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Stranski-Krastanow transition and epitaxial island growth

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A detailed examination is presented of the way in which the Stranski-Krastanow epitaxial islanding transition can be controlled by strain due to elemental segregation within the initially-formed flat ''wetting'' layer. Calculations using a segregation model are shown to accord well with experimentally measured critical wetting-layer thicknesses for the $In_xGa_{1-x}As/GaAs$ system ($x=0.25$–1). The strain energy associated with the segregated surface layer is determined for the complete range of deposited In concentrations using atomistic simulations. The segregation-mediated driving force for the Stranski-Krastanow transition is considered also to be important for all other epitaxial systems exhibiting the transition.

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The growth of thin epitaxial films upon crystalline substrates can occur in one of three modes: (i) two-dimensional (2D) layer-by-layer growth proposed by Frank and Van der Merwe,[1] (ii) 3D island growth proposed by Volmer and Weber,[2] and (iii) 2D layer growth followed by 3D islanding, first described by Stranski and Krastanow (SK).[3] 2D layer-by-layer growth typically occurs in systems with either zero or small lattice mismatch, while 3D island growth usually occurs for systems with highly mismatched and dissimilar materials. For epitaxial systems with similar materials and high lattice mismatch, the two-stage SK growth mode is common. In this latter case, a very thin, flat epitaxial layer is formed first, and then a transition to 3D island growth takes place at a certain critical thickness. This growth mode has received in-depth experimental study across wide materials areas from metals to semiconducting materials (see Venables *et al.*[4] for early work on mainly metal-related deposition systems). In the semiconductors area, the transition has assumed some importance since the islands formed can be employed as quantum dots in advanced electronic devices. Accordingly, a number of semiconductor epitaxial systems exhibiting the SK growth mode have been carefully studied, including $In_xGa_{1-x}As/GaAs$,[5–11] $InP/In_xGa_{1-x}P$,[12,13] GaSb/GaAs,[14] and SiGe/Si.[15–19] The initially-formed SK islands are coherent[15] although incoherent (dislocated) islands are produced[6] when island sizes increase during growth.

Much work has been devoted to the formulation of theoretical models based upon energy calculations and rate equations relating to surface growth structures[20–27] in order to explain the features of the 2D-3D transition. It is often concluded that 2D islands tend to transform into 3D islands when they exceed a certain critical size, and such arguments have been employed to model the transition. However, there has been little consideration of the growth of the initial wetting layer and the factors that control the critical thickness which it must attain before the islanding transition can take place. Recently, careful measurements by Walther *et al.*[28,29] of SK island and wetting-layer composition were carried out for the $In_xGa_{1-x}As/GaAs$ system using electron energy-loss imaging. Based upon these measurements, it was proposed[28,29] that segregation of elemental In to the surface of the initial flat wetting-layer controls the critical point at which the transition to island growth occurs (hereafter referred to as the WCNH mechanism). In principle, this provides a natural explanation for the general features of the transition and it is described in some detail here. The mechanism is fundamentally applicable to all materials systems exhibiting the SK transition and is considered now with special reference to the $In_xGa_{1-x}As/GaAs$ system.

For layer growth in the $In_xGa_{1-x}As/GaAs$ system, either an alloy or, for $x=1$, a binary material (InAs) is deposited. In the WCNH mechanism proposed for the SK transition, as the initial flat epitaxial layer forms, emphasis is placed upon the strain-related effects of vertical segregation of the largest atomic species (In) in the deposited material. This has been simulated using the Fukatsu/Dehaese segregation model,[30,31] employing parameters taken from the original work.[31,32] The model considers exchange of the group-III species between the top two layers during growth so that the surface layer exhibits a very substantial deviation from the deposition flux concentration. If a relatively dilute ($x=0.25$) alloy is deposited, Fig. 1 shows the way in which the In concentration is predicted by the theory to evolve within the growing flat layer. It is immediately evident that segregation of In to the surface enhances the In concentration in the surface monolayer rapidly above that of the deposition flux so that, for only ~ 1 nm of layer growth, the surface In concentration is already above 40%. It continues to increase as deposition proceeds and is estimated to attain a saturation value of 80–85% for layer thicknesses in excess of ~ 2.5 nm.[33]

In Fig. 1, the continuous line tracks the In concentration in the surface layer during growth. It is then important to determine the variation in predicted surface In concentration as a function of deposition flux composition. This is presented in Fig. 2 where the curves show this quantity for deposition fluxes containing from 5% to 100% In. For each deposition condition, the surface In concentration rises progressively to a saturation value, which itself rises with increasing deposition flux concentration.

