The role of surface tension in the growth of strained quantum wire arrays[a]

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The critical radius of a strained quantum wire and the potential strain stabilization of quantum wire arrays has been investigated for the $In_xGa_{1-x}As/GaAs$ system. The critical radius of the quantum wire was calculated using an energy balance approach. The wire was found to be more stable than the corresponding two-dimensional quantum well structure. The use of surface tension as a stabilization force during the growth of strained quantum wire arrays is expected to have beneficial effects for arrays with greater than 7% InAs.

I. INTRODUCTION

With improvements in lithography and crystal growth technology, it is now possible to fabricate one- and zero-dimensional semiconductor systems: quantum wires and quantum dots. Recent work has also focused on the fabrication of one- and two-dimensional arrays of quantum wires using *in situ* growth techniques such as molecular-beam epitaxy (MBE) or metalorganic chemical vapor deposition (MOCVD). Research on the growth of wire arrays presently exploits the relatively strain-free AlGaAs/GaAs material system and relies on the preferential bonding of Al atoms to surface step ledges. This may be attributed to the relative surface-free energies of the group III metals, Al and Ga.[1] Recently, Berger et al.[2] and Srolovitz[3] have demonstrated that the presence of stress during strained semiconductor film growth can lead to the destabilization of layer-by-layer growth in favor of island growth. It has also been shown that surface tension modifies the critical layer thickness of a single strained overlayer.[4] In compressively strained overlayers, such as InGaAs on GaAs, the critical layer thickness is increased by the presence of surface tension. In the present paper, we consider the role of surface-free energy (or surface tension) in promoting the growth of strained quantum wire arrays with wavelengths determined by the competition between surface tension and stress relaxation.

The best known method for the *in situ* growth of quantum wires begins with the preparation of a terraced substrate.[5,6] Ideally, straight parallel monolayer steps bound flat terraces which run from one edge of the substrate to the other, as shown in Fig. 1. The terrace width determines the center-to-center wire spacing. Growth proceeds in a layer-by-layer fashion at the advancing step edges while maintaining the terrace structure of the substrate. Upon completion of a GaAs buffer layer, half-monolayers of AlAs and GaAs are alternately deposited. This builds up AlAs only on AlAs and GaAs only on GaAs. The sequence is continued until the height of the AlAs pillars equals their width. Continuing the growth with only GaAs results in the production of an array of AlAs wires with square cross sections, the edge dimension of which equals the interwire spacing and is one half of the terrace width. Alternatively, if the buffer and cap layers are AlAs, an array of GaAs wires in an AlAs matrix results.

The above model for quantum wire array growth is based upon the energetics of atom bonding at terrace edges. However, since the dimensions involved in terrace growth are so small and the capillary (surface tension) driving force scales as the interfacial energy divided by the appropriate length scale (radius of curvature) we should expect that surface tension plays a major role in the formation of these structures. It has been observed that while terrace edges are not initially straight and parallel, the growth of vertical (Al,Ga)As superlattices tends to enhance both properties. This result suggests that the line tension of the terrace edge is minimized when the edge is straight and that the Al-Ga interfacial energy is greater than the Ga surface energy. Therefore, these experimental results support the idea that interfacial/surface tension play a major role in determining growth modes.

