Effect of molecular beam epitaxy growth conditions on the Bi content of $GaAs_{1-x}Bi_x$

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We describe how the Bi content of $GaAs_{1-x}Bi_x$ epilayers grown on GaAs can be controlled by the growth conditions in molecular beam epitaxy. Nonstandard growth conditions are required because of the strong tendency for Bi to surface segregate under usual growth conditions for GaAs. A maximum Bi content of 10% is achieved at low substrate temperature and low arsenic pressure, as inferred from x-ray diffraction measurements. A model for bismuth incorporation is proposed that fits a large body of experimental data on Bi content for a wide range of growth conditions. Low growth rates are found to facilitate the growth of bismide alloys with a low density of Bi droplets.
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The bismide alloy, $GaAs_{1-x}Bi_x$, has a number of interesting properties that make it potentially useful for devices. For example, bismuth incorporation produces a much larger reduction in the band gap of GaAs than In or Sb alloying, for the same increase in lattice constant.[1] Also, Bi is the heaviest nonradioactive element, therefore, it has a large spin orbit splitting, which is useful for spin-based semiconductor devices. Applications of this new alloy have been held back by practical difficulties in growing films with high Bi content, due to the strong tendency for Bi to surface segregate and form droplets on the surface under conventional GaAs growth conditions. The highest Bi content reported to date in $GaAs_{1-x}Bi_x$ is 8%.[2,3] In this paper, we explore the influence of the growth conditions on the Bi content in molecular beam epitaxy (MBE) growth of $GaAs_{1-x}Bi_x$, with the goal of identifying conditions for making films with large Bi concentrations. In particular, we show how the Bi concentration depends on the Bi and As fluxes and the substrate temperature.

The $GaAs_{1-x}Bi_x$ samples were grown on undoped GaAs (100) substrates in a solid source MBE system, equipped with effusion cells for Ga and Bi, and a two-zone valved cracker source of As_2. The substrate temperature is monitored during growth by optical band gap thermometry.[4] The Ga flux was measured with a retractable ion gauge, and calibrated from the film thickness measured after growth using x-ray diffraction. The As flux was obtained from the flux gauge reading and the calibrated Ga flux using literature values for the relative ionization efficiency of Ga and As.[5] The Bi flux was calibrated by depositing a Bi film on an unheated wafer and estimating the total amount of deposited Bi from the volume of the Bi islands observed in atomic force microscope (AFM) images. The Bi flux is believed to be a combination of monomers and dimers.[6] With *in situ* diffuse light scattering, we were able to detect the formation of metallic droplets on the surface during growth.

Earlier experiments showed that the Bi incorporation is substitutional.[7] In this case, x-ray diffraction measurements of the lattice constant can be used to determine the Bi content of the $GaAs_{1-x}Bi_x$ epilayers. The Bi content and epilayer thicknesses were determined by fitting high resolution [004] θ-2θ scans using RADS MERCURY software from Bede Scientific. The surface morphology was measured by AFM.

Figure 1 shows θ-2θ x-ray diffraction scans with Cu $K\alpha$ radiation for three $GaAs_{1-x}Bi_x$ epilayers with Bi content x=1.4%, 5%, and 10%. The weak x-ray interference fringes observed in the x-ray scans compared with the simulations are believed to be due to non-uniformity in the Bi content in the growth direction as reported earlier.[7] One source of non-uniformity in composition in the growth direction is the delay associated with the buildup of a Bi surface layer after the Bi shutter is opened. Under steady state growth, the surface is typically saturated with Bi. A typical AFM image of a $GaAs_{1-x}Bi_x$ epilayer is shown in Fig. 2. This sample is 30 nm thick with a Bi concentration of 3.6%. The rms surface roughness is 0.76 nm, with surface features elongated in the

