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Effects of elastic relaxation on aspect ratios during island growth of isotropic films

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The effect of misfit strain on the equilibrium aspect ratio of isotropic islands has been investigated by using numerical calculations of the elastic strain energy of spherical caps on a substrate. The effects of three dimensionless quantities were investigated: the ratio of the surface energy to strain energy, the modulus mismatch and the ratio of the interfacial energy to the surface energy of the island. It was shown that values of these parameters that tended to increase the strain energy dominance resulted in larger equilibrium aspect ratios (height-to-width ratio). The effect of modulus mismatch was also studied. It has been shown that as the modulus of the substrate increases relative to the island (keeping all other parameters constant), the aspect ratio increases. Furthermore, it has also been shown that island-to-island interactions occur over very short ranges, becoming negligible when the midpoint of the islands are separated by more than two diameters.

1. Introduction

Heteroepitaxial films are becoming increasingly important for use in optical and microelectronic applications. In order to ensure optimal performance of these devices, it is essential to grow uniform, defect-free films. Therefore, over recent years there has been considerable interest in understanding the physics governing the growth of these films. Three primary mechanisms have been identified: (i) uniform layer-by-layer growth, (ii) isolated island growth and (iii) an intermediate regime in which three-dimensional clusters grow on top of a uniform deposit. These three modes of growth are often referred to as the Frank–van der Merwe, Volmer–Weber and Stranski–Krastinov modes, respectively [1, 2].

Which mechanism dominates depends on the kinetics of film growth, the relative magnitudes of the interfacial energies between the film, substrate and environment, and the stress in the film. For example, classical theories of wetting predict complete coverage of the substrate by the film if

$$\gamma_{sv} \geqslant \gamma_{sf} + \gamma_{fv}, \tag{1}$$

where γ is the specific interfacial energy and the subscripts "sf", "sv" and "fv" denote the substrate–film, substrate–vapour and film–vapour interfaces respectively. Gilmer and Grabow [3] used molecular-dynamics techniques to consider the effects of the misfit strain in the film, and the ratio between the film–substrate interaction energy and the self-interaction energy of the film, W. They showed that if the misfit strain is non-zero, so that the overall strain energy of the film can be reduced by the formation of clusters [4–8], Volmer–Weber growth occurs for low values of W, while Stranski–Krastinov growth occurs at higher values. One way of quantifying the strain-energy reduction of different island shapes is to use the concept of an effective misfit strain. For example, this concept was developed by Luryi and Suhir [5] for a two-dimensional laterally-limited structure, while Christiansen *et al.* [6, 7] have developed a similar function for three-dimensional faceted structures of varying aspect ratios and facet angles.

The investigations described above have concentrated on the reduction of strain energy of the system. However, the total energy of a film–substrate system must include surface-energy terms. The effect of γ_{fv} on the stability of a completely wetting film has been examined by a number of authors [9–13]. It has been demonstrated that, while the strain energy of a completely wetting film can be lowered by the formation of surface roughness, the process occurs at the cost of an increased surface energy. Therefore, there is a natural length scale for roughening which emerges from this competition. For example, if the film and substrate have identical elastic properties, the critical wavelength for surface roughness at which the growth of small perturbations on the film surface are energetically favoured is given by [12, 13]

$$\lambda_{cr} = 11.98\gamma_{fv} G_f/\sigma_0^2 \tag{2}$$

where G_f is the shear modulus of the film and σ_0 is the residual stress in the film.

The effects of a competition between strain and surface energies are also expected to control the evolution of the growth mode when the substrate is not completely covered. In this regime, additional terms associated with the substrate–film interface and the substrate–vapour interface are expected to be significant. A simple model in which it is assumed that the surface energies of the substrate–film interface and the substrate–vapour interface are identical (i.e. the contact angle between the film and substrate is 90°), and that a hemispherical cap can support no elastic strain is given by Tu *et al.* [1]. By comparing the total strain and surface energies of a uniform film to the surface energy of a series of hemispherical islands of the same total volume, they demonstrate that clusters with a volume greater than a critical size V_c will always have a lower energy than the equivalent uniform film. This critical volume is given by

$$\frac{V_c^{1/3}}{h} = (18\pi)^{1/3}\left[\frac{E_f\varepsilon_0^2 h}{(1-\nu)\gamma_{fv}} + 1\right]^{-1} \qquad (3)$$

where E_f is Young's modulus, ν_f is Poisson's ratio, ε_0 is the misfit strain and h is the thickness of the equivalent uniform film (i.e. the volume of film per unit area of substrate).