The WCNH mechanism proposes that a critical surface concentration of In (and associated strain) must build up before the SK-islanding transition can take place. Since a deposition flux of 25% In is approximately the lowest that will induce the SK transition, it is possible to identify the corre-

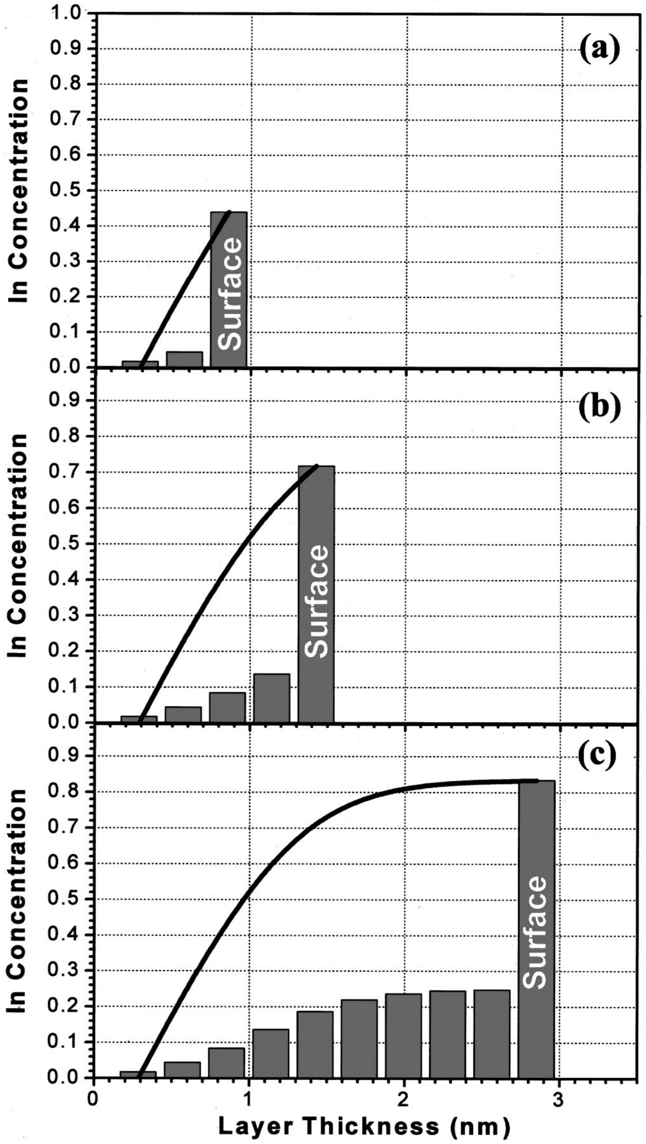

FIG. 1. Composition variations in the near-surface $In_xGa_{1-x}As$ monolayers (shown by bars), driven by In segregation to the surface (In concentration variation in the surface monolayer is tracked by the solid line). Deposition flux is 25% In and different total-growth thicknesses are: (a) 3 monolayers, (b) 5 monolayers, and (c) 10 monolayers.

sponding critical surface In concentration from the associated curve in Fig. 2: the critical concentration would be predicted to be 80–85% In in the surface layer. For any particular deposition flux, it is predicted that the SK transition will take place after the surface In concentration rises to this critical level. Thus the islanding transition points for layers grown over the complete range of deposition fluxes can be estimated from plots of the type given in Fig. 2, so that it is possible to estimate the critical transition thickness of the initial flat wetting layer as a function of deposited In concentration. This then gives the continuous "theoretical" curve in Fig. 3, which extends from 2.5 nm thickness for a deposition flux of 25% In to 0.3 nm thickness for InAs deposition.

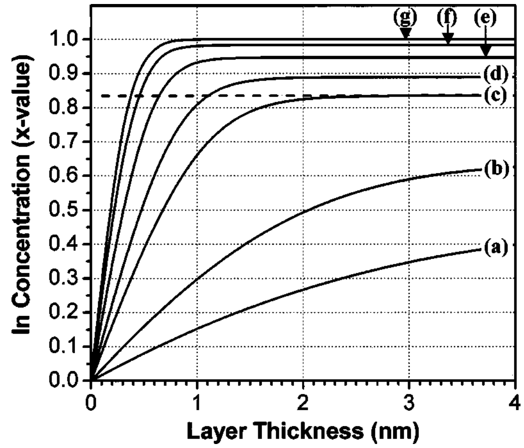

FIG. 2. Composition variations in the surface monolayer, driven by In segregation to the surface, for deposition fluxes with (a) 5% In, (b) 10% In, (c) 25% In, (d) 35% In, (e) 55% In, (f) 80% In, and (g) 100% In.

