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Growth of high Bi concentration $GaAs_{1-x}Bi_x$ by molecular beam epitaxy

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The incorporation of Bi is investigated in the molecular beam epitaxy growth of $GaAs_{1-x}Bi_x$. Bi content increases rapidly as the As_2:Ga flux ratio is lowered to 0.5 and then saturates for lower flux ratios. Growth under Ga and Bi rich conditions shows that Bi content increases strongly with decreasing temperature. A model is proposed where Bi from a wetting layer incorporates through attachment to Ga-terminated surface sites. The weak Ga-Bi bond can be broken thermally, ejecting Bi back into the wetting layer. Highly crystalline films with up to 22% Bi were grown at temperatures as low as 200 °C.
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Alloying GaAs with Bi has the potential to allow longer wavelength and higher performance devices to be fabricated on GaAs and InP substrates.[1–3] Bi incorporation in $GaAs_{1-x}Bi_x$ alloys grown by molecular beam epitaxy (MBE) is limited by weak Ga-Bi reactivity[4] and the strong tendency for Bi to surface segregate.[5] This paper shows how to grow $GaAs_{1-x}Bi_x$ with up to 22% Bi, by reducing the growth temperature and As_2:Ga flux ratio. The important physical mechanisms are clarified with a model for Bi incorporation.

Samples were grown in a MBE reactor on semi-insulating GaAs (100) substrates. Ga-type effusion cells were used as sources of Ga and Bi, and a two-zone valved cracker was used for As_2. Substrate temperature was measured using optical bandgap thermometry with an accuracy of ±5 °C. Reflection high energy electron diffraction (RHEED) and elastic light scattering were used to monitor the surface reconstructions and roughness during growth. The beam equivalent pressure (BEP) of the sources was measured with a retractable ion gauge. After thermal desorption of the native oxide and the growth of a ~500 nm thick GaAs buffer layer, a growth interrupt was used to adjust the substrate and source temperatures and measure source BEPs, and then $GaAs_{1-x}Bi_x$ epilayers were grown 15–700 nm thick. *Ex-situ* x-ray diffraction (004) $\omega/2\theta$ scans were performed on all samples to determine composition and (224) reciprocal space maps were carried out on selected samples to check for relaxation. Composition was obtained by dynamical simulation of the (004) scans, assuming Vegard's law and a GaBi lattice constant of 6.33 Å extrapolated from Rutherford backscattering spectrometry measurements.[5]

Fig. 1 shows the dependence of Bi content on As_2:Ga beam equivalent pressure ratio (BEPR) for samples grown at substrate temperatures of 220–230 °C, 265 °C, and 330 °C, with Bi:Ga BEPRs of 0.47, 0.35, and 0.09, respectively. The 330 °C samples were grown at a growth rate of 1.0 μ/h while the other samples were grown at 0.13 μ/h. The three data sets show similar behaviour. Below an As_2:Ga BEPR of ~2.25, the Bi incorporation is saturated, and further lowering of the As_2:Ga ratio does not result in an increase of Bi incorporation. For BEPRs between 2.25 and 3.6, the Bi content decreases strongly with increasing As_2:Ga BEPR. Above an As_2:Ga BEPR of 4.5, no Bi incorporation was detected with x-ray diffraction (<0.1% detection limit). Growths at substrate temperatures of 265 °C and 330 °C with As_2:Ga BEPRs > 4.5 showed no Bi and (1 × 3) RHEED pattern, while the Bi containing samples showed (2 × 3), (2 × 1), or (2 × chevrons) RHEED patterns. Samples grown at 220–230 °C with As_2:Ga BEPRs < 3.6 showed (2 × 1), (1 × 1), and spotty RHEED patterns, while the sample grown with As_2:Ga BEPR above 4.5 showed no observable RHEED pattern. The curves in Fig. 1 are discussed in connection with the growth model below.

