Adatom Densities on GaAs: Evidence for Near-Equilibrium Growth

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We examine the equilibrium of a compound semiconductor surface under molecular beam epitaxy (MBE) conditions, both theoretically and experimentally. For GaAs, the Ga chemical potential and adatom density depend sensitively on As pressure as well as temperature. Our results suggest that MBE growth may take place under conditions much closer to equilibrium than has been believed. We also show that standard one-component models cannot, even in principle, reproduce both the adatom density and its temperature dependence. [S0031-9007(96)02150-3]

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Because of its relative simplicity, molecular beam epitaxy (MBE) provides an ideal process for studying fundamental issues in growth. Recently, such studies have proven their value: computer simulations can now reproduce certain features of semiconductor growth in considerable detail [1–3]. In principle, this understanding should translate into improved growth, which would be technologically important. However, the models used are generally restricted to a single component, whereas the primary application of MBE is in growth of compound semiconductors. The quality of MBE-grown GaAs depends critically on the relative amounts of Ga and As supplied during growth [4,5]. Yet the interplay of the two components is not understood in detail [6].

The most important determinant of growth, as discussed below, is the Ga adatom density on the surface. Here we derive explicit formulas relating this density to the temperature, As pressure, and deposition rate. We also report measurements of the adatom density, which lend considerable support to the analysis.

While our theory and experiment primarily address thermodynamic equilibrium, the results have profound implications for growth. It is often claimed that MBE growth takes place very far from equilibrium. However, as we show below, under typical conditions the Ga adatom density on the surface may be extremely high even in equilibrium, so that the additional Ga arriving in the growth flux represents a tiny perturbation.

Thus, in fact, MBE growth can take place close to equilibrium. The interplay of temperature and As pressure also accounts for the trend toward lower As pressure in MBE growth to compensate for the effects of lower temperature. These results place MBE growth in a new light and suggest that many of the powerful tools of thermodynamics [6,7] can be applied directly to the surface during growth.

Our results also have important implications for the modeling of growth. The most successful attempts to simulate growth of compound semiconductors [1] have relied on mapping this problem onto the simpler one-component case. In the case of GaAs or similar compounds, this is justified by noting that growth is Ga limited. Thus, in a one-component model, that component implicitly refers to the Ga, with its properties suitably "renormalized" by its interaction with the As. However, we show here that the crucial Ga adatom density cannot be described even in principle by an effective one-component model. We also suggest how this shortcoming can be corrected without introducing any unknown parameters.

We begin by treating the thermodynamic equilibrium of the surface and later extend the discussion to actual growth. In order to treat this complex problem in a useful and transparent way, we make several simplifying assumptions, all of which are consistent with what is known about MBE growth of GaAs (especially at moderate temperature). More generally, the model should describe many compound semiconductors over a range of conditions.

We assume that the vapor pressure of Ga is so small that one can neglect evaporation of Ga from the surface, that Ga diffuses on the surface as individual adatoms occupying discrete sites, and that the surface is in equilibrium with the crystal and with the As vapor. (We generalize below to include a directed As flux.) We consider that there are ν_{Ga} equivalent sites per unit area where Ga may sit. Because the surface is reconstructed in a complex way, the density ν_{Ga} is typically somewhat smaller than, but of the same order as, the surface atom density. We neglect all contributions to the Ga adatom entropy other than permutations of the Ga atoms among the allowed sites.

Minimizing the free energy with respect to Ga adatom density, the equilibrium adatom density is [6]

$$\eta_{\mathrm{Ga}} = \nu_{\mathrm{Ga}} e^{-(E_{\mathrm{Ga}} - \mu_{\mathrm{Ga}})/kT}, \tag{1}$$

as long as $\eta_{\mathrm{Ga}} \ll \nu_{\mathrm{Ga}}$. Here μ_{Ga} is the Ga chemical potential and E_{Ga} is the energy of a Ga adatom.

We take the isolated free atoms as our zero of energy, so $E_{\mathrm{Ga}} = -B_{\mathrm{Ga}}$, where B_{Ga} is the binding energy of a free Ga atom to the surface. Also, from equilibrium with

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the crystal,

$$\mu_{\mathrm{Ga}} + \mu_{\mathrm{As}} = -B_{\mathrm{GaAs}}\,, \tag{2}$$

where B_{GaAs} is the cohesive energy of GaAs, per two atoms.

