1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

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MATERIALS ISSUES IN MOLECULAR BEAM EPITAXY

J.Y. TSAO

Sandia National Laboratories

Dept 1311-0603

Albuquerque, NM 87185-5800

Introduction

The technology of crystal growth has advanced enormously during the past two decades; among those advances, the development and refinement of molecular beam epitaxy (MBE) has been among the most important. Crystals grown by MBE are more precisely controlled than those grown by any other method, and today form the basis for many of the most advanced device structures in solid-state physics, electronics and optoelectronics.

In addition to its numerous device applications, MBE is also an enormously rich and interesting area of materials science in and of itself. In this paper, we discuss a few examples of some of these materials issues, organized according to whether they involve bulk, thin films, or surfaces [1].

Bulk Phase Equilibria

As a first example, consider bulk phase equilibria in the binary GaAs alloy. There are four phases that must be considered. The first phase is crystalline GaAs, which is usually what one wants to grow by MBE. The second phase is liquid Ga, which is usually what one doesn't want to form, except under special conditions (e.g., during migration enhanced epitaxy, which relies on enhanced Ga adatom diffusivities on Ga-rich surfaces). The third phase is solid As, which is also usually what one doesn't want to form, except under other special conditions (e.g., during low-temperature GaAs growth, which relies ultimately on precipitation of excess solid As). The fourth phase is the vapor, which has in it both elemental Ga and a mixture of As species.

The question we ask is: under what conditions does crystalline GaAs want to form from the vapor, but the other condensed phases, liquid Ga and solid As, not want to form?

To answer that question, consider the composition-temperature phase diagrams [2] for binary GaAs shown in Figure 1. In particular, consider the high pressure phase diagram shown at the left. One sees that at very high temperatures, only the vapor is stable, and at slightly lower temperatures, only the liquid is stable. In between, because As has so much higher a vapor pressure than Ga, there is a broad two-phase region in which Ga-rich liquid co-exists with As-rich vapor. At lower temperatures, the condensed phases become the more stable phases. On the left there is a two-phase region in which the 50:50 crystal coexists with Ga-rich liquid, and on the right there is a two-phase region in which the 50:50 crystal coexists with As-rich liquid.

At even lower temperatures, the liquids become unstable, and on the left the 50:50 crystal coexists with Ga solid, or gamma, and on the right the 50:50 crystal coexists with As solid, or alpha.

At the top and bottom of Figure 1 are also shown snapshots of the molar Gibbs free energies of the various phases at a couple of temperatures. These are the free energies from which the phase diagrams are actually constructed. Three phases have fairly sharp minima (solid GaAs, Ga and As), and two phases have fairly broad minima (liquid and vapor). The common tangent constructions that determine which phases will actually be present are also drawn.

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Consider now the lower pressure phase diagram shown at the right of Figure 1. As pressure decreases, the vapor becomes increasingly stable relative to the condensed phases, and so its region of stability expands to fill some of the regions that used to be occupied by those condensed phases. In particular, a two-phase region opens up which has the 50:50 crystal coexisting with As-rich vapor. This is precisely the window in which MBE of GaAs is allowed. Everywhere else, some other condensed phase has a tendency to form -- if the temperature is too high or there's too much Ga, Ga-rich liquid forms, and if the temperature is too low solid As precipitates form.

Figure 1

What happens if the pressure is decreased even further? Basically, as shown on the left in Figure 2, the vapor continues to get more and more stable, and the vapor region continues to grow at the expense of the liquid region. The "MBE window" within which MBE is possible also moves down as the pressure decreases. Physically, the lower the As overpressure, the lower the temperature can be at the bottom boundary before solid As precipitates tend to form, and the lower the temperature must be at the top boundary in order to suppress As loss from the surface that would lead to Ga-rich liquid.

Note that this "MBE window" varies quite a bit with alloy material. For GaAs it is a fairly wide window with about 250-300 degrees of play in it. However, for III/V alloys composed of heavier elements, the windows get narrower and narrower, mainly because the vapor pressures of the group V elements get lower and lower. By the time one gets to InSb, the window, for reasonable growth rates, is as narrow as 10-20 degrees.

Also note that if the pressure is decreased even further, below the so-called congruent sublimation pressure [3], the two-phase liquid plus vapor region above the MBE window disappears entirely.

As shown on the right of Figure 2, as the crystal is heated, it sublimates congruently into vapor rather than decomposes incongruently into a liquid-vapor mixture.

Figure 2

Physically, what is the origin of such a congruent sublimation point? The right side of Figure 3 shows the vapor pressures of Ga over the 50:50 crystal (the solid curve) and over the Ga liquid (the dot-dashed curve). The intersection of the two curves defines the congruent sublimation pressure and temperature. Above the congruent sublimation temperature, the vapor pressure of Ga over the 50:50 crystal is higher than that over Ga liquid. That means that Ga vapor, once formed from the crystal, will have a tendency to condense into liquid. Below the congruent sublimation temperature, the vapor pressure of Ga over the 50:50 crystal is lower than that over Ga liquid. That means that Ga vapor, once formed from the crystal, will not have a tendency to condense into liquid.

