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Mass-action control of AlGaAs and GaAs growth in molecular beam epitaxy

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GaAs evaporation during molecular beam epitaxy (MBE) is measured using reflection high-energy electron diffraction (RHEED). On the (001) surface there is a first-order phase transition from a 2×4 to 1×1 reconstruction. Upon crossing the phase boundary into the 1×1 structure, layer-by-layer evaporation of GaAs is observed. This evaporation affects the rate of growth of GaAs and $Al_xGa_{1-x}As$ by MBE. The dependence of the growth rate on substrate temperature and on As, Al, and Ga fluxes is followed by measuring RHEED intensity oscillations. The results agree quantitatively with the mass-action analysis of Heckingbottom [R. Heckingbottom, J. Vac. Sci. Technol. B **3**, 572 (1985)]. At substrate temperatures above 850 K no differences between As_2 and As_4 incident fluxes are observed.

An important component process in the high-temperature molecular beam epitaxial (MBE) growth of GaAs and $Al_xGa_{1-x}As$ is the evaporation of gallium. Fischer *et al.*[1] observed a decrease in the net growth rate of GaAs above 900 K which they attributed to Ga evaporation. They also showed that the growth rate at high substrate temperature was affected by the addition of small Al concentrations. Heckingbottom[2] explained the main features of their results with the equilibrium thermodynamic argument but was unable to obtain complete confirmation because of the range of As_4 fluxes used to obtain the data. In the following we report the direct observation of the evaporation of Ga using reflection high-energy electron diffraction (RHEED).[3] Using RHEED intensity oscillations we measure the growth rate of AlGaAs and GaAs versus the growth parameters. Both show quantitative agreement with Heckingbottom's mass-action analysis.

The diffraction and growth apparatus have been described elsewhere.[4] The samples were oriented to within 0.7 mrad of the (001) and showed less than 0.7 mrad of curvature. The thermocouple was held firmly against the back of the sample block and was calibrated at the Al-Si eutectic. Absolute and relative temperatures were determined to within 1°. The Ga and Al fluxes were determined from the RHEED oscillations. The As flux was measured by an ion gauge in the growth chamber but which had been calibrated to give the beam equivalent pressure of a gauge near the sample position. Most of the results were obtained using As_4. Some comparisons were made to As_2, which was prepared by passing As_4 through a hot Mo tube.

On the GaAs (001) surface there is a first-order phase transition[5] between a 1×1 and an antiphase-disordered 2×4 (Ref. 6) surface reconstruction. The phase boundary is shown in the insert of Fig. 1. For the measurements shown in this figure no Ga flux was present. This boundary was determined by measuring the (0 1/4) RHEED beam intensity as a function of substrate temperature and As_4 flux when going from the 2×4 to the 1×1 structure. The enthalpy of transition between the two structures is 4.5 ± 0.2 eV.

Upon crossing this boundary from the 2×4 to the 1×1, either by increasing substrate temperature or by decreasing the As_4 flux, we observe intensity oscillations in the specular RHEED beam. We interpret these oscillations to correspond to the layer-by-layer evaporation of GaAs. The observed oscillations correspond to the cyclic alternation in the diffraction from smooth and rough surfaces. A cycle begins with nucleated evaporation that creates holes somewhere on the long terraces of these well oriented surfaces. Evaporation from the newly created steps and additional nucleated desorption progressively increase and then decrease the roughness until the surface is nearly a perfect plane once again. The change in the diffracted intensity results from destructive interference between scattering from the different surface levels that become exposed. On the (001) surface one period corresponds to the time to remove $a/2$ or 2.83 Å. To check this interpretation we have measured the shape of the diffracted beam[7] as a function of time after the phase boundary is crossed. At an angle of incidence where diffraction from different surface levels is constructive, and hence insensitive to monolayer steps, the diffracted beam remains sharp. At angles of incidence where the scattering from different levels is destructive, a broad component is added to the initially sharp diffracted beam as soon as evaporation begins. This is the signature of surface steps.[8] As the evaporation proceeds the relative contribution of the broad

