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Critical dimensions for the plastic relaxation of strained axial heterostructures in free-standing nanowires

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We consider strained layers at the top of free-standing nanowires. We show that there exists a radius-dependent critical layer thickness below which no interfacial dislocation should be introduced. This critical thickness becomes infinite for radii less than some critical value, below which arbitrarily thick coherent layers should be obtainable. Implicit equations allowing the calculation of these critical dimensions from material parameters are given. These are derived from an evaluation of the elastic energy stored in the system with a coherent interface, the areal density of which is shown to be much less than in a laterally infinite system.

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Semiconductor wires perpendicular to a substrate and having micrometric diameters were first fabricated more than 40 years ago.[1] Using modern epitaxy techniques, homogeneous wires with much smaller diameters are now grown. We shall call them nanowhiskers to distinguish them from nanowires growing along a substrate. Whisker materials include elemental semiconductors,[2,3] III-V and II-VI compounds,[4–7] and oxides.[8] These whiskers have lengths up to several tens of micrometers and diameters in the nanometer-micrometer range. The interest in these nanowhiskers ranges from fundamental physics (growth processes,[7,9,10] electrical transport,[6] optical properties[4,8]) to their possible applications in nanoelectronics and nanooptics.

For basic studies as well as applications, it is vital to master the fabrication of whiskers containing strained heterostructures. In this work, we consider axial heterostructures, where the materials are stacked along the wire axis, as opposed to radial heterostructures, where one material surrounds the other.[11,12] Whiskers are particularly promising in this respect since they have free surfaces not only at the top but also at the side, which should allow efficient *lateral* stress relaxation. It is already known that, thanks to lateral relaxation, the same material can grow thicker on a given substrate as a quantum dot (QD) than as a uniformly thick layer [hereafter termed a two-dimensional (2D) layer] before the onset of plastic relaxation. The critical thickness beyond which interfacial dislocations appear is therefore larger for a QD (Refs. 13 and 14) than for a 2D layer.[15,16] For a misfitting layer at the top of a whisker, lateral relaxation should be even easier than for a QD, since its effective "substrate" has the same finite diameter instead of being infinite. The critical thickness should consequently be higher. Indeed, semiconductor nanowhiskers containing strongly misfitting dislocation-free layers with thicknesses well above the corresponding 2D critical thicknesses have already been grown.[6,17,18]

However, so far, the increase in critical thickness has neither been demonstrated theoretically nor calculated. The present work shows that the critical thickness depends sensitively on the whisker diameter and derives the relationship between these two dimensions as a function of the misfit of the layer with respect to its whisker substrate. To this end, we compare the energies of the system without and with dislocations. We thus adopt a thermodynamic equilibrium approach, in line with the standard theories of critical thickness for 2D layers,[15,16,19] without treating the kinetics of dislocation incorporation.

The whisker considered (Fig. 1, inset) is a semi-infinite circular cylinder of radius r_0. Between its two parts, the whisker substrate ($-\infty \leq z \leq 0$) and the layer ($0 \leq z \leq h$), exists a purely dilatational misfit ϵ_0, taken as positive for layers under compression (in cubic materials, ϵ_0 is the relative difference of lattice parameter between the two materials). We ignore the bulk substrate present at the base of the whisker. Calculations are carried out in the framework of linear isotropic elasticity, taking identical Young's moduli E and Poisson's ratios ν for both materials. In all numerical evaluations, we take $\nu=1/3$.

Let us first consider the system without interfacial extended defects. For want of an exact solution for its elastic strain state, we search an approximate analytical solution. We start from the exact integral solution for a misfitting layer of finite height in an infinite circular cylinder, which was derived long ago by Barton[20] but overlooked in recent work.[21,22] This solution satisfies the boundary conditions of our problem as regards stresses on the lateral free surface