As an extension of the analysis described above, the purpose of this paper is to examine the effects of (i) the relative magnitudes of the γ_{sf}, γ_{sv} and γ_{fv}, and (ii) the residual elastic strain energy associated with an island on a substrate. This is done for an isotropic material by assuming that the island is in the form of a spherical cap. The surface energy of this shape can be computed analytically, while the strain energy arising from a misfit strain must be computed numerically. (It should be emphasized that, in these calculations, the strain energy includes a contribution from the substrate [6, 7]. The strain in the substrate is zero only when a film uniformly covers a very thick substrate. When a film breaks up into islands, the strain in the film is reduced, but localized regions of strain are induced within the substrate.) The equilibrium configuration of an island is found by determining the aspect ratio at which the total energy is minimized for a given volume, misfit strain and combination of interfacial energies.

As an approximate analysis for an isotropic material, this search for minimum-energy configurations has been limited to shapes that consist of spherical caps. The assumption that the shape can be approximately described by a spherical cap considerably eases the computational aspect of the search for an equilibrium configuration. The island can be completely characterized by only two parameters, the volume and a contact angle between the film and substrate (Fig. 1). In practice, it is recognized that the island will not, in general, be exactly spherical. The equilibrium configuration is dictated by the condition that the chemical potential must be constant over the entire surface, as any difference in potential will result in atomic diffusion to restore equality. The chemical potential at any point on the surface of a cap is given by

$$\mu = \mu_0 + \Omega[\gamma_{fv}(\kappa_1 + \kappa_2) + W_s] \qquad (4)$$

where μ_0 is a reference potential, Ω is the atomic volume, κ_1 and κ_2 are the principal curvatures, and W_s is the strain-energy density at the surface. Only if the surface strain energy is constant everywhere, will the equilibrium shape be a spherical cap for an isotropic material (and a faceted island for non-isotropic surface energies). In general, there will be gradients of strain energy owing to local stress concentrations, and a complete solution to this problem would require finding a minimum-energy configuration when both the shape and aspect ratio vary. The deviation from a spherical surface is expected to become particularly pronounced in the region of contact between the film and substrate, since it is in this region that the strain gradients are highest. For the purposes of this paper, it is assumed that the details of the shape provide a second-order effect to the total energy of the system, while the first order effects are provided by the general aspect ratio of the island. It is assumed that this aspect ratio is captured by an effective contact angle, $\hat{\theta}$. Islands with a low height-to-width ratio are denoted by a small contact angle, those with a higher aspect ratio are denoted by a larger effective contact angle. As shown schematically in Fig. 1, this effective contact angle is unrelated to the actual microscopic contact angle at the triple junction between the substrate, vapour and island which is established by the three interfacial quantities.

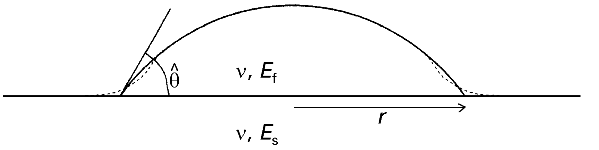

Figure 1 Schematic illustration of the configuration analysed in this paper. An island of volume V is in the form of a spherical cap, and is elastically bonded to a substrate with an effective contact angle $\hat{\theta}$. This effective contact angle is, in general, different from the microscopic contact angle at the triple junction between film, substrate and vapour. The Young's modulus of the island is denoted by E_f, that of the substrate by E_s. Poisson's ratio of both are assumed to be equal to ν.