A plot of the Bi content as a function of the growth temperature is shown in Fig. 2. Samples were grown with As_2:Ga BEPR in the range 0.81–1.7, below where the Bi

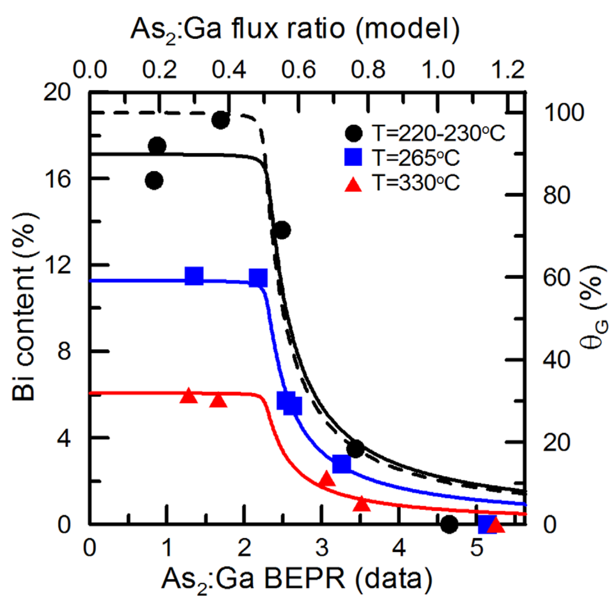

FIG. 1. Bi content as a function of As_2:Ga BEPR. The solid curves are model calculations of Bi content as a function of the flux ratio on the top scale. The broken curve is a plot of θ_G for $P_A = 0.12$ and $P_G = 0.001$ in the absence of Bi.

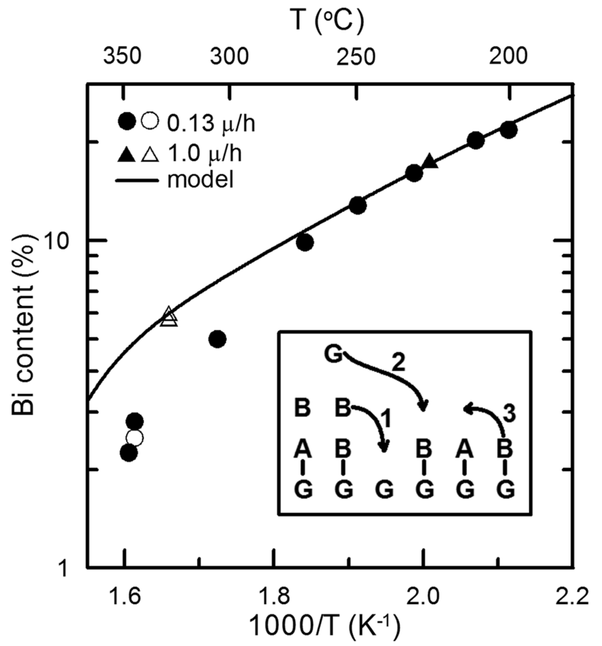

FIG. 2. Temperature dependence of Bi content for samples grown with As_2:Ga flux ratios <0.5. Bi:Ga BEPRs were: 0.59 ± 0.06 for the solid data points, 0.09 for the open triangles, and 6.5 for the open circle. The inset shows the crystal termination and Bi surfactant layers and illustrates: (1) incorporation of Bi on a Ga site, (2) incorporation of Ga on a Bi site, and (3) thermal ejection of incorporated Bi.

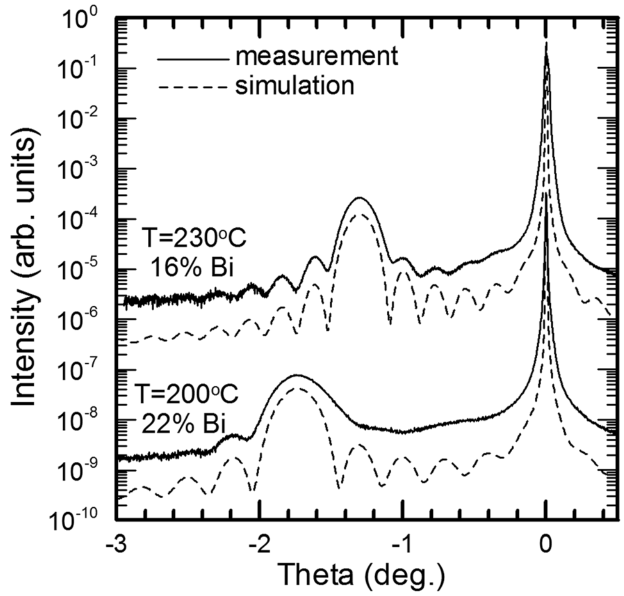

FIG. 3. (004) x-ray diffraction $\omega/2\theta$ scans and dynamical simulations for $GaAs_{1-x}Bi_x$ samples containing 16% and 22% Bi, corresponding to the 200 °C and 230 °C data points from Fig. 2.

incorporation has saturated, as indicated in Fig. 1. Ga fluxes would have resulted in 0.13 and 1.0 μ/h growth rates, had the low As_2:Ga ratio not resulted in Ga droplets. The solid data points were grown with a large Bi:Ga BEPR of 0.59 ± 0.06. These conditions are expected to yield Bi incorporation, which is maximized with respect to As_2:Ga and Bi:Ga BEPR, however, they also guarantee Ga and Bi droplets on the surface. Bi incorporation was found to increase with decreasing temperature, with the lowest growth temperature of 200 °C resulting in 22% Bi. An exponential fit to the data below 270 °C gives an activation energy of 0.25 ± 0.01 eV.