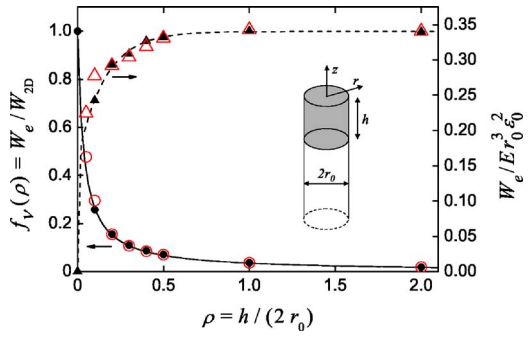

FIG. 1. (Color online) Nanowhisker with a misfitting top layer. Variations with the layer aspect ratio of the total elastic energy of the system (triangles, fitted by dashed line; right scale) and of the same energy, normalized to the energy of a portion (having the same volume as the whisker layer) of an identical 2D layer grown on a semi-infinite substrate (disks, solid line; left scale) ($\nu=1/3$). Closed and open symbols correspond, respectively, to the method indicated in the text and to finite-element calculations.

($\sigma_{rr}=0$, $\sigma_{rz}=0$ for $r=r_0$) but not on the upper free surface ($\sigma_{zz}=0$, $\sigma_{rz}=0$ for $z=h$). However, we may insert in the infinite whisker additional misfitting layers. The total strain field is then the sum of Barton's solutions for each layer. Hence, provided all added layers are located above $z=h$, they do not modify the strain field on the lateral surface for $-\infty \leq z \leq h$, which remains free. In practice, we insert a small number of such additional layers and optimize numerically their positions, heights, and misfits so that the resultant stresses nearly cancel the stresses generated by the original layer on section $z=h$, which becomes nearly free. This method has the advantage of yielding explicit integral expressions of the elastic fields for use in future calculations. The total elastic energy $W_e(r_0,h,\epsilon_0)$ stored in the region $-\infty \leq z \leq h$ is then computed numerically from the strain and stress fields. More details will be given elsewhere. We checked the validity of this procedure by performing finite-element calculations that give very close results, minor discrepancies being noted only for the smallest layer aspect ratios $\rho=h/(2r_0)$ (Fig. 1).

For given whisker radius and misfit, the energy W_e increases with layer height h (Fig. 1, triangles). However, at variance with the case of a 2D layer, W_e tends toward a finite value when $h\to\infty$. This is easily understood: when the layer reaches a thickness of the order of its diameter, its upper part nearly recovers its strain-free state and will retain it as growth proceeds, without any extra elastic energy being generated. In linear elasticity, the strain field depends only on the relative dimensions of the system. In the present case, it is thus determined by aspect ratio ρ and misfit. Therefore, for given ρ and ϵ_0, W_e scales with the volume of the layer and hence with r_0^3, so that the variations of W_e with ρ shown in Fig. 1 are universal, given the normalization chosen (right scale).

Figure 1 (disks) also gives the variation with aspect ratio of $f_\nu(\rho)=W_e/W_{2D}$, where $W_{2D}=E\pi r_0^2 h\epsilon_0^2/(1-\nu)$ is the energy stored in the same volume cut in a 2D strained layer coherently grown on a semi-infinite substrate with misfit ϵ_0. This ratio must tend to 1 when $\rho\to 0$, since the section of the whisker is then effectively infinite, and to 0 when $\rho\to\infty$, since W_{2D} scales with h. f_ν measures the effect of lateral strain relaxation, which is huge. Even at low aspect ratios, the elastic energy is considerably reduced, for instance to a quarter of its 2D value for $\rho\simeq 0.1$. The function f_ν depends weakly on Poisson's ratio but on neither Young's modulus nor misfit. We find that a good approximation (solid line in Fig. 1) is $f_\nu(\rho)=1/(1+A_\nu\rho)$ (with $A_\nu=27.3\pm 0.55$ for $\nu=1/3$). Hence

$$W_e=\frac{E}{1-\nu}f_\nu(\rho)\pi r_0^2 h\epsilon_0^2\simeq\frac{E}{1-\nu}\frac{\pi r_0^2 h\epsilon_0^2}{1+A_\nu\rho}. \tag{1}$$