The chemical potential of As is determined by equilibrium with the As vapor, which consists of As_2 molecules. However, for generality, and to facilitate application of these results to different compounds, we consider a vapor of As_m molecules. From the Clausius-Clapeyron equation [7],

$$m\mu_{\mathrm{As}} \approx kT\,\ln(P/P_0) - mB_m\,, \tag{3}$$

where B_m is the cohesive energy per atom of an As_m molecule, P is the pressure, and P_0 is a constant of the As vapor phase.

Combining (2) and (3) gives

$$\mu_{\mathrm{Ga}} = B_m - B_{\mathrm{GaAs}} - kT\,\ln(P/P_0)/m\,, \tag{4}$$

and with (1) this gives

$$\eta_{\mathrm{Ga}} = \nu_{\mathrm{Ga}}(P/P_0)^{-1/m}e^{-E_x/kT}. \tag{5}$$

Here

$$E_x = B_{\mathrm{GaAs}} - B_{\mathrm{Ga}} - B_m \tag{6}$$

is simply the energy needed to create a Ga adatom, while $(P/P_0)^{-1/m}$ reflects the increase in entropy when As goes from the crystal to the vapor.

The Ga adatom density (5) depends exponentially on temperature, in the usual way. However, the activation energy E_x involves properties of the crystal, the adatoms, and the vapor molecule. Equally important, the Ga adatom density depends sensitively on the As pressure, as $P^{-1/m}$. We believe this is why the Ga diffusion length on GaAs increases with decreasing As pressure [5].

Direct measurement of adatom densities is extremely difficult, but recently there has been some progress in this. We introduced a method [8] in which the surface is equilibrated under conditions similar to those of MBE and then quenched. Ga adatoms which are far from any step on the surface condense into monolayer GaAs islands, by reacting with the plentiful free As. Thus the areal density of these islands, measured far from any steps, provides a direct and reasonably accurate measure of the Ga adatom density. To facilitate interpretation, we take care to work only in the range of temperature and pressure where the surface keeps the As-rich $c(2 \times 4)$ reconstruction. Details of our method have been given elsewhere [8].

Before comparing theory and experiment, we must address one technical issue regarding the As vapor. In the actual experiment, the dominant source of As is not the ambient vapor, but rather a flux F_{As} of As_4 directed onto the sample. When As molecules from either the flux or vapor are adsorbed onto the surface, they promptly dissociate into the stable surface species. (This is presumably As_2, but it does not matter here.) Eventually, these either react or desorb into the As_m vapor. This situation is equivalent to equilibrium with an As_m vapor of pressure P_{eff}, where P_{eff} is that pressure which would give the same As desorption rate in equilibrium as actually occurs under the experimental temperature and flux. For a flux F_{As}, with sticking coefficient of unity and negligible ambient pressure, one has

$$P_{\mathrm{eff}} \propto F_{\mathrm{As}}T^{1/2}. \tag{7}$$

Though the real situation is inevitably more complex, the temperature dependence is dominated by the term $e^{-E_x/kT}$; so the details are unimportant, beyond the fact that $P_{\mathrm{eff}} \propto F_{\mathrm{As}}$ for the flux-dominated case.

Figure 1 shows the measured Ga adatom density on GaAs(001) as a function of temperature, for a nominal pressure $P_{\mathrm{nom}} \sim 2 \times 10^{-6}$ Torr. (The nominal pressure, measured as described in [8], is assumed to be proportional to the pressure P_{eff} defined above. We take care to analyze the data in such a way that the unknown constant of proportionality is unimportant.)

From the slope of the linear fit in Fig. 1, $E_x \approx 2.7$ eV. This initially seemed unreasonable. In a one-component model, one would have

$$\eta_{\mathrm{Ga}} = \nu_{\mathrm{Ga}}e^{-E_x/kT}.$$

But with $E_x \approx 2.7$ eV, this would give an adatom density roughly 15 orders of magnitude too small compared to our measurements. The analysis above reconciles the large activation energy with the high adatom density.

Detailed measurements of the pressure dependence would provide a valuable test of our analysis. Unfortunately, the range of accessible pressure is limited; but such data as we have obtained strongly support our interpretation. Figure 2 shows that the Ga adatom density increases with decreasing As pressure. More specifically, since As