Fig. 3 shows high resolution x-ray diffraction (004) $\omega/2\theta$ scans and dynamical simulations for $GaAs_{1-x}Bi_x$ epilayers containing 16% and 22% Bi. Pendellösung fringes indicate good composition uniformity and abrupt interfaces, despite being grown at 230 °C and 200 °C and at flux conditions resulting in Ga and Bi droplets on the surface. The fringes indicate epilayer thicknesses of 24 and 17 nm, respectively, typical thicknesses for the samples shown in Fig. 2. Reciprocal space mapping of the (224) off-axis peak of a 20 nm thick sample containing 20% Bi (not shown) indicated that the epilayer is fully strained. This film has a 2.4% lattice mismatch with GaAs and greatly exceeds the predicted critical thicknesses of less than 5 nm according to the Matthews-Blakeslee criterion.

A plot of the Bi content as a function of the Bi:Ga BEPR is shown in Fig. 4. The highest Bi:Ga BEPR sample was grown with an As_2:Ga BEPR of 3.3. At low Bi flux, the Bi content is proportional to the Bi:Ga BEPR, consistent with Ptak *et al.*,[7] however, eventually the surface becomes saturated with Bi and then the maximum incorporation is determined by the As_2:Ga BEPR and the growth temperature. It is expected that Bi droplets start to appear as the Bi coverage approaches unity. The relationship between Bi:Ga BEPR and the atom flux ratio was determined from the linear portion of the figure, assuming that at low Bi:Ga ratios the Bi content is equal to the flux ratio. The resulting relationship is 1.5 times less than what was determined by profilometry measurements on a masked Bi metal film. The profilometry yielded the relationship: $F_{Bi}/F_{Ga} = (0.51 \pm 0.05)$ (Bi:Ga BEPR). The value obtained from Fig. 4 is used in the model discussed below.

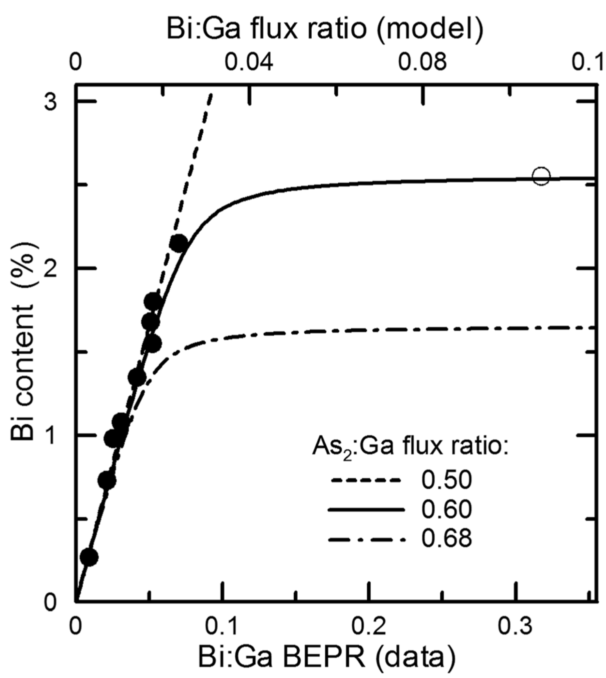

FIG. 4. Bi:Ga BEPR dependence of Bi content for samples grown at 330 °C and 1.0 μ/h with As_2:Ga BEPR between 2.5 and 3.3. The sample corresponding to the open circle has droplets on the surface, while the other samples do not. The curves are model calculations as a function of the Bi:Ga flux ratio indicated at the top.