Next, we must calculate the energy of the system at the onset of plastic relaxation. As in a 2D layer, interfacial dislocations reduce the misfit between substrate and layer to a new value ϵ_0' (with $|\epsilon_0'|<|\epsilon_0|$), thereby reducing W_e. On the other hand, their own strain field and their core energy increase the total energy of the system. To insure biaxial in-plane strain relaxation, we place in the heterointerface a single pair of orthogonal dislocations. To preserve at best the symmetry of the system, we take them as intersecting on the whisker axis; this ensures that they are of maximal length and thus most efficient. We denote by **b** their Burgers vector (BV) and by b_{eff} the edge component of the latter in the interface. As a first approximation, and in accordance with the method usually followed for the calculation of the critical thickness of a 2D layer,[16] we assume that the total energy is the sum of the energy W_d of the same dislocations in a homogeneous whisker and the elastic energy $W_e(r_0,h,\epsilon_0')$ calculated from Eq. (1) for the reduced misfit. We shall consider these two contributions to the energy in turn.

No exact solution could be found for the strain in a whisker with such dislocations, so that we have to resort to some approximation. The elastic energy for dislocations parallel to an *infinite* planar free surface can be calculated as a function of the distance of the dislocations from the surface.[23] On the other hand, no closed-form solution exists for faceted elongated QDs, but Ovid'ko, effectively treating them as wires parallel to the substrate, has proposed to use the same formulas after replacing the distance between dislocation and planar free surface by the distance between the dislocation and the nearest free surface.[24] Our case is more complex since the distance to the nearest free surface varies along the dislocation line (as it indeed does in true QDs). We extend Ovidko's method by considering that for a thin layer at the top of a whisker, the relevant distance is the distance to the top surface, whereas for a thicker layer it is the *average* distance to the lateral surface, namely, $\bar{d}=\beta r_0$ with $\beta=2/\pi$. We thus define an effective distance $\bar{h}$ by

$$\bar{h}=h \quad \text{if } h\leq\beta r_0, \quad \bar{h}=\beta r_0 \quad \text{if } h\geq\beta r_0. \tag{2}$$

We then substitute $\bar{h}$ by the distance between dislocation and planar free surface in the standard formula giving the energy in the 2D case[23] to obtain an energy per unit length of dislocation line equal to

$$w_d=\frac{E(1-\nu\cos^2\theta)b^2}{8\pi(1-\nu^2)}\left(1+\ln\frac{\bar{h}}{b}\right) \tag{3}$$

where θ is the angle between the dislocation line and its BV and $b=|\mathbf{b}|$ is as usual taken as the core cutoff radius for the calculation of the elastic energy.[16,23] In Eq. (3), the terms of the sum in parentheses correspond, respectively, to the core and elastic energies of the dislocations. The total dislocation energy is simply $W_d=4r_0 w_d$.

We must now compute the elastic energy W_e for the reduced misfit ϵ_0'. However, defining which part $\epsilon_a=\epsilon_0-\epsilon_0'$ of the misfit is accommodated by the dislocation pair requires some care. For a 2D layer with a square grid of interfacial dislocations of period d, we simply have $\epsilon_a=b_{\text{eff}}/d=b_{\text{eff}}\ell/2$, where ℓ is the length of dislocation per unit surface.[16] Keeping the same formula in the whisker case ensures in particular that we recover the standard 2D critical thickness when $r_0\to\infty$. Since, in the whisker case, $\ell=4/(\pi r_0)$, we are led to consider that the misfit accommodated is $\epsilon_a=\alpha b_{\text{eff}}/(2r_0)$, with $\alpha=4/\pi$.