The left side of Figure 3 shows the molar Gibbs free energy curves that correspond to the vapor pressures on the right side of that Figure. Consider first a temperature higher than the congruent sublimation temperature, as in the top panel. If the 50:50 crystal and the vapor are to be in equilibrium, then their free energy curves must just be tangent. However, at this high temperature, the liquid is just stable enough to drop below the vapor in free energy, and so will tend to form. Consider now a temperature lower than the congruent sublimation temperature, as in the bottom panel. Again, if the 50:50 crystal and the vapor are to be in equilibrium, then their free energy curves must just be tangent. However, at this low temperature, the liquid is not stable. It lies everywhere above the vapor in free energy, and so will not tend to form.

Figure 3

Thin Film Structure and Microstructure

As a second example, consider a strained thin film epitaxial layer. Consider, in particular, a ternary alloy composed of elements having different atomic sizes, and hence different propensities to incorporate into lattices to form strained alloys. For concreteness, Figure 4 shows a calculation of the forces which ensue when one tries to create a small tetrahedral cell having two In atoms and two Ga atoms in the corners and one As atom in the center. The In-As bonds are longer than the Ga-As bonds, so there will be a tendency for the As atoms to want to move down from the center of the cube. At the same time, as the As atom moves downwards, the tetrahedral sp^3 bonding associated with the As atoms surrounding each of the group V atoms gets distorted, and so there will be a tendency for the As atom to want to stay smack in the center of the cube [4].

The one extreme of behavior, where the As atom moves down to preserve bond lengths is called the covalent radius approximation, and the other extreme of behavior, where the As atom stays centered to preserve bond angles is called the virtual crystal approximation. In reality, the covalent radius approximation is the more accurate one, since bonds tend to be stiffer against stretching than against bending. The net result is that the downward movement of the As atoms within these tetrahedra of mixed composition creates a fair amount of microscopic strain energy (on the order of 0.1 eV/at-pr), and that strain energy tends to make the alloy want to phase separate [5].

Figure 4

In fact, all of the pseudobinary III-III/V and III/V-V alloys have a tendency to phase separate, and hence have positive mixing enthalpies. Figure 5 shows, e.g., measured mixing enthalpies for a number of III/V pseudobinary alloys, plotted versus those which one would expect solely on the basis of microscopic strain considerations. The agreement is fairly good, and indicates that microscopic strain is the dominant factor in determining the mixing enthalpies in these alloys [6]. Note that the greater the size mismatch the greater the mixing enthalpy. InP and InAs don't have that large a size difference, so InPAs has a relatively low mixing enthalpy, and in practice is relatively easier to grow uniformly. InAs and InSb do have a large size difference, so InAsSb has a relatively high mixing enthalpy, and in practice is relatively more difficult to grow uniformly.

Figure 5

Note that growth of actual thin films of these pseudobinary alloys is complicated by that fact that, even though all the pseudobinary bulk alloys have a tendency to phase separate, they are often constrained from doing so by what are called coherency constraints [7]. One way to see these constraints is to imagine the following. Suppose one is growing a thin film on a substrate that is infinitely flexible and accommodating. Suppose, in particular, one is growing a 50:50 InGaAs film with an average lattice constant of 5.85 Å, with a tendency to phase separate laterally into a GaAs region with a smaller lattice constant of 5.65 Å and an InAs region with a larger lattice constant of 6.05 Å. Because the substrate stretches infinitely flexibly, those regions are free to adopt their natural lattice constant, and there will not be a barrier to phase separation.

In fact, usually one grows on a substrate that is rigid. That means the GaAs regions will not be able to freely adopt a 5.65 Å lattice constant, and the InAs regions will not be able to freely adopt a 6.05 Å lattice constant. Both of those regions will be highly strained, and that strain will add to their energies and keep them from forming, or at least keep them from forming to the extent that they otherwise would.

Surface Morphology

As a final example, consider the evolution of surface morphology during growth. In a simplified view of that evolution, one supposes that there are two main "entities" that move on surfaces, steps and adatoms. The relative rates at which those two move determines, to first order, the growth mode that one can expect [8].

First, how fast do the steps move? If adatoms are being deposited at a rate of j monolayers per second and the steps are spaced by L , then the steps move to the right at a rate of L every $1/j$ seconds, or at a velocity of $v_{\text{step}} = jL$. Second, how fast do the adatoms move? If an adatom lands on a terrace and executes a random walk to get to the nearest step, then the average time it takes to get to that step will be approximately L^2/D , where D is the diffusivity, and so its average velocity will be $v_{\text{adatom}} = L/(L^2/D) = D/L$. The ratio between these two velocities, $v_{\text{step}}/v_{\text{adatom}} = jL^2/D$, is called the Peclet number, in that it is a measure of the relative importance of "convective" flow, that is, how fast steps move to adatoms, vs "diffusive" flow, that is, how fast adatoms move to steps.