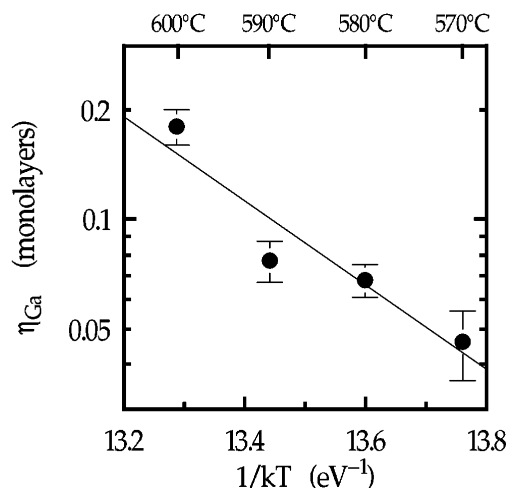

FIG. 1. Ga adatom density η_{Ga} (in monolayers) vs temperature. Data are for nominal As pressure $P_{\mathrm{nom}} \sim 2.2 \times 10^{-6}$ Torr. Solid line is least-squares fit, giving activation energy of 2.7 eV. Error bars represent sample-to-sample variations and do not include any estimate of systematic error.

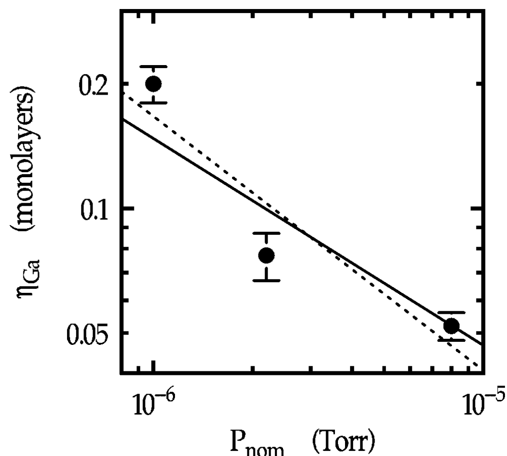

FIG. 2. Ga adatom density η_{Ga} (in monolayers) vs nominal As pressure P_{nom} at 590 °C. Solid line is expected power law $\eta_{Ga} \propto P^{-1/2}$. Dotted line is least-squares fit and has slope -0.6 close to the expected value of -0.5. Error bars are as in Fig. 1.

desorbs as As_2, and this is the equilibrium vapor phase, we expect [from Eq. (5) with $m = 2$] that the Ga adatom density should vary with As pressure as $P^{-1/2}$. Figure 2 shows that the data obey this power law rather well. Figure 2 also includes an unrestricted least-squares fit, which gives an exponent of -0.6, in very satisfactory agreement with our prediction.

We now turn from equilibrium to the important problem of growth. During MBE growth, Ga is deposited on the surface, leading to a supersaturation of Ga adatoms. We assume here that As never plays a rate-limiting role; incorporation of Ga into the crystal is limited by diffusion of Ga across the terraces, or by incorporation at the step edge. Thus it is the magnitude of the Ga supersaturation which determines whether growth occurs near to or far from equilibrium.

At large supersaturation, new monolayer islands nucleate readily, so that the surface is rougher than in equilibrium. Also, the approach to equilibrium by island coarsening or curvature-driven step motion is effectively suppressed. In contrast, for sufficiently small supersaturation the growing surface is indistinguishable in structure from a surface at equilibrium. Which regime prevails depends on a competition between the adatom supersaturation and the energy of the steps which define the island edges. While the step energies are not known, we can see how the supersaturation depends upon the growth rate, temperature, and As pressure.

Consider growth under a flux F of Ga, with Ga adatom diffusion coefficient D, and a characteristic distance L between steps. (In equilibrium, these steps could be due either to the misorientation of a vicinal surface relative to the atomic planes or to thermal fluctuations.) We allow for the possibility of a barrier to adatom diffusion at the step edge, reducing the probability of a diffusional "hop" to the step itself by a factor α. At the step itself, the Ga adatom density has its equilibrium value η_e. (Bear in mind that below, F refers to Ga flux and P to As pressure, unless specifically indicated otherwise.)

Solving the steady-state diffusion equation $F + Dd^2\eta/dx^2 = 0$ with the boundary condition $\nabla\eta = \alpha(\eta - \eta_e)/a - Fa/D$ at the step (where a is the surface lattice constant) gives a maximum adatom density midway between the steps of

$$\eta_m = \eta_e + \frac{FL}{2D}\Big(\frac{a}{\alpha} + \frac{L}{4}\Big). \tag{8}$$

The corresponding supersaturation, i.e., the excess chemical potential relative to the equilibrium density η_e, is

$$\begin{aligned}\Delta\mu &= kT\,\ln(\eta/\eta_e)\\ &= kT\,\ln\Big[1 + \frac{FL}{2D\eta_e}\Big(\frac{a}{\alpha} + \frac{L}{4}\Big)\Big]\\ &\approx kT\,\frac{F}{2D\eta_e}\,L\Big(\frac{a}{\alpha} + \frac{L}{4}\Big),\end{aligned} \tag{9}$$

where the last expression is an expansion for small $\Delta\mu$, valid whenever η_e/F is sufficiently high. (If η_e/F is too small, then the terrace length is not fixed by the surface misorientation or thermal fluctuations, but instead depends on nucleation of new atomic layers. In that case the problem must be treated self-consistently.)