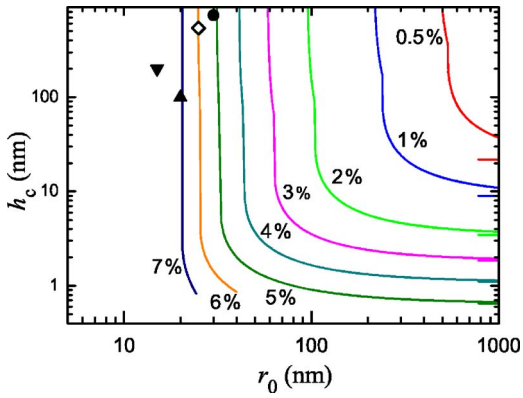

FIG. 2. (Color online) Variations of the critical thickness of a misfitting layer growing on top of a nanowhisker as a function of the whisker radius, for various values of the misfit (given in percent near each curve) and $\nu=1/3$. In the plastically relaxed state, misfit is accommodated by 60° dislocations ($b=0.4$ nm). Each segment at the right gives the asymptote of the curve immediately above for $r_0\to\infty$, which is the 2D critical thickness. Symbols give the dimensions of layers grown without (full symbols) or with (open symbol) dislocations, for $\epsilon_0\simeq 0.9\%$ (disk) (Ref. 17), 3.2% (up triangle) (Ref. 6), 3.7% (down triangle) (Ref. 18), and 7.1% (diamond) (Ref. 4).

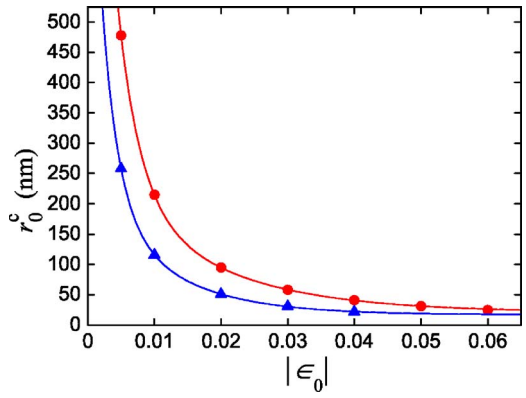

FIG. 3. (Color online) Critical radius above which infinitely thick misfitting layers could grow coherently, as a function of misfit. Triangles and disks correspond to plastic relaxation by, respectively, edge and 60° dislocations. b and ν as in Fig. 2.

Under these assumptions, using Eqs. (1) and (3), the excess energy of the state with the dislocation pair with respect to the state with a fully coherent interface is

$$\Delta W(r_0,h)=\frac{Er_0}{1-\nu}\left[f_\nu\left(\frac{h}{2r_0}\right)\pi r_0 h\left(\frac{\alpha^2 b_{\text{eff}}^2}{4r_0^2}-\frac{\alpha b_{\text{eff}}}{r_0}\epsilon_0\right)+C\left(1+\ln\frac{\bar{h}(r_0,h)}{b}\right)\right] \tag{4}$$

where $C=(1-\nu\cos^2\theta)b^2/[2\pi(1+\nu)]$ and where the dependencies of f_ν and $\bar{h}$ on whisker dimensions are specified. Equation (4) includes terms of second order in b_{eff}, which are essential for critical thickness calculations.[25] If $\Delta W>0$, the coherent interface is stable whereas if $\Delta W<0$, it is favorable to introduce dislocations.

Hence, equation $\Delta W(r_0,h_c)=0$ defines implicitly the critical thickness h_c as a function of radius r_0. If the layer thickness is less than $h_c(r_0)$, the stable state is free of interfacial dislocations whereas plastic relaxation should occur above $h_c(r_0)$. We calculated this radius-dependent critical thickness for pure edge ($\theta=\pi/2$, $b_{\text{eff}}=b$) and 60°dislocations ($\theta=\pi/3$, $b_{\text{eff}}=b/2$). Both types pertain to face-centered cubic crystals. For a given radius, the critical thickness is less for edge dislocations since they relieve misfit more efficiently. These defects are seldom found in low-misfit 2D films but may occur for higher misfits;[16] the same should happen in whiskers.

The variations of the critical thickness with r_0 for 60° dislocations are shown in Fig. 2 for several values of the misfit, taking $b=0.4$ nm, a value pertaining to GaAs and a good approximation for many semiconductors. For each misfit, the $h_c(r_0)$ curve separates, in the (r_0,h) plane of layer dimensions, the coherency domain (below, left) from the domain of plastic relaxation (above, right).