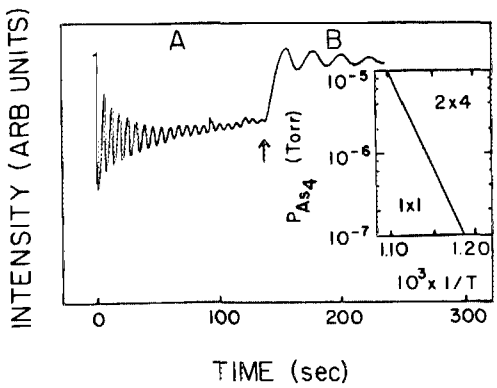

FIG. 1. RHEED intensity oscillations during growth and evaporation. The series of oscillations with period 7.2 s was measured during growth. The Ga flux was then shuttered (arrow), and the oscillations due to evaporation were observed. Along with the intensity oscillations there is a cyclic broadening of the diffracted beams. The insert shows the transition between the 2×4 and 1×1 surface reconstructions.

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and sharp components alternates in importance. Similar intensity oscillations have been observed during epitaxial growth.[9] This new result provides a direct measure of the loss of Ga from a surface at typical MBE growth temperatures.

The period of the evaporation oscillations, which is the time required to desorb a monolayer of GaAs, depends upon the substrate temperature and As_4 flux. An example at $T_{sub} = 938$ K and at an As_4 flux corresponding to 1.4×10^{-6} Torr is shown in Fig. 1. Here a film was grown at a temperature and pressure in the 1×1 region of Fig. 1, where evaporation is important. The specular beam intensity was measured versus time during growth and after the Ga flux was interrupted. One can see two types of intensity oscillations: those with period 7.2 s that correspond to growth and those associated with 25 s per layer evaporation. The arrow indicates the time when the Ga flux was interrupted, at which point there is a short anneal. During this annealing time the residual roughness from the preceding growth decreases while the surface atoms evaporate and diffuse to form predominantly large terraces. Evaporation periods between 1 and 1000 s have been observed. No evaporation oscillations are observed in the 2×4 region even though the period would be measurable. In addition, at very low As fluxes, where the surface structure changes to $C(8 \times 2)$ and Ga is believed to accumulate on the surface, evaporation oscillations are not observed.

The picture that emerges resembles the bulk phase diagram. The 1×1 reconstruction might correspond to the single phase region[10] inside the binary solidus. In this region there are two degrees of freedom so that one partial pressure and the substrate temperature are each independently controllable. In contrast, in the $C(8 \times 2)$ a Ga phase is present and in the 2×4 an As phase is present, both with only one degree of freedom. In these latter regions of the phase diagram, the evaporation rate cannot be controlled by independent variation of substrate temperature and As flux. Note that it is difficult to distinguish kinetic from equilibrium effects and that these additional phases could be surface phases distinct from their bulk counterparts.

Even though not equilibrium, the evaporation rate depends on substrate temperature and As flux according to the mass-action analysis of Heckingbottom.[2] Assuming that all incident As_4 molecules crack at the surface and that the activity is unity, the law of mass action can be written as

$$P_{Ga} P_{As_2}^{1/2} = K_p, \tag{1}$$

where K_p is the equilibrium constant. Since the sticking coefficient of Ga is near unity, we follow the detailed balance argument of Heckingbottom[2] and take P_{Ga} in Eq. (1) to be the evaporation rate in the absence of an incident Ga flux. If there are no significant kinetic barriers to growth, then Eq. (1) should give the temperature and As flux dependence of the period of the measured evaporation oscillations.