For comparison with theory, in the present work $In_xGa_{1-x}As$ alloy layers were grown on (001) $\pm 1°$ GaAs by molecular-beam epitaxy, and the thicknesses of wetting layers at the SK 2D-3D transition point were measured directly in the transmission electron microscope (TEM). Growth took place upon heat-cleaned (001) substrates exhibiting the As (2×4) reconstruction under an As overpressure and with a relatively high substrate temperature of 540 °C, chosen to encourage segregation whilst In desorption can still be considered insignificant. Growth was terminated and each substrate rapidly cooled under As flux slightly before the transition in the reflection high-energy electron-diffraction (RHEED) pattern from 2D "streaked" to 3D "spotty" was complete, since the pattern change is a little insensitive to the precise SK-islanding transition point. Structural and compositional studies of these layers have been carried out using a JEOL 2010F field emission gun TEM, employing samples thinned to electron transparency in cross-sectional configuration by sequential mechanical polishing and low-voltage

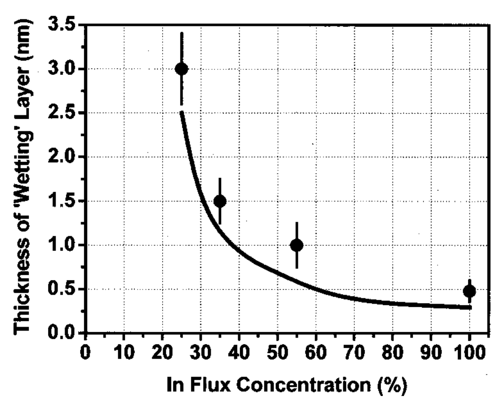

FIG. 3. Variation in the flat-layer critical thickness for the islanding transition as a function of In concentration in the deposition flux: measured values given as data points and theoretically predicted values based upon the WCNH mechanism presented as continuous curve.

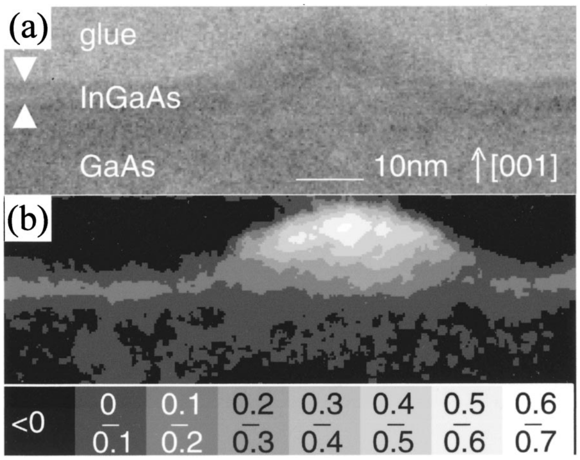

FIG. 4. Cross-sectional TEM images of initial quantum dot formed for $In_xGa_{1-x}As$ growth upon GaAs with a deposition flux having 25% In: (a) bright-field image with arrows indicating the wetting layer and (b) image showing In composition variations in quantized steps (modified from Ref. 28).

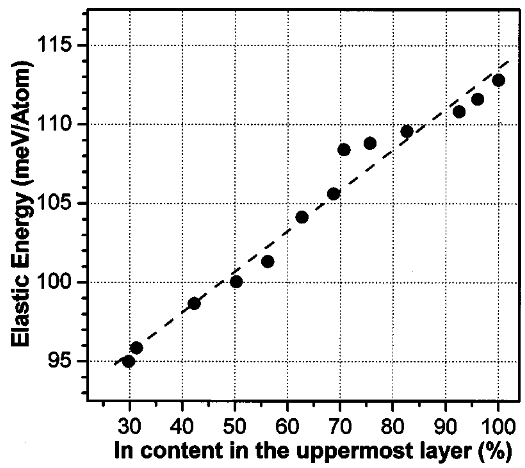

FIG. 5. Variation in calculated elastic energy-per-atom for the uppermost continuous monolayer as a function of the local In concentration.

ion milling. Figure 4(a) shows a cross-sectional view of a typical sample grown with 25% In deposition flux, and the critical wetting-layer thickness was measured directly from such images: in this case, the thickness is ~3 nm, as indicated by the arrows. (The In within the wetting layer is visible in Fig. 4(b), together with the nonuniform In distribution within a typical growth island.[28]) Similar observations have been made for growth with In flux concentrations of 35% and 55%, which have yielded critical wetting layer thicknesses of ~1.5 nm and ~1.0 nm, respectively. It is anticipated that these measurements may be modestly depressed below the real values due to likely consumption of surface/near surface monolayers (containing high concentrations of In) by the initial island nuclei. The experimental thicknesses are also plotted in Fig. 3, together with a critical wetting-layer thickness of 0.4 nm (1.6 monolayers[11]) for InAs deposition. Other measurements of wetting-layer thickness have been reported,[13] but they appear to have relied wholly upon RHEED observations which, due to insensitivity, may have resulted in overestimates of the critical thickness values.