2. Analysis and discussion

The geometry considered in the analysis presented in this section is shown in Fig. 1. An axisymmetric spherical cap with a volume V and a contact angle $\hat{\theta}$ is elastically bonded to a substrate of infinite depth. The Young's modulus of the film and substrate are E_f and E_s, respectively; Poisson's ratio of the two are assumed to be identical and equal to ν. (In this study, we did not investigate the effect of a Poisson's ratio mismatch between the film and substrate.) The strain energy of this configuration was calculated using the ABAQUS finite-element program with the misfit strain, ε_0, being modelled by assigning different coefficients of thermal expansion to the film and substrate, and then subjecting the system to a temperature rise. The effects of contact angle, modulus mismatch ($\Sigma = E_f/E_s$), and volume of the film on the strain energy were investigated numerically. Owing to the stress singularity at the edge of the island, a series of mesh refinements was used to ensure that a mesh-independent strain energy was obtained. The strain energy, which is normalized by $E_f\varepsilon_0^2V/(1-\nu)$, is presented in Fig. 2 as a function of effective contact angle and modulus mismatch for a single, isolated island. Fig. 3 shows the effects of the interaction between neighbouring islands, assuming axisymmetry. This has been plotted for three different values of modulus mismatch and a contact angle of 90°. Calculations for other contact angles show similar effects; in particular, it will be noted that any interaction between neighbouring islands is of extremely short order.

The surface energy of the substrate and island is given by

$$U_s = A_{fv}\gamma_{fv} - A_{sf}(\gamma_{sv} - \gamma_{sf}) \quad (5)$$

plus an arbitrary constant, where A represents the interface area. Both A_{fv} and A_{sf} can be readily determined as analytical expressions of the contact angle and volume of a spherical cap. The normalized surface energy, $U_s/\gamma_{fv}V^{2/3}$, is plotted as a function of the effective contact angle for different values of the parameter $\eta = (\gamma_{sv} - \gamma_{sf})/\gamma_{fv}$ in Fig. 4. It will be noted that the minimum energy condition is given by the well known Young–Dupré equation:

$$\theta_e = \cos^{-1}\eta \quad (6)$$

The total energy of the system, U_{tot}, is given by the sum of the surface and strain energies. It depends on three non-dimensional parameters, η, Σ, and

$$\xi = \gamma_{fv}(1-\nu)/E_f\varepsilon_0^2 V^{1/3}, \quad (7)$$

which measures the relative importance of the strain and surface energies. The effects of these three parameters on the normalized total energy of the system, $U_{tot}(1-\nu)/E_f\varepsilon_0^2 V$, are illustrated in Fig. 5a–c.

2.1. Equilibrium configuration

The equilibrium shape of an isolated island deposited on a substrate will be that which gives the minimum total energy of the system. This equilibrium configuration can be obtained by an examination of the data summarized in Fig. 5. A summary of the effects of both η and ξ (the parameters which measure the relative interfacial energies and the relative importance of the strain- and surface-energy terms) on the aspect ratio of an isolated island is presented in the three-dimensional plot of Fig. 6. This figure shows the aspect ratio for which the total energy of a substrate –island system (with identical elastic constants) is minimized as a function of both η and ξ. It will be observed from the plot that, at low values of ξ, the island takes up a very large aspect ratio to minimize the strain energy. Conversely, at large values of ξ, surface-energy considerations dominate. For all