Fast adatoms. If the adatoms are really fast, so that the Peclet number is much less than one, then growth proceeds by by "simple" step flow, although the evolution of perturbations in surface morphology can be quite complex [9]. Suppose, as shown in Figure 6, that there's a perturbation in step density. The step position and height are x and h , respectively, and one can see that the steps are bunched up in the center. L refers to the terrace widths between the steps, and one can see that the terrace width distribution has a corresponding dip in the center.

How those step positions and terrace widths evolve is determined by wave equations, and the parameters in the wave equations depend in a complicated way on whether adatoms have a higher probability of attaching at up or down steps, and on whether adatoms have a higher probability of crossing over up or down steps. In the example shown in Figure 6, the adatoms are assumed not to cross over steps, and to have a higher probability of attaching at up than at down steps. Then, the wave equations have second order terms which cause the perturbation to damp as it propagates up.

If adatoms do cross over steps, then the shape changes can be much more complicated, with higher-order dispersive terms entering into the wave equation.

Figure 6

Medium-fast adatoms. Now suppose that the adatoms move at about the same rate that the steps do, so that the Peclet number is of order unity. Then there will be a delicate balance between adatoms moving to steps and steps over-running adatoms, and the step flow becomes, in a sense, "convective." This regime is more difficult to treat, since now adatom concentrations and diffusion between steps must be treated in addition to the motion of the steps themselves [10]. Figure 7 shows a simple example in which one assumes that adatoms annihilate strongly at step edges. Then, even as adatoms rain down on the terrace, their concentration at the step edges remains zero. As more adatoms arrive, and as more annihilate at the step, the step begins to move a little. Then, the step begins to pick up more and more speed, and as it begins to over-run the adatoms, the adatom concentration becomes skewed. Finally, the step has over-run a large fraction of the adatoms and it begins to slow down.

This overall sequence gives rise to a step velocity that oscillates in time, as shown in the middle panel of Figure 7, and that can also manifest itself as surface diffraction intensities that oscillate in time, as shown in the right panel of Figure 7.

Figure 7

Slow Adatoms. Now suppose that the adatoms move more slowly than the steps do, so that the Peclet number is greater than unity. Then the adatoms don't have time to diffuse to pre-existing step edges, and instead will nucleate into clusters between the steps. Those clusters will grow, and eventually coalesce. This is the classic 2D cluster nucleation, growth and coalescence regime in which layer-by-layer surface diffraction oscillations most often occur [11].

Figure 8 shows a couple of numerical simulations of that kind of growth. The top panel shows mobile adatom coverages, the next panel shows cluster densities, the next panel shows immobile adatom coverages, and the bottom panel shows simulated surface diffraction intensities. The simulation on the left is for the case where the attachment rate of adatoms at down steps is a little higher than that of adatoms at up steps, the simulation on the right is for the opposite case. One can see that the monolayer-by-monolayer oscillations in the surface diffraction intensity are more pronounced in the first case than in the second. The reason is that enhanced attachment of adatoms at down steps suppresses nucleation of new clusters on top of existing clusters, so that growth tends to be more two dimensional, or layer-by-layer, rather than three dimensional, or multi-layered.

Figure 8

Statistical Growth. Now suppose that the adatoms move much more slowly than the steps do, so that the Peclet number is much greater than unity. In other words, suppose the adatoms stick wherever they land. This is the regime of statistical roughening. For MBE, it is probably the least interesting regime, although occasionally one may be forced to grow there. However, mathematically, it may be the most studied regime of them all.

If growth is purely vertical, as it is in MBE, then all one has are column probabilities, without regard for lateral correlations. Those column probabilities will initially obey Poisson arrival statistics, and eventually, because of the law of large numbers, also obey Gaussian statistics. In Figure 9, e.g., one can see that as the average coverage increases from 0.5 to 1.5, the distribution becomes more and more symmetric as it eventually approaches a Gaussian. At the same time, the surface diffraction intensity decreases rapidly, and by the time the average coverage reaches 1, is nearly zero.

However, if growth is not purely vertical, as perhaps in chemical vapor deposition, then one doesn't just have column probabilities. If growth, e.g., is proportional to actual surface area, rather than surface area projected onto the substrate plane, then perturbations in growth rate can evolve in extremely interesting ways. And if there are both components to the growth, the evolution can be exceedingly complex, and can be characterized by fractal exponents of various kinds.

Figure 9

Summary

MBE is an enormously rich and interesting area of materials science. One way of organizing the materials issues which are important to MBE is according to whether they involve bulk, thin film, or surface issues.

Of primary importance are materials issues that have to do with bulk phase equilibria, in that they define, to first order, the "MBE window." Next in importance are materials issues that have to do with thin films. Even if the right bulk phase is forming, its thin film structure and microstructure may or may not be what one wants, particularly if one is dealing with ternary and quaternary alloys, and with strained thin films. Last (but not least) in importance are materials issues that have to do with surfaces. It is important to emphasize, though, that even the least important of these issues can have important effects on the performance of MBE-grown devices.

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