From Fig. 3, it is immediately apparent that the theoretically and experimentally derived curves exhibit exactly the same form and are displaced from one another by no more than 0.1–0.5 nm, depending upon In flux concentration. This small displacement of the curves may result, at least in part, from the fact that the theoretical curve does not allow for any induction period required prior to the formation of island nuclei after the wetting layer has achieved its critical surface In concentration. Furthermore, it is possible that use of appropriately calibrated multilayer segregation theory[33] would give an even closer fit to experiment. Of particular significance, the near coincidence of the curves lends strong support for the importance of segregation in determining the SK 2D-3D transition point, as proposed in the WCNH mechanism.[28,29] Segregation to the initial flat growth surface of large amounts of In would be expected to produce a heavily strained surface layer. The magnitude of this strain was estimated by atomistic simulation of the dependence of the elastic energy of the uppermost continuous monolayer on its In composition. Optimized Tersoff potentials[34–36] were employed to model the interactions of 8000 atoms, arranged in a rectangular box of dimensions $6\times6\times6$ nm, with a rigid boundary at the bottom, open boundary at the top, and periodic boundaries in the [100] and [010] directions. The structure consisted of 10 monolayers of GaAs and 10 monolayers of $In_xGa_{1-x}As$ with increasing In concentration, as predicted using the kinetic segregation model[31] for the 25% In deposition flux. An As-stabilized (2×4) reconstructed $In_xGa_{1-x}As$ (001) surface with As-As dimers[37] and with varying In content was reproduced by the atomic model. The structures were relaxed using the OXON code,[38] and the elastic energy of the uppermost continuous monolayer was evaluated directly from the components of the strain tensor.[39,40] The results are shown in Fig. 5, where it is clear that there is a continuous increase in the elastic energy stored in the surface, and hence also in the strain, as the concentration of In increases. The WCNH mechanism proposes that this surface strain, in part, inhibits the incorporation of In (and Ga) on lattice sites, thereby raising the number density of mobile surface atoms and increasing the probability of island nucleation on the surface. Beyond a critical point, 3D islands would be expected to form, yielding strain relief within the islands primarily by lateral expansion of unconstrained vertical lattice planes.[41]

The increasing surface-strain energy, resulting from the increasing surface In concentration, has a clear effect upon layer surface growth structures. For example, for a low deposition flux In concentration of 15%, it has been shown[10] that the layer-by-layer growth results in the formation of a very flat surface with evenly spaced monolayer surface steps and few, if any, monolayer islands. However, an increase in the deposition flux In concentration to 20% results in a strong change in surface-step configurations with the formation of narrow protuberances running ahead of step fronts and the production of significant numbers of monolayer islands.[10] Such step-front distortions would be expected to yield elastic relaxation by unidirectional expansion across the narrow protuberances. The monolayer islands are the expected[21] precursors of 3D islands produced by the SK transition when the deposition-flux In concentration is increased by a further 5%. Similar ribbonlike wetting-layer surface structures are seen in other systems (e.g., AlSb/GaAs, GaSb/GaAs, and InSb/GaAs) for layers undergoing the SK-islanding transition.[14] For deposition of InAs on GaAs, an initial delay in the increase of the surface In concentration to 100% [curve (g) in Fig. 2] results from the exchange of In atoms with Ga atoms in the GaAs surface. In this latter case, partial completion of the second monolayer is required before the surface In concentration and associated strain become high enough to trigger the SK 3D-islanding transition. Once again, before the transition occurs, layer growth processes are severely disturbed by the increasing surface strain.[11]

It is interesting that, for $In_xGa_{1-x}As/GaAs$, the SK transition takes place[37] only on the As-stabilized (2×4) reconstructed (001) surface and, as shown above, requires a surface In concentration close to 100%. It is possible that the group-III-stabilized (4×2) reconstruction on (001) and the (110) and (111) crystal orientations confer altered surface energies so that segregation buildup of even 100% In is insufficient to initiate the SK-islanding transition.

In summary, the way in which the WCNH segregation mechanism can drive the SK transition is considered in detail. For the (001) $In_xGa_{1-x}As/GaAs$ epitaxial system, theory and experiment give critical wetting-layer thicknesses which are in excellent agreement, thus providing strong support for the segregation-based mechanism. It is considered that, for all other epitaxial systems exhibiting the SK transition, elemental segregation within the wetting layer will be a key factor determining the critical point at which islanding occurs.

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