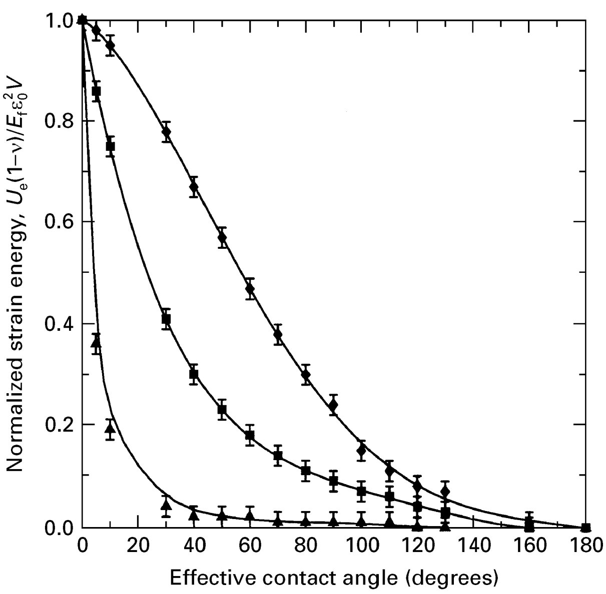

Figure 2 Normalized strain energy plotted as a function of effective contact angle for different values of the modulus-mismatch ratio. The error bars indicate the approximate magnitudes of the errors associated with the numerical calculations. Key: ◆ $\Sigma = 0.1$; ■ $\Sigma = 1$; ▲ $\Sigma = 10$.

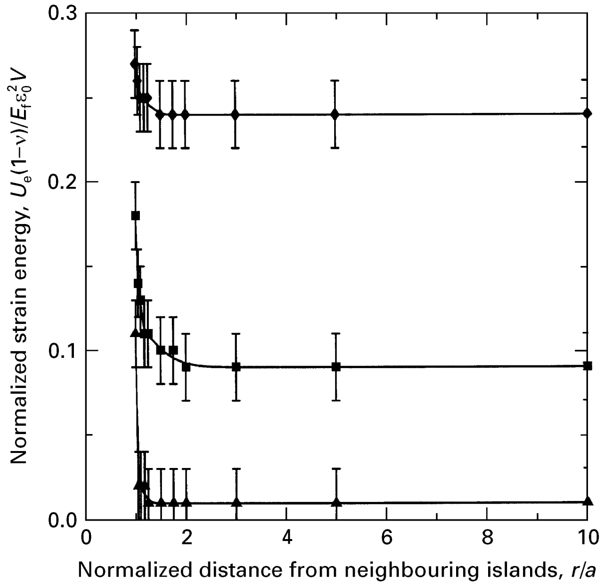

Figure 3 Normalized strain energy plotted as a function of distance from neighbouring islands for different values of the modulus-mismatch ratio. The radius of the island is r, while the distance to the midpoint between two islands is given a. These calculations have been conducted assuming cylindrical symmetry. $\hat{\theta} = 90°$. Key: ◆ $\Sigma = 0.1$; ■ $\Sigma = 1$; ▲ $\Sigma = 10$.

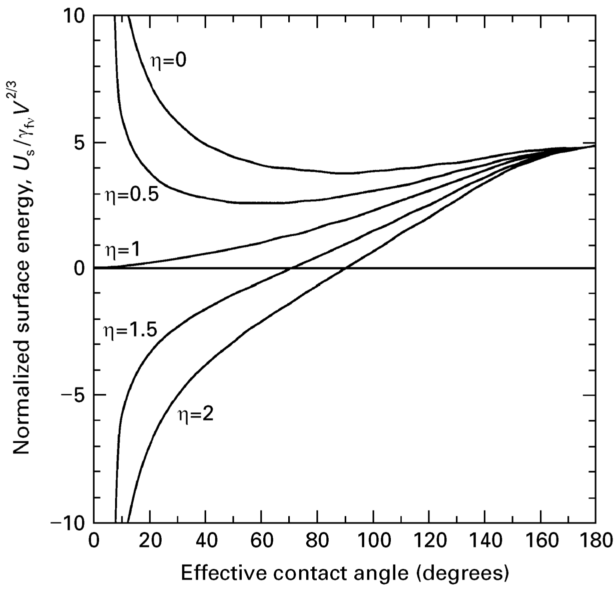

Figure 4 Normalized surface energy plotted as a function of the effective contact angle.