The effectiveness of mass-action control of the evaporation rate is shown in Fig. 2. The period of the evaporation oscillations is plotted versus reciprocal temperature for three different As_4 pressures. From the slopes of the straight lines, the enthalpy of formation is 4.6 ± 0.2 eV, in good agreement with the bulk data.[11] Although As_4 molecules were incident

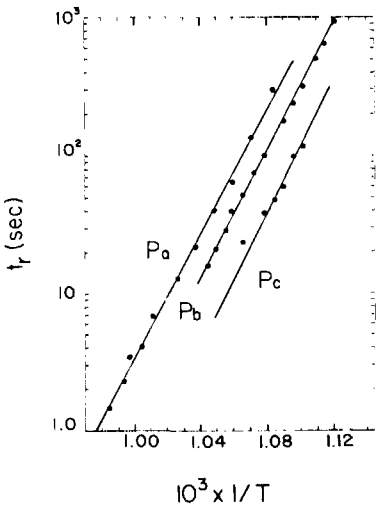

FIG. 2. Dependence of Ga evaporation rate on substrate temperature at several As_4 fluxes. These data agree with $P_{Ga} P_{As_2}^{1/2} = K_p$ using an enthalpy of 4.6 eV. Here $P_a = 8 \times 10^{-6}$ Torr, $P_b = 1.6 \times 10^{-6}$ Torr, and $P_c = 1.6 \times 10^{-7}$ Torr.

in these measurements, no changes in the transition temperatures, oscillation periods, or enthalpies were observed if As_2 was used. At these substrate temperatures there appears to be sufficient cracking at the sample that equilibrium arguments apply even though As_4 rather than As_2 is used in the growth.

Evaporation oscillations have been observed with $Al_xGa_{1-x}As$ films for initial mole fractions of $0 \leqslant x \leqslant 0.7$. In contrast, for pure AlAs no evaporation oscillations are observed even at substrate temperatures as high as 1020 K, suggesting that Al does not desorb. This is also inferred from the time behavior of the oscillations from a film with some initial mole fraction of Al. At a given As flux and sample temperature, the period of the evaporation increases and the amplitude decay quickens as the Al content is increased. We interpret this to mean that the oscillations result only from Ga desorption from the first few monolayers of the film. As Ga leaves, the Al concentration is enriched until a largely AlAs surface prevents further desorption. Kawabe and Matsuura have previously suggested this based upon photoluminescence measurements.[12]

The preferential evaporation of Ga is clearly seen in the net growth rate of the epitaxial film. Figure 3 shows the measured oscillation period during the growth of both GaAs and AlGaAs as a function of substrate temperature. The ordinate is the oscillation period normalized to that at low temperature where evaporation of Ga is not significant. The As_4 flux is held fixed for each. The closed symbols are the measured periods during growth; the curves are a calculation based on the mass-action analysis. For GaAs, the calculated growth rate R is given by $1 - \tau_{Ga}^{inc}/\tau_{Ga}^{evap}$, where the incident Ga flux is measured at low temperature and the evaporating flux is calculated from the equilibrium constant and the measured As_4 pressure via Eq. (1). Because of the uncertainties in As pressure measurement, the curves were fit at one point. The growth rate of $Al_xGa_{1-x}As$ was calculated with the approximation that the activity of GaAs is $1 - x$, so that Eq. (1) becomes

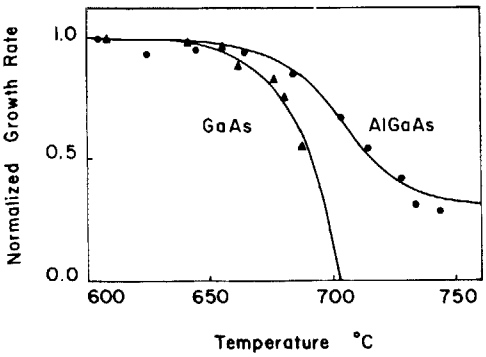

FIG. 3. Normalized growth rate for GaAs and $Al_{0.3}Ga_{0.7}As$ vs temperature. The closed symbols are the measured growth oscillation period normalized to the low-temperature period where evaporation of Ga is not significant. The curves are a calculation based on Eqs. (1) and (2). $P_{As_4} = 1.8 \times 10^{-6}$ Torr and $\tau_{870\,K} = 3.3$ s for the AlGaAs, and $P_{As_4} = 1.2 \times 10^{-6}$ Torr and $\tau_{870\,K} = 4.2$ s for the GaAs.