Since surface tension helps determine the growth morphology, in the present paper we investigate methods by which surface tension can be optimally utilized to enhance the growth of quantum wire arrays. In order to do this, we build on the suggestions of Berger et al.[2] and Srolovitz[3] in order to exploit the competition between strain energy destabilization and surface energy stabilization of surfaces. This competition results in the periodic modulation of the surface morphology. This type of relaxation requires the presence of a stress in the overlayer and hence this approach may only be utilized below the critical thickness for the formation of interfacial dislocations. The present paper focuses on the estimation of the critical dimensions for strained quantum wires and dots, and for the case of InGaAs/GaAs system, defining the conditions under which surface tension will enhance the growth of wire arrays.
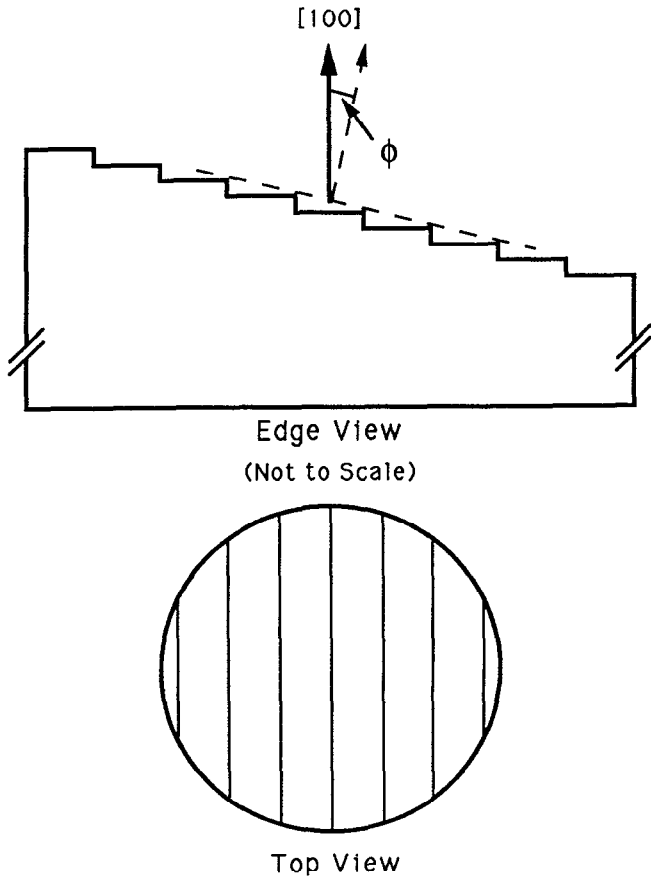
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[100]

φ

Edge View
(Not to Scale)

Top View

FIG. 1. An ordered terrace structure with monolayer step heights prior to the initiation of film growth.

II. CRITICAL RADII

In order to utilize surface tension to stabilize quantum wire and dot arrays, it is imperative that the strain in the wires or dots is not relieved by the formation of interfacial dislocations. Although there is evidence that a force balance method for determining critical dimensions is more accurate than energetic methods,[7] utilization of energy methods are more easily applied since they require no assumptions regarding the dislocation mechanism. For this reason, we employ the simpler energy methods for the quantum wire and dot critical radius computations.

In the energy balance method, the critical dimension for interfacial dislocation formation is determined by equating the strain energy of the unrelaxed system with the energy of the interfacial dislocation network. If we assume that the elastic constants do not vary through the material, the elastic strain energy (per unit volume) of the strained phase in an infinite medium is independent of the shape of the strain phase and may be written as

$$E_\epsilon = 2G(1 + v)/(1 - v)\epsilon^2, \qquad (1)$$

where G is the shear modulus, v is the Poisson's ratio, and ϵ is the elastic misfit strain. It is important to note that since the elastic energy of the solid is proportional to ϵ^2 rather than ϵ, the same results are obtained for compres-

sion as for tension (i.e., linear elastic solids are harmonic). The elastic energy of the an interfacial dislocation array (per unit area) is[8]

$$E_i = \frac{Gb}{2\pi^2} \{1 + \beta - (1 + \beta^2)^{1/2} - \beta \ln[2\beta(1 + \beta^2)^{1/2} - 2\beta^2]\}, \qquad (2)$$

where $\beta = \pi\epsilon/(1 - v)$ and b is the magnitude of the Burgers vector of the dislocations.

The critical quantum well layer thickness is obtained by equating the strain energy per unit area [i.e., the product of the layer thickness h and Eq. (1)] with the interfacial dislocation network energy per unit area [i.e., twice Eq. (2) since the quantum well has two interfaces]. The critical quantum well layer half-thickness, $h_c^{(1/2)} = h_c/2$, is quoted since it will be compared with quantum wire and dot radii

$$h_c^{(1/2)} = \frac{b}{4\pi^2\epsilon^2} (1 - v)/(1 + v)\{1 + \beta - (1 + \beta^2)^{1/2} - \beta \ln[2\beta(1 + \beta^2)^{1/2} - 2\beta^2]\} \qquad (3)$$

This result is identical to that obtained by Matthews.[9]