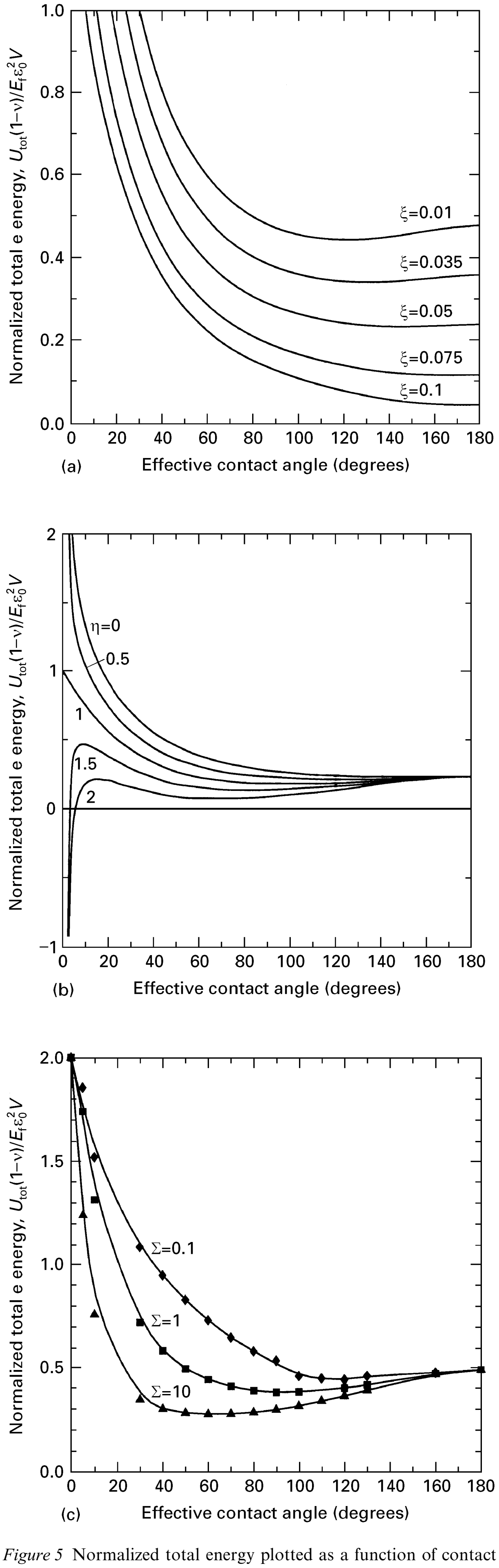

Figure 5 Normalized total energy plotted as a function of contact angle for (a) different values of interfacial-energy ratio ($\Sigma = 1$ and $\eta = 0$), (b) surface-to-strain-energy ratio ($\Sigma = 1$ and $\xi = 0.05$) and (c) modulus-mismatch ratio ($\eta = 0.5$ and $\xi = 0.1$).

values of η above 1, the minimum energy tends to minus infinity at the point when the substrate is completely wetted ($\hat{\theta} = 0$). There are, however, local minima that may exist in the total-energy/contact-angle plot as shown in Fig. 5. So, in principle, a spreading island may be trapped in a metastable equilibrium at a finite contact angle. The local minimum will be shallow for high values of ξ and η, and will probably be overcome by any thermal energy of the film. When ξ and η are large enough, the minima disappear completely and the total energy decreases monotonically as the effective contact angle decreases to zero.

The effect of the modulus mismatch can be deduced from Fig. 2. This figure demonstrates that, for a given film modulus, the strain energy of the system increases as the modulus of the substrate is increased (i.e. as Σ decreases). Hence for a given value of the interfacial-energy ratio, ξ, the contribution of the strain energy to the total energy of the system increases as Σ decreases. This will tend to move the equilibrium contact angle to higher values as shown in Fig. 7.

The continuum calculations have some immediate relevance to the experimental observations of LeGoues *et al.* [14] in which the growth of germanium islands on a silicon substrate was observed in an ultra-high-vaccum transmission-electron microscope. These observations indicated that growth occurred in a discrete fashion: the projected area of an island increased only with the nucleation of individual misfit dislocations. The authors proposed that this implied that the height and, hence, the aspect ratio of the islands increased with volume while the effective misfit strain stayed constant. The introduction of a dislocation decreased the effective misfit strain, allowing the aspect ratio to drop spontaneously. The accompanying model relied on a balance between the surface energy, a dislocation energy and a strain energy which was assumed to be proportional only to volume and not dependent on shape. The present work shows that similar oscillations would be predicted from continuum considerations in which the strain energy is assumed to be sensitive to the shape of the island. The effect of adding additional material at constant strain is to decrease ξ and, consequently, to increase the equilibrium aspect ratio. The introduction of an interfacial misfit dislocation reduces the misfit strain by the ratio of the Burgers vector to the radius of the interfacial area. This increases ξ and, hence, the equilibrium aspect ratio of the island decreases.