$$P_{Ga}^{evap} = \frac{K_p(1-x)}{P_{As_2}^{1/2}}. \quad (2)$$

Note that x, the mole fraction of Al, also depends upon the evaporation rate of Ga. The mole fraction is given by τ_{growth}/τ_{Al}, where τ_{growth} is the measured period for the combined Ga and Al fluxes and τ_{Al} is the period for the Al flux only. The important point is that, like the curves of Fig. 2, the net growth rates of GaAs and AlGaAs depend not only upon total column III flux but also upon substrate temperature and As flux. The main temperature dependence is due to the exponential dependence in K_p. As in the previous two figures, no differences between As_2 and As_4 were observed.

In conclusion, we have observed (1) a layer-by-layer evaporation of GaAs and AlGaAs and (2) As flux dependent and substrate temperature dependent net growth rates of GaAs and AlGaAs. Both obey an equilibrium mass-action analysis. Neither depends on whether the source of As is As_2 or As_4. The evaporation is only observed for the 1×1 surface reconstruction.

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[1]R. Fisher, J. Klem, T. J. Drummond, R. E. Thorne, W. Kopp, H. Morkoç, and A. Y. Cho, J. Appl. Phys. **54**, 2508 (1983).
[2]R. Heckingbottom, J. Vac. Sci. Technol. B **3**, 572 (1985).
[3]J. M. Van Hove, P. R. Pukite, G. J. Whaley, A. M. Wowchak, and P. I. Cohen, presented at the 12th Conference on the Physics and Chemistry of Semiconductor Interfaces, Tempe, AZ, January 1985.
[4]J. M. Van Hove, C. S. Lent, P. R. Pukite, and P. I. Cohen, J. Vac. Sci. Technol. B **1**, 741 (1983).
[5]P. R. Pukite, C. S. Lent, and P. I. Cohen, Surf. Sci. (in press).
[6]J. M. Van Hove, P. I. Cohen, and C. S. Lent, J. Vac. Sci. Technol. A **1**, 546 (1983).
[7]P. R. Pukite, C. S. Lent, and P. I. Cohen, Surf. Sci. (in press); J. M. Van Hove, Ph.D. thesis, University of Minnesota, 1985 (unpublished).
[8]C. S. Lent and P. I. Cohen, Surf. Sci. **139**, 121 (1984).
[9]J. M. Van Hove, P. R. Pukite, and P. I. Cohen, J. Vac. Sci. Technol. B **3**, 563 (1985).
[10]D. L. Smith, Prog. Cryst. Growth Charact. **2**, 33 (1979).
[11]C. Pupp, J. J. Murray, and R. F. Pottie, J. Chem. Thermodyn. **6**, 123 (1974).
[12]M. Kawabe and N. Matsuura, Jpn. J. Appl. Phys. **23**, L351 (1984).

Pair-groove-substrate GaAs/AlGaAs multiquantum well lasers by molecular beam epitaxy

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We investigated molecular beam epitaxial growth characteristics on (001) GaAs substrates with a pair of etched grooves along the $\langle 1\bar{1}0 \rangle$ direction. It is found that, as the growth proceeds, the mesa width between the pair of grooves gradually decreases and that the grown mesa surface becomes slightly concave. These results offer great advantages for precisely defining the lateral width of index guided lasers during growth. A pair-groove-substrate GaAs/AlGaAs multiquantum well laser has been newly developed, which shows stable fundamental transverse mode oscillation and a high external differential quantum efficiency of 68% as well as a low threshold current of 23 mA.

Single and multiquantum well (MQW) lasers have been developed by using multilayers grown by molecular beam epitaxy (MBE) and they show low threshold,[1,2] high characteristic temperature.[3] However, there have been few studies concerning the built-in optical waveguide in quantum well lasers.[4–6] One of the convenient techniques for fabricating lateral waveguides is epitaxial growth on preferentially etched substrates. Although several attempts have been re-

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