In the growth model proposed by Lu *et al.*,[6] the dependence of Bi content on the As flux results from As displacing incorporated Bi. The observation that the Bi content is independent of As_2:Ga ratio at low As_2:Ga BEPRs and then decreases much faster than the Ga:As_2 BEPR cannot be explained entirely by incoming As_2 displacing incorporated Bi. In this paper, it is proposed instead that the Bi incorporation depends on the surface Ga:As ratio of the growing film. Eq. (1) is proposed for the rate of Bi incorporation into the crystal at the surface

$$\frac{dx}{dt} \propto \theta_G \theta_B - a_1 x F_G - a_2 x e^{\frac{-U_1}{k_B T}}, \tag{1}$$

where x is the Bi content in the crystal termination layer, θ_G is the fraction of the surface that is Ga-terminated, θ_B is the Bi surfactant coverage, F_G is the Ga flux, and a_1 and a_2 are constants. A Ga-terminated surface site corresponds to an incorporated Ga atom that is not terminated with As or Bi. The Bi surfactant is assumed to exist on top of the crystal termination layer as an additional layer so that $0 \le \theta_B \le 1$. The normalization condition of the termination layer is $\theta_G + \theta_A + x = 1$, where θ_A is the corresponding fraction of the termination layer that is As-terminated. The Bi content of the crystal termination layer (x) is assumed to be equal to that of the bulk.

Eq. (1) has three terms, which are illustrated as processes 1, 2, and 3 in the inset of Fig. 2: 1 is the incorporation of a Bi atom, which acts to increase the Bi content of the growing layer, and is assumed to be proportional to the probability of finding a surfactant Bi on a Ga-site ($\theta_G \theta_B$); 2 is a free Ga atom attaching to an incorporated Bi atom, which reduces the surface Bi content. This process is necessary for the growth of the crystal without creating vacancies; 3 is the thermal ejection of incorporated Bi atoms from the surface back into the surfactant layer. The activation energy, U_1, is the energy difference between an incorporated Bi atom (bonded to Ga) and a surfactant Bi atom. Following Lu, θ_B is assumed to have the form of a Langmuir isotherm, in which the rate of Bi incorporation is subtracted from the incident Bi flux[6,8] as shown in Eq. (2). F_B is the Bi flux and U_0 is the Bi desorption energy, taken to be 1.8 eV.[8] The constant b is equal to $2\pi\sigma_o/\omega_o$, where $\sigma_o = 0.2$ nm^2 is the Bi site area as reported by Young *et al.*[8] and $\omega_o/2\pi$ is assumed to be 10^{12} s^{-1}

$$\theta_B = \frac{b(F_B - xF_G)e^{\frac{U_0}{k_B T}}}{b(F_B - xF_G)e^{\frac{U_0}{k_B T}} + 1}. \tag{2}$$

To obtain an expression for the Ga surface coverage θ_G, a growth model that allows hopping of Ga and As atoms on the GaAs surface is proposed. Analogous solid on solid models have previously been used to calculate surface stoichiometry and other features of GaAs growth using Monte Carlo simulations.[9,10] Incident As_2 molecules are assumed to dissociate into 2 As adatoms which diffuse on the surface. In the absence of Bi, As adatoms will permanently attach if they land on a Ga site, converting the site into an As site. If As lands on an As site, it will either evaporate with probability P_A or hop to a new site with probability $1 - P_A$. Ga adatoms undergo a similar process, sticking when they land on an As site. Ga evaporation is negligible in this temperature range,[11] however, there is a small probability (P_G) on each hop that the Ga atom will be lost to droplet formation. This becomes important at low As_2:Ga ratios, where Ga atoms undergo many hopping events in search of As sites. Assuming these processes are fast compared to the deposition rate (i.e., no interaction between mobile adatoms), the rate of change of the As coverage, θ_A is given by Eq. (3) in the absence of Bi

$$\frac{d\theta_A}{dt} = F_A(1-\theta_A)\sum_{n=0}^{\infty}[\theta_A(1-P_A)]^n - F_G\theta_A\sum_{n=0}^{\infty}[(1-\theta_A)(1-P_G)]^n. \tag{3}$$

In this equation, F_G is the Ga flux and F_A is the As flux, which is twice the As_2 flux. The sums in Eq. (3) are geometric series, which are easy to evaluate.