2.2. Clustering

The discussion above has been concerned with the spreading of an isolated island of fixed volume. Since Fig. 3 demonstrates that interaction effects between neighbouring islands are very localized, these results can be used to determine approximately the critical island size at which clustering is energetically favoured over uniform film growth. Equation 3 presents the critical radius with the assumption that an island can support no elastic strain. Here, a modification to the analysis of Tu *et al.* [1] is presented in which the effects of a non-zero strain are incorporated.

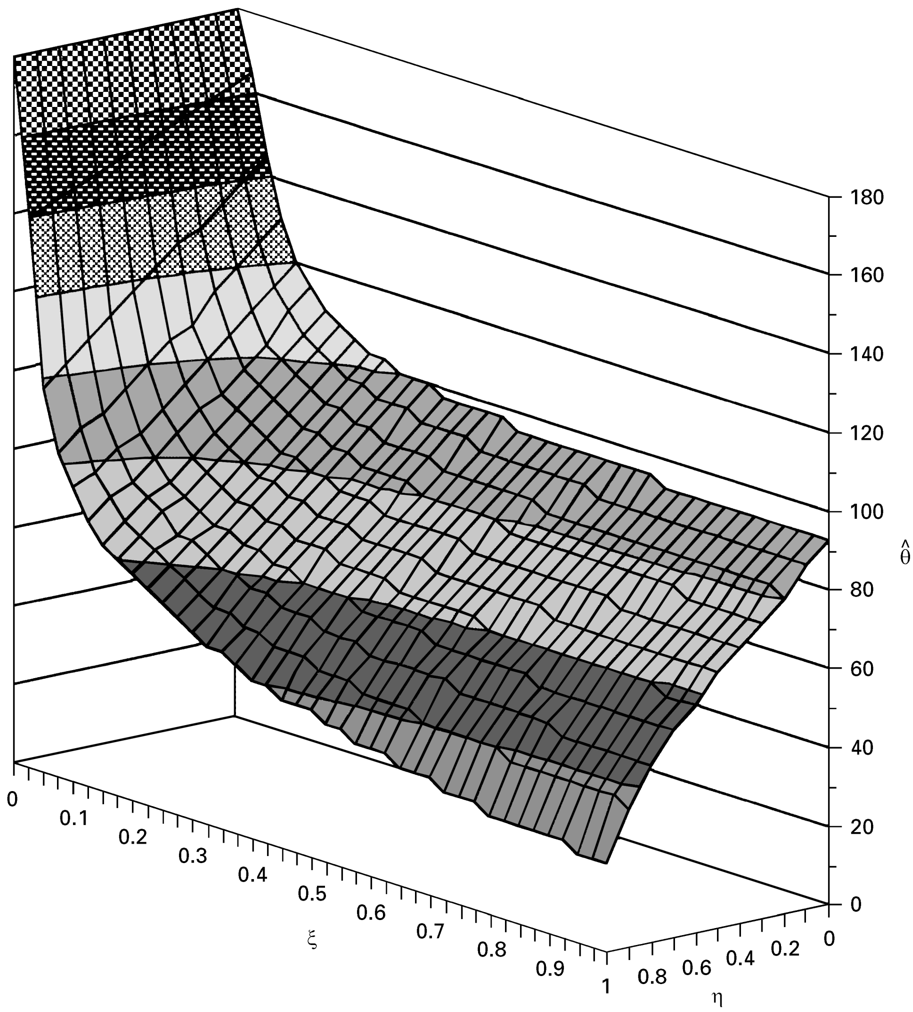

Figure 6 Plot showing equilibrium effective contact angle as a function of both ξ and η for $\Sigma = 1$.