As for the quantum well case, the critical quantum wire radius, R_c^c, is determined by equating the strain energy per unit length of a cylinder [i.e., the product of Eq. (1) and πR^2] and the interfacial dislocation network energy per unit length of a cylinder [i.e., the product of Eq. (2) and $2\pi R$]:

$$R_c^c = \frac{b}{2\pi^2\epsilon^2} \left(\frac{1 - v}{1 + v}\right) \{1 + \beta - (1 + \beta^2)^{1/2} - \beta \ln[2\beta(1 + \beta^2)^{1/2} - 2\beta^2]\}. \qquad (4)$$

The critical radius of the quantum wire is exactly twice the half-critical thickness of the quantum well. A similar calculation for the quantum dot (sphere) geometry yields

$$R_c^s = \frac{3b}{4\pi^2\epsilon^2} \left(\frac{1 - v}{1 + v}\right) \{1 + \beta - (1 + \beta^2)^{1/2} - \beta \ln[2\beta(1 + \beta^2)^{1/2} - 2\beta^2]\}. \qquad (5)$$

The critical radius of the quantum dot is exactly three times that of the half-critical thickness of the quantum well and 50% larger than that for the quantum wire.

Figure 2 shows the critical half-thickness for a quantum well, the critical radius for a quantum wire, and the critical radius of a quantum dot made of $In_xGa_{1-x}As$ in a GaAs matrix as a function of In mole fraction x. In the calculation of these curves, a Burgers vector of a 60° dislocation with $b = 0.4$ nm was employed and Poisson's ratio was chosen as 0.31. Clearly, as the dimensionality of the structure shifts from the quantum well ($d = 2$) to the quantum dot ($d = 0$) greater InAs concentrations can be accommodated at the same critical length.

Also shown in Fig. 2 is the half-thickness for a quantum well as calculated from force balance considerations.[7] The half-thickness of the quantum well, as calculated from the force balance method is approximately 2.75 times
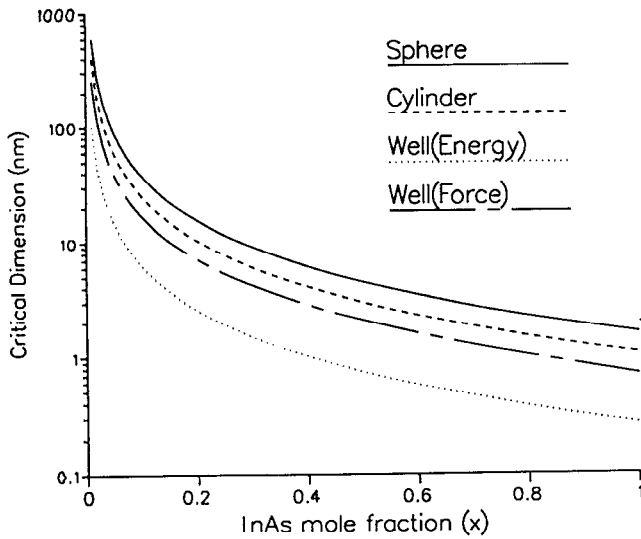
FIG. 2. Critical dimensions for a quantum well, quantum wire (cylinder), and quantum dot (sphere) calculated using the energy method. For the quantum wire and dot this dimension is the radius and for the well it is the half-thickness. For comparison, the critical dimension of the quantum well calculated using the force method is also shown.

greater than the energy balance results over the entire InAs concentration range. We expect a similar factor to apply to the quantum wire and quantum dot results on going to a force balance approach.

III. SURFACE TENSION AND ELASTIC INSTABILITY

Now that the appropriate critical lengths for the strained quantum wire and quantum dot have been determined, the potential use of surface tension and the elastic instability to enhance growth can be investigated. The basis of this study is the destabilization of flat, thin strained films and an evaluation of the wavelengths at which the destabilization occurs the fastest.