Combining (5) and (9) gives

$$\Delta\mu \approx \nu_{Ga}^{-1}(P/P_0)^{1/m}kTe^{E_x/kT}\,\frac{F}{2D}\,L\Big(\frac{a}{\alpha} + \frac{L}{4}\Big). \tag{10}$$

Thus decreasing As pressure *or* increasing temperature explicitly reduces the Ga supersaturation, leading to near-equilibrium growth. To maintain a constant supersaturation when the temperature is lowered or the Ga flux is increased, the As pressure must be decreased as

$$P_{As} \propto F_{Ga}^{-m}T^{-m}e^{-mE/kT}, \tag{11}$$

where the energy in the exponent is E_x plus the diffusion activation energy (including that implicit in α, when that term is dominant). In terms of As flux rather than pressure (again assuming perfect sticking), this would be $F_{As} \propto F_{Ga}^{-m}T^{-(2m+1)/2}e^{-mE/kT}$. In practice, the distinction between As pressure and flux is unimportant in this context, since the extra factor of $T^{1/2}$ is negligible compared with the exponential dependence on T.

There has been a trend in recent years toward growing GaAs and other III-V semiconductors at progressively lower temperature and lower As pressure. Lower temperature has many advantages, but may lead to poor crystalline quality because of the reduced diffusion. Equation (11) shows how reducing the As pressure can compensate for low temperature, keeping growth close to equilibrium. The implication seems to be that crystal quality is best when growth occurs under near-equilibrium conditions, or at least not too far from equilibrium.

In fact, more than one recent study supports the thesis that technological growth conditions are much closer to equilibrium than had been believed. Theis and Tromp [3] analyzed MBE growth of Si(001) and showed that at reasonable temperatures the critical nucleus for a monolayer island can be quite large. This indicates that the adatom supersaturation is small and that growth occurs very near equilibrium. Kisker *et al.* [9] showed that the critical nucleus for a monolayer island in chemical vapor deposition growth of GaAs at 480 °C is much larger than had been believed, of order 20 atoms or more. Again this indicates near-equilibrium growth.

The crucial difference between GaAs and Si is that, for a compound semiconductor, the adatom density is not determined strictly by temperature. This gives growers the added flexibility of tuning two parameters independently. Thus the near-equilibrium growth regime may be extended to even lower temperatures for GaAs than would be expected from analogy with Si. The only limitation is the As pressure at which our assumptions break down. At sufficiently low As pressure the crystal decomposes into As vapor and metallic Ga [6]. Even before that point, As may become rate limiting. Also, low As pressure can lead to a Ga-rich surface reconstruction that appears to be less favorable for growth. There is some evidence that the best growth occurs at the lowest As pressure for which the As-rich surface reconstruction persists [4].

We now consider the implications of our results for numerical simulations of growth. There is great interest in modeling the growth of compound semiconductors, in order to determine the optimal conditions for growth, and to understand the problems which arise. However, to date such efforts have typically been restricted to simple one-component models. In many ways this is well justified; but our analysis indicates one serious problem.

In a one-component model, the equilibrium adatom density is automatically of the form

$$\eta_{\rm Ga} = \nu_{\rm Ga} e^{-E_x/kT}.$$

In contrast, the actual result (5) has a very large prefactor which depends on $P_{\rm eff}$. Thus a one-component model could not even in principle describe correctly both the adatom density and its dependence on temperature.

To formulate an *effective* one-component model which corrects this problem, the Ga adatom formation energy could be made to depend explicitly on As pressure via the chemical potential of As,

$$E_x \leftarrow E_x + kT \ln(P/P_0)/m .$$

This would not introduce any additional free parameters into the model, since the thermodynamic properties of the vapor (including the value of P_0) are well known [6].

In conclusion, we have shown that the Ga chemical potential and adatom density depend sensitively upon As pressure as well as temperature. Typically, As pressure is kept low enough to give an unexpectedly high Ga adatom density. Thus growth occurs under conditions closer to equilibrium than was believed. We have also shown how one-component models must be modified to be applicable to the growth of compound semiconductors.

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