Assume a unit area of substrate, A_0 has a volume V_0 of film deposited over it, and that $\eta = 0$. When the film is in the form of a uniform layer, it will be of a thickness $h = V_0/A_0$ so h represents the volume per unit area deposited on the substrate. A comparison can be made between the total energies of the system when the film covers the substrate uniformly, and when it clusters into n equal sized islands per unit area. The total energy for uniform coverage is given by

$$\frac{U_{\rm tot}(1-\nu)}{E_{\rm f}\varepsilon_0^2 V_0} = 1 + \frac{A_0}{n^{1/3}V_0^{2/3}}\,\xi \tag{8}$$

The total energy for n islands can be obtained from the data for the minimum-energy configuration as a function of ξ (for $\eta = 0$) presented in Fig. 5. By comparing these two results, a critical value for n at which the energy for clustering becomes lower than the energy of a uniform film can be determined and a relationship between the normalized critical island size, $V_{\rm cr}/h$, and ξ can be obtained. This is plotted in Fig. 8, and compared with the results of Equation 3 which can be re-expressed as

$$\frac{V_{\rm cr}^{1/3}}{h} = \left(\frac{2}{3\pi}\right)^{1/3}\left[\frac{1}{\xi}\left(\frac{V_{\rm cr}^{1/3}}{h}\right)^{-1} + 1\right] \tag{9}$$

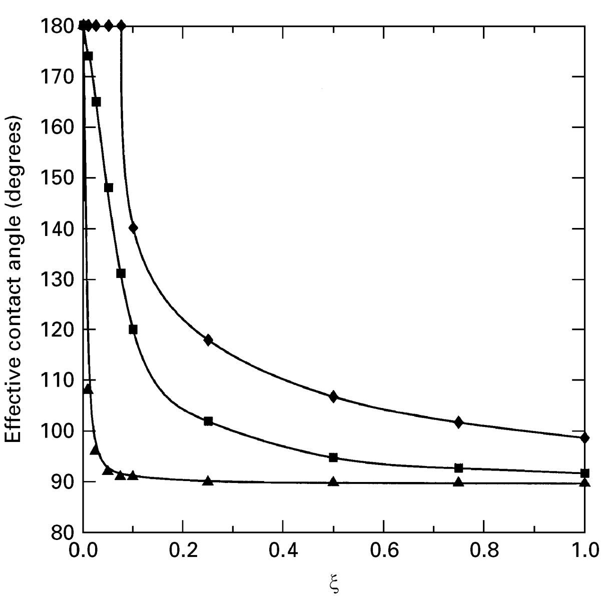

Figure 7 Plot showing the equilibrium effective contact angle as a function of ξ, for three different values of the modulus-mismatch ratio. $\eta = 0$. Key: ◆ $\Sigma = 0.1$; ■ $\Sigma = 1$; ▲ $\Sigma = 10$.

2.3. Surface-tension induced stress

The results presented in this paper have ignored any consideration that, in addition to any misfit strain that may exist, a residual stress will be induced in the island in response to the surface tension and any surface

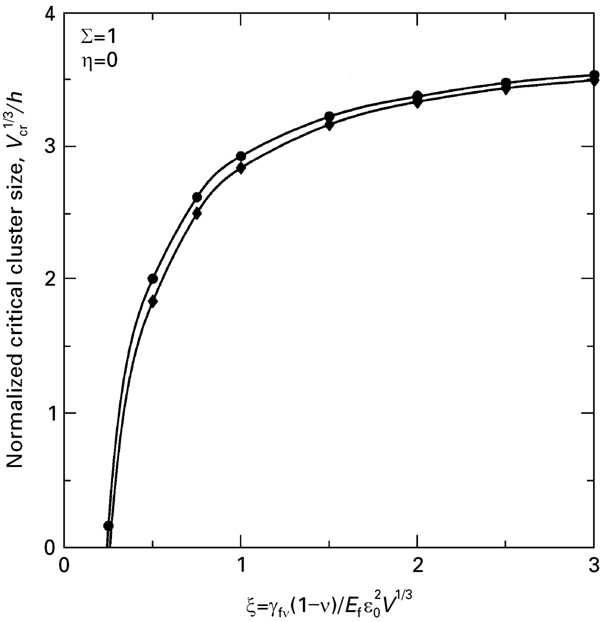

Figure 8 Plot showing the critical volume of an island above which island growth is more energetically favourable than a uniform layer, as a function of the interfacial-energy ratio, ξ. $\Sigma = 1$ and $\eta = 0$. Key: ● including strain energy; ◆ ignoring strain energy.