A flat surface bounding a strained elastic body is unstable and can develop ripples for all wavelengths longer than $\lambda_0 = \pi M \gamma / \sigma^2$, where M is the elastic modulus along the surface, γ is the surface tension, and $\sigma(= -M\epsilon)$ is the stress in the body. This result was derived by Asaro and Tiller,[10] in connection with their study of stress corrosion cracking, and independently by Srolovitz,[3] in connection with a strained film growth study. The actual wavelength of the surface profile which develops depends on the kinetic mechanism which controls matter transport to/from/along the surface. For surface diffusion controlled growth, such as MBE or MOMBE, the wavelength of the fastest growing mode is $\frac{4}{3}\lambda_0$. For growth controlled by evaporation and condensation from the vapor, such as MOCVD, the maximally unstable mode occurs at $2\lambda_0$.

In calculating the maximum stable wavelength, λ_0, several assumptions are made. The seminal analysis assumes a flat surface, as opposed to a terraced surface, as in the present case. The effect of a nonplanar surface on the determination of the elastic stability of the film is considered to be negligible as long as λ_0 is much greater than the

step height at the terrace edge. The surface tension used throughout is calculated for a flat (100) GaAs surface. The variation in the surface tension with the addition of In is assumed to be negligible compared to the other errors in the calculation. It is further assumed that the line tension of the step edge, which is neglected in the present analysis, will stabilize a quantum wire array along the length of the wire as in the case of the AlAs/GaAs system (see Ref. 16 for an analysis of the effect of step edge line tension in homoepitaxial growth). If this is not the case, then one should be able to engineer the growth of a two-dimensional quantum dot array using arguments similar to those presented below for quantum wires. Finally, it is assumed that the elastic stability analysis is valid only up to the point at which the stress in the film is relieved by misfit dislocation formation.

In order to calculate the maximally unstable wavelength as a function of InAs concentration, the surface elastic modulus and the surface tension of the film must first be determined. The surface elastic moduli of GaAs has been calculated by Brantley[11] for different surface orientations. For the (100) GaAs surface, M is 1.24×10^{12} dyne/cm^2.

Since no experimental data on the surface tension or surface energy per unit area γ of GaAs is available, we estimate using the method of Mezey and Giber[12]:

$$\gamma = \frac{\alpha \Delta G^*}{\phi}, \tag{6}$$

where

$$\Delta G^* = \Delta G + RT \ln(RT/PV(T)),$$

$$\alpha = (\sqrt{z_b} - \sqrt{z_s})/\sqrt{z_b},$$

and where z_b is the bulk coordination number, z_s is the surface coordination number, ϕ is the molar surface area, ΔG^* is the molar free energy of atomization, $V(T)$ is the volume of the evaporated surface, P is the vapor pressure, R is the gas constant, and T is the temperature. In determining the constants necessary to calculate γ, we assume that the surface tension is controlled by the arsenic atoms due to the higher vapor pressure.

