{d}\right). \tag{6}$$

For $\xi > 1$, $g(\xi)$ is defined by

$$g(\xi) = \int_{\xi_0}^{\xi}\sqrt{\frac{1}{s}\ln(es) - \frac{1}{\xi}\ln(e\xi)}\mathrm{d}s. \tag{7}$$

ξ_0 is the lower zero of the integrand. (Note that as $k \to \infty$ so does T_c; as mentioned above infinite stiffness would suppress phase transition.)

Equations (6) and (7) link critical temperature to the plastic limit. Figure 2 depicts the behavior of T as a function of the threshold for dislocations x_p, assuming all the other parameters are constant. One would deduce that in general stability can be achieved at higher temperatures by pushing higher the single crystalline threshold. Yet the phase transition was obtained in the limit $d/L \to 0$. Consider now (4) and (5) for L/d large but finite. For $T > T_c$, where T_c is the critical temperature, there are clearly no nanowires, as there are still no bound states. When $T < T_c$, the operator in (5) has (at least) one bound state, and yet the density operator does not just project on the ground state; it leaves some probability $p \propto e^{-(L/d)|E^o_\beta|}$ of a jump from the bound state to the continuum spectrum, a jump activated by the small "pseudotemperature" d/L. In the proximity of T_c, we obtain (see later) $E^o_\beta = \pi^2\epsilon_o d^2(T_c - T)^2/2T_c^3$; p is thus a Gaussian in $T - T_c$ of relative width

$$\frac{\Delta T_c}{T_c} = \frac{1}{\pi}\sqrt{\frac{T_c}{\epsilon_o L d}}, \tag{8}$$

which implies a gray zone of coexistence of both islands and wires of the order of $10^{-1}T_c$ (if we assume k of the same order as $\epsilon_o d$, $L/d \sim 10^2$, and $x_p/d \sim 10 - 100$). Notice that the width in (8) increases with T_c. That makes it possible for a region of coexistence of islands and wires to be accessible even when T_c is beyond practical reach. This seems to be the case in Ref. [14], as explained later.

It is interesting to explore the behavior of the critical temperature with deposition. In general the plastic limit as well as ϵ_o, k, and d depend on island height h, surface energy, and strain. Tersoff and Tromp found $d/e = \phi h \exp(\Gamma/2ch)$ and $\epsilon_o = 2ch/d$, where Γ is proportional to the surface energy, c to the strain energy, and ϕ is a number which depends on the contact angle [10]. Clearly, the linear elastic constant $k = \chi h$ is also proportional to the island height. In the simpler approach, the energy balance $x_p[V(x_p) - V(x_p/2)] = \Gamma_p$ provides a criterion for the formation of a defect of energy (per unit length) Γ_p, which gives $x_p/d = 4\exp(\Gamma_p/2ch - 1)$. So, if we neglect the dependence of Γ_p upon temperature, we can relate critical temperature with the island height and thus obtain the critical line

$$T_c(h) = \frac{2e\phi}{\pi}\sqrt{\chi c}\,h^2 e^{\Gamma/2ch} g\left(\frac{4}{e}e^{\Gamma_p/2ch}\right). \tag{9}$$

In Fig. 3 we plot (9) as a phase diagram for a nanowire or nanoisland under the above assumptions, along with experimental results of Zhou *et al.* [14]. One sees that below a certain temperature $T_{c,\min}$ the growth of a nanowire by further deposition is always stable. Above $T_{c,\min}$, deposition will cause growth in height until a critical value is encountered, above which the wire becomes unstable. Equation (9) also predicts a region of wire stability for

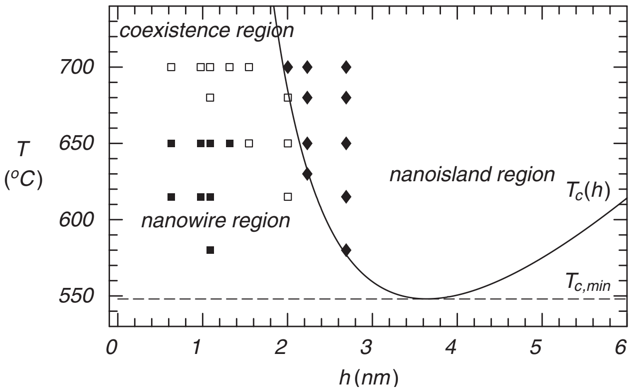

FIG. 3. Phase diagram (T, h) from (9) and the experimental findings of Zhou *et al.* [14]. Filled boxes denote nanowires, empty boxes regions of coexistence, while diamonds correspond to nanoislands (the relative coverage is 0.29, 0.73, 0.87, 1.16, 1.45, 2.03, 2.32, 2.90 monolayers). We have chosen our parameters arbitrarily (yet reasonably) to provide a decent superposition with Q. Cai's results [14]: $\frac{\Gamma_p}{2c} = 6$ nm, $\frac{\Gamma}{2c} = 1$ nm, $T_{c,\min} = 548\,^\circ$C. Note that for low h, where T_c diverges, the region of coexistence of islands and wires is still experimentally accessible, as discussed theoretically in the text. Note also the region of nanowire stability with no transition for $T < T_{c,\min}$ and for large heights $h > 3.5$ nm.

higher values of h. As Fig. 3 shows, the interval of instability in h decreases in size with the temperature, until it disappears below $T_{c,\min}$. Depending on materials, kinetic parameters, and other physical circumstances, only a portion of the phase diagram of Fig. 3 might be accessible.

Our predictions explain the experimental results of Cai's group on the self-organization of erbium silicide on Si(001). They obtained phase transitions from nanowires to nanoislands, both when increasing postannealing temperatures at fixed coverage [13] and when increasing coverage (and thus the height of nanostructures) at fixed postannealing temperatures as in Fig. 3 [13,14]. In a yet different approach, the same group was able to control the efficiency of the chemical synthesis of the silicide via different deposition techniques, and could obtain nanostructures of different heights (2.0, 1.5, 0.5 nm) at the same temperature; again transition from nanowires to nanoislands was observed as the height increased [15], as well as the coexistence zone.

Finally, let us tie up some loose ends. The WKB method seems appropriate to compute the critical temperature but not for critical exponents. It is clearly so for a case that can be solved exactly, the square well. And yet, as the length scale diverges at the transition, one expects the actual shape of the well to become irrelevant to the exponents. With the approximation $g(\xi) \simeq (\xi - 1)/2$, which works fine for ξ of the order of 3–10, one finds that our critical temperature corresponds to that of a square well of depth ϵ_o and size a such that $4\epsilon_o a^2 = \epsilon_o(x_p - d)^2$. The problem for the square well potential can be solved easily and returns for the ground state $E^o_\beta = \frac{\pi^2}{2}\epsilon_o d^2(T_c - T)^2/T_c^3$, and then $1/\bar{x} \sim t$ and thus $f \sim t^2$ for $t < 0$ while $f = 0$ for $t > 0$; f has no kinks; hence entropy is continuous at the transition and there is no latent heat, but a discontinuity in the specific heat. One can check that on the contrary a WKB study of a square well (and also for our truncated well) returns different exponents, $1/\bar{x} \sim t^{1/2}$, and thus a latent heat.

In conclusion, we have studied the stability of nanowire fabrication under thermal fluctuations. We find phase transitions from wires to islands, both by increasing temperature and the height of the nanostructure. Plasticity of extended films plays a crucial role in our analysis. Our results show that the transition can be more or less sharp depending on the average length of the wires, and is preceded by regions of coexistence of wires and islands.

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