curvature. This was investigated using finite-element calculations but the effect was found to be negligible for the parameters considered. In this section a simple dimensional argument will be presented to illustrate the conditions over which the effect should be considered. First, it should be recognized that the effect of the surface tension on the residual stress can be modelled by assuming tractions are applied over the surface with a magnitude given by $\gamma_{fv}(\kappa_1 + \kappa_2)$, where κ_1 and κ_2 are the principal curvatures at any point. The assumption that the island maintains a spherical shape means that this effect can be modelled with a uniform pressure applied over the surface of the island. The strain energy associated with the surface tension is, therefore, approximately given by $U_1 = 2\gamma_{fv}^2 V^{1/3} g_1(\theta)/E_f$, whereas the surface energy term is given by $U_2 = \gamma_{fv} V^{2/3} g_2(\theta)$. A comparison between these two terms indicates that the surface-energy induced stress can probably be ignored provided the quantity $\gamma_{fv}/E_f V^{1/3}$ is very small. For example, if a surface energy of about $1\ \mathrm{J m^{-2}}$ and a modulus of about 100 GPa are assumed, the surface-tension induced stress is negligible when the island radius is greater than about 1 nm.

3. Conclusions

Using an approximation that the shape of an isotopic island sitting on a substrate can be modelled as a spherical cap, the effect of aspect ratio on strain energy was numerically computed. The results of the computation were combined with analytical expressions for the surface energy so as to obtain the total energy of isolated islands with different aspect ratios. The approximate equilibrium configuration was then deduced by equating it to the minimum-energy configuration. It was shown that as the effective contact angle increases (i.e. the aspect ratio of the island height to contact-width increases), the strain-energy term decreases. Hence, it was shown that if the relative importance of the strain-energy term is increased by, for example, increasing the magnitude of the misfit strain or the island volume, the equilibrium aspect ratio increases so as to counteract the strain-energy effect. Conversely, increasing the surface-energy term tends to decrease the equilibrium aspect ratio. The effects of modulus mismatch, surface-energy-to-misfit-strain ratio, and different interfacial energies were shown to influence the aspect ratio in a similar fashion.

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References

1. K. N. TU, J. W. MAYER and L. C. FELDMAN, "Electronic Thin Film Science for Electrical Engineers and Materials Scientists" (Macmillan, New York, 1992).
2. M. OHRING, "The Materials Science of Thin Films" (Academic Press, London 1992).
3. G. H. GILMER and M. H. GRABOW, *J. Metals* **39** (1987) 19.
4. N. CABRERA, *Surf. Sci.* **2** (1964) 320.
5. S. LURYI and E. SUHIR, *Appl. Phys. Lett.* **49** (1986) 140.
6. S. CHRISTIANSEN, M. ALBRECHT, H. P. STRUNK and H. J. MAIER, *ibid.* **64** (1994) 3617.
7. S. CHRISTIANSEN, M. ALBRECHT, H. P. STRUNK, P. O. HANSSON and E. BAUSER, *ibid.* **66** (1995) 574.
8. L. J. GRAY, M. F. CHISHOLM and T. KAPLAN, *ibid.* **66** (1995) 1924.
9. D. J. SROLOVITZ, *Acta Metall.* **37** (1989) 621.
10. H. GAO, *Int. J. Solids* **28** (1991) 703.
11. C. RATSCH and A. ZANGWILL, *Surf. Sci.* **293** (1993) 123.
12. W. H. YANG and D. J. SROLOVITZ, *Phys. Rev. Lett.* **71** (1993) 1593.
13. L. B. FREUND and F. JONSDOTTIR, *J. Mechs. Phys. Solids* **41** (1993) 1245.
14. F. K. LEGOUES, M. C. REUTER, J. TERSOFF, M. HAMMAR and R. M. TROMP, *Phys. Rev. Lett.* **73** (1994) 300.

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