The variable α describes the bond cutting between surface atoms and bulk atoms. For a GaAs lattice, the bulk coordination number is 4. In the first approximation, a surface As atom will have two dangling bonds, with a coordination number of 2. However, surface reconstruction as observed by reflection high-energy electron diffraction (RHEED) leads to a surface coordination number of three.[13] Using these numbers, α is found to be 0.13. During growth, the GaAs surface is assumed to be arsenic stabilized with a 2×4 reconstruction (2 arsenic surface atoms per unit cell) such that $\phi \approx 9.6 \times 10^8$ cm^2/mole. However, since the surface reconstruction varies with substrate temperature and incident arsenic flux during growth, both α and ϕ may vary. Following Overbury et al.[14] we determine ΔG^* as half the molar heat of sublimation[15] (GaAs$_{(s)} \rightarrow$ Ga$_{(g)}$ + As$_{(g)}$); $\Delta G^* = 77.5$ kcal/mole. With the above results, a surface tension of 0.45 J/m^2 is obtained
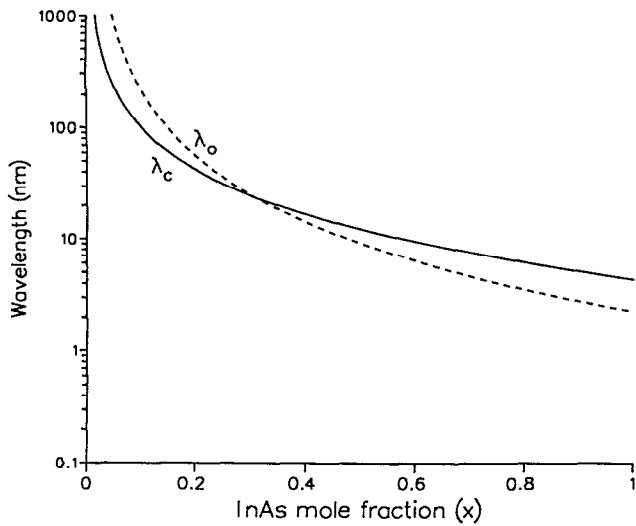
FIG. 3. The critical wavelength (i.e. $4 \times R_c^c$) λ_c and the shortest unstable wavelength λ_0 vs the InAs mole fraction in the quantum wires.
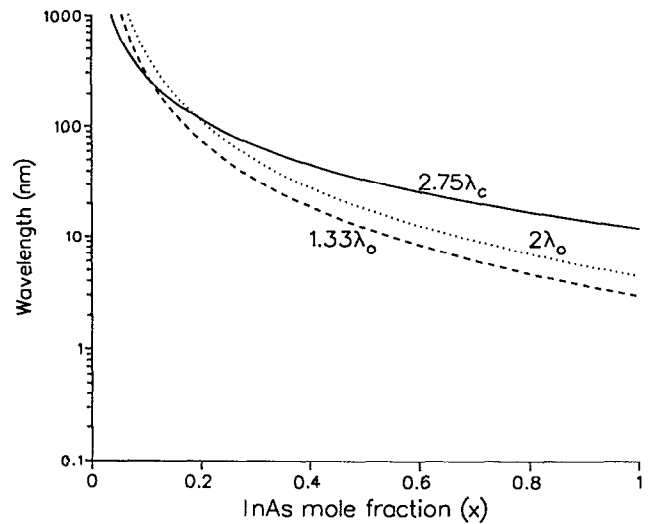

FIG. 4. The estimated true critical wavelength (i.e., $2.75 \times \lambda_c$) and the maximally unstable wavelengths for evaporation/condensation controlled kinetics (i.e., $2\lambda_0$) and surface diffusion controlled kinetics (i.e., $\frac{4}{3}\lambda_0$) vs the InAs mole fraction in the quantum wires.

for GaAs at room temperature. This is surprisingly close to the recently measured value of 0.46 J/m^2 for molten GaAs at its melting point.[17]

Employing the determined value of γ, the minimum wavelength for unstable (nonflat) film growth λ_0 for a pseudomorphic $In_xGa_{1-x}As$ overlayer on GaAs can now be determined. For the case of equally spaced quantum wires with wire spacing equal to the wire diameter, the maximum period of the array is equal to four times the critical radius for dislocation relaxation. This period corresponds to a critical wavelength, λ_c. λ_0 and λ_c are compared in Fig. 3. For InAs mole fraction greater than 0.33, flat, pseudomorphic thin films are unstable with respect to elastic relaxation while a quantum wire array is thermodynamically stable.

Extending the preceding arguments, a set of design constraints may be proposed for strained quantum wire arrays. The appropriate quantities to focus on in setting such constraints are the critical wavelength and the wavelength of the fastest growing unstable mode. In Fig. 4 we plot the 2.75 times the critical wavelength determined above (to account for the difference between the energy and more accurate force methods) and the wavelengths of the fastest growing modes $2\lambda_0$ (evaporation-condensation) and $\frac{4}{3}\lambda_0$ (surface diffusion) versus InAs mole fraction. The maximally unstable wavelength for a thin film is proposed to be the maximum stable wavelength for a wire array. Assuming, as in the case of thin strained films, that the energy balance underestimates the critical radius of the wire by a factor of 2.75, surface tension is predicted to stabilize the wire arrays for InAs mole fractions greater than 0.07. These curves indicate that elastic relaxation effects are important for wavelengths less than 430 nm. This raises the question of what are the limitations imposed by technologically practical terrace widths. The terrace width as a function of tilt (or miscut) angle away from the (001) orientation in either a $[1n0]$ or $[11n]$ direction is plotted in

Fig. 5 for a step height of one monolayer. In the equal diameter/spacing geometry, a terrace width of 30 nm is obtained for tilt angles of 0.4–0.6 degrees. This approaches the tilt angular uncertainty typical of GaAs substrates. Hence for small InAs mole fractions or large interwire spacings, tilt angle control becomes a serious practical limitation.