When Bi is included in the model, As and Ga adatoms can also land on incorporated Bi sites. Interactions with the Bi surfactant layer and free As and Ga atoms are neglected. When an As atom lands on an incorporated Bi site there are two extreme possibilities: the Bi site behaves like an As site, so the As either evaporates or hops to a new site; or the site behaves as a Ga site in which case the Bi is displaced by the As adatom. Whether the Bi site is chosen to behave as an As site or a Ga site has a negligible effect on the surface coverages and the Bi content predicted by the model. It is assumed that from the perspective of an As atom, the Bi site behaves like an As site and that As does not displace Bi. As Bi and Ga tend to react weakly, it is expected that when a Ga atom lands on an incorporated Bi site, the probability that it will attach is $\ll 1$. From the perspective of a Ga atom, the Bi site looks like a Ga site. This assumption is required to reproduce the observation in Fig. 1 that the Bi content saturates at low As_2:Ga flux ratios. With these assumptions, the rate of change of θ_A in the presence of Bi is given by Eq. (4)

$$\frac{d\theta_A}{dt} = F_A(1-\theta_A-x)\sum_{n=0}^{\infty}[(\theta_A+x)(1-P_A)]^n - F_G\theta_A\sum_{n=0}^{\infty}[(1-\theta_A)(1-P_G)]^n. \tag{4}$$

A steady state solution for θ_G is obtained from Eq. (4), noting that $\theta_A + \theta_G + x = 1$. The Ga coverage θ_G is plotted as a function of As_2:Ga flux ratio as a dashed line in Fig. 1 without Bi, where P_A and P_G were chosen to be 0.12 and 0.001, respectively. A larger value for P_A would result in θ_G decreasing more slowly above the As_2:Ga flux ratio of 0.5. Choosing P_G to be very small, results in $\theta_G \approx 1$ for As_2:Ga ratios less than 0.5.

The rates of Bi incorporation and thermal ejection (terms 1 and 3 in Eq. (1)) are assumed to be large compared to the rate of Ga attaching to incorporated Bi. Based on this assumption, the second term in Eq. (1) is neglected. With θ_G and the above relation for θ_B (Eq. (2)), a steady state solution for the Bi content (x) is obtained from Eq. (1). The curves in Figs. 1, 2, and 4 were obtained by setting $P_A = 0.12$, $P_G = 0.001$, $U_1 = 0.28$ eV, and $a_2 = 3300$. P_A is determined by the ratio of the As evaporation and hopping rates, which increases with increasing temperature, however, a temperature independent value is adequate to fit the data in this study.

The Bi content plotted as a function of As_2:Ga BEPR and the model plotted as a function of As_2:Ga flux ratio in Fig. 1 agree well if an As_2:Ga flux ratio of 0.5 is equal to a BEPR of ~2.25. This is in reasonable agreement with a corresponding BEPR of 1.7 calculated from Preobrazhenskii *et al.*[12] A larger value ($2.25 > 1.7$) could mean that the sticking coefficient for As_2 is less than 1, which would shift the data to higher BEPR. The lack of Bi incorporation at the highest As_2:Ga ratios in Fig. 1 could be associated with the reconstruction changing to (1×3),[13] suggesting Bi does not incorporate with the (1×3) reconstruction. The Bi fluxes from the data and used to draw the model curves in Fig. 1 were high enough to maintain Bi-saturated surfaces ($\theta_B \approx 1$) for samples grown at 220–230 °C and 265 °C. Thus, the Bi incorporation is saturated with respect to the Bi flux in these conditions, and so the Bi content is primarily dependent on the growth temperature and the As_2:Ga ratio. For the lowest two As_2:Ga ratio samples grown at 330 °C, the Bi flux was only adequate to produce $\theta_B \approx 1$ after accounting for the fact that at such a low As_2:Ga ratio approximately half the Ga flux is lost to droplet formation, thus, increasing the effective Bi:Ga flux ratio. The 330 °C model curve was drawn assuming a Bi saturated surface ($\theta_B = 1$).

The U_1 and a_2 values of 0.28 eV and 3300 were obtained by fitting to data at temperatures below 270 °C in Fig. 2. The small value of U_1 indicates incorporated Bi atoms are weakly bound. The fall-off in the model curve for $T > 350$ °C is due to the onset of Bi evaporation, and consequent loss of Bi surface saturation. Increasing the Bi flux 11 times (open circle) at 350 °C did not increase the Bi content, showing that the surface is saturated with Bi at the lower Bi flux in the experimental data.

The model curves in Fig. 4 show the Bi incorporation increases linearly with Bi:Ga BEPR until the surface saturates with Bi. The data shown in Figs. 1 and 2 were all grown with surfaces saturated with Bi, indicating that the Bi content is dependent on the As_2:Ga ratio and the growth temperature when the surface is saturated with Bi.

The proposed model indicates Bi incorporation is highly sensitive to the stoichiometry of the crystal surface during growth, explaining why careful control of the As_2:Ga flux ratio is required. Low temperature is required as the weakly bound incorporated Bi atoms can be thermally ejected back into the Bi surfactant layer.

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