In most strained axial heterostructures fabricated so far, the layers have been kept below their 2D critical thicknesses.[11,26] However, there are a few reports of layers grown beyond this limit.[4,6,17,18] In each case, our calculations correctly predict the state (coherent or with dislocations) experimentally observed (symbols in Fig. 2).

Figure 2 suggests that, for each misfit, the critical thickness h_c tends to infinity for some critical value r_0^c of the whisker radius. Examination of Eq. (4) confirms that, since $\rho f_\nu(\rho)\to 1/A_\nu$ when $\rho\to\infty$ [from Eq. 1], a critical radius indeed exists (provided the misfit is not too high) and is the solution of the following equation:

$$\frac{2\pi}{A_\nu}\left(\frac{\alpha^2 b_{\text{eff}}^2}{4}-\alpha b_{\text{eff}}\epsilon_0 r_0^c\right)+C\left(1+\ln\frac{\beta r_0^c}{b}\right)=0. \tag{5}$$

The variations of the critical radius with misfit calculated from Eq. (5) for edge and 60° dislocations are shown in Fig. 3. These values are of the order of the typical radii of current nanowhiskers. Ertekin *et al.* estimated a similar quantity via a different method:[22] they considered a heterostructure made of two semi-infinite misfitting cylinders and posited an elastic displacement field depending on parameters that they found by minimizing the associated elastic energy. Moreover, they considered only edge dislocations, the energy of which was calculated for an infinite matrix. At variance with this approach, we use Barton's exact solution,[20] take into account the free surfaces, and, most importantly, derive a simple formula [Eq. (5)] allowing the direct calculation of the critical radius from the material parameters. Since Ertekin *et al.* do not give such a formula, we can only compare our results with the numerical values given by these authors in their Fig. 4 for specific sets of parameters, namely, $\nu=0.25$ and $b=0.1$, 0.2, and 0.4 nm. The critical radii agree to within ±6%. On the other hand, our critical radii for 60° dislocations are about twice larger (Fig. 3).

Moreover, the very existence of a critical radius can be demonstrated independently of the particular expressions chosen for the energies involved, as follows. We saw earlier

that for any misfit and for a given aspect ratio ρ, the elastic energy W_e scales with r_0^3. This is true in particular for its limit when $\rho \to \infty$ (Fig. 1). On the other hand, the total dislocation energy W_d is *larger* than the energy of the dislocation cores, because of the added elastic energy, *whatever its form*. Since the core energy depends on the atomic structure of the dislocation,[23] it is proportional to the dislocation length and hence to r_0 (neglecting further relaxation at the intersections with the lateral surface, which involves a few atoms at most) and independent of layer height; this remains true irrespective of the precise location of the defects in the interface and even of their number. From these different power dependencies upon r_0 it follows that, for infinitely thick layers, the dislocation energy always dominates, provided r_0 is small enough. In other words, there exists a critical radius below which plastic relaxation is forbidden and coherent layers of arbitrary thickness should be obtainable. The general features of the $h_c(r_0)$ curves (Fig. 2), in particular the vertical and horizontal asymptotes, are thus independent of the expressions used in the calculations.

In Eqs. (1), (4), and (5), A_ν is the only parameter that has to be evaluated numerically (more values will be given elsewhere). Given A_ν, the radius-dependent critical thickness and the critical radius are readily calculated.

We chose maximal length dislocations in the plastically relaxed state. This hypothesis is not critical. If smaller segments are considered, their energy is reduced but so is also the misfit effectively accommodated. Moreover, we have just seen that the existence of the critical radius does not depend on the details of the dislocation geometry. As for the neglect of the presence of a bulk substrate at the foot of the whisker, it is legitimate as soon as the distance between heterointerface and substrate exceeds the length upon which the strain field decays from the interface, which is of the order of the whisker diameter.

To summarize, for strained layers at the top of nanowhiskers, elastic relaxation at the lateral free surface is very efficient. The critical thickness for the introduction of misfit dislocations depends on the radius and becomes infinite below some critical value of the latter. Equations allowing the calculation of these critical dimensions have been derived. Our predictions agree with the few experimental results currently available.

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