IV. CONCLUSIONS

We have proposed guidelines for the surface tension and elastic strain enhancement of the growth of strained quantum wire arrays. In so doing, we have also estimated the surface tension of GaAs and the critical dimensions of
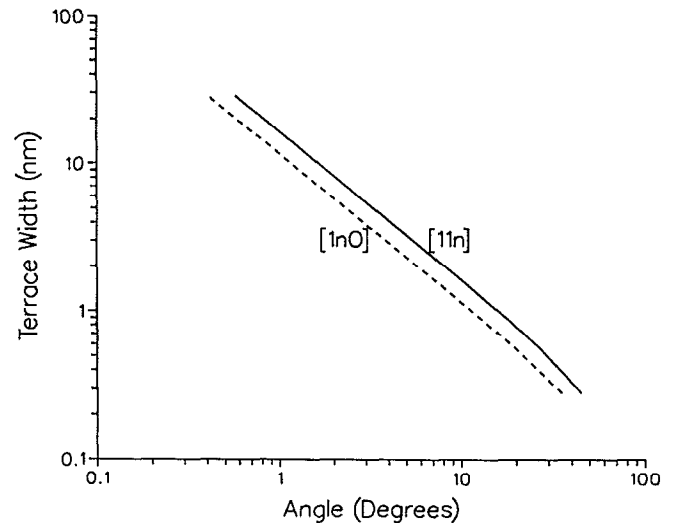

FIG. 5. Terrace width as a function of misorientation angle with the surface tilted away from the (001) plane in a $[1n0]$ or $[11n]$ direction.

strained quantum wire and quantum dot systems. Enhanced quantum wire array growth is predicted over practically obtainable InAs mole fraction and wire spacing ranges. Although approximate, these calculations support the concept that surface tension is an important design parameter for the fabrication of strained low-dimensional systems.

ACKNOWLEDGMENTS

[1] M. Tsuchiya, P. M. Petroff, and L.A. Coldren, Appl. Phys. Lett. **54**, 1690 (1989).

[2] P. R. Berger, K. Chang, P. Bhattacharya, J. Singh, and K. K. Bajaj, Appl. Phys. Lett. **53**, 684 (1988).

[3] D. J. Srolovitz, Acta Metall. **37**, 621 (1989).

[4] D. J. Arent, K. Denefee, C. Van Hoof, J. De Boeck, and G. Borghs, J. Appl. Phys. **66**, 1739 (1989).

[5] T. Fukui and H. Saito, J. Vac. Sci. Tech. B **6**, 1373 (1988).

[6] J. M. Gaines, P. M. Petroff, H. Kroemer, R. J. Simes, R. S. Geels, and J. H. English, J. Vac. Sci. Tech. B **6**, 1378 (1988).

[7] T. G. Andersson, Z. G. Chen, V. D. Kulakovskii, A. Uddin and J. T. Vallin, Appl. Phys. Lett. **51**, 752 (1987).

[8] W. A. Jesser, Philos. Mag. **19**, 993 (1969).

[9] J. W. Matthews, in *Dislocations in Solids*, edited by F. R. N. Nabarro, (North-Holland, Amsterdam, 1979), Vol. 2, Chap. 7.

[10] R. J. Asaro and W. A. Tiller, Met. Trans. **3**, 1789 (1972).

[11] W. A. Brantley, J. Appl. Phys. **44**, 534 (1973).

[12] L. Z. Mezey and J. Giber, Jap. J. Appl. Phys. **21**, 1569 (1982).

[13] P. K. Larsen and D. J. Chadi, Phys. Rev. B **37**, 8782 (1988).

[14] S. H. Overbury, P. A. Bertrand, and G. A. Somorjai, Chem. Rev. **75**, 547 (1975).

[15] J. R. Arthur, J. Phys. Chem. Solids **28**, 2257 (1967).

[16] G. S. Bales and A. Zangwill, Phys. Rev. B **41**, 5500 (1990).

[17] R. Shetty, R. Balasubramanian, and W. R. Wilcox, J. Cryst. Growth **100**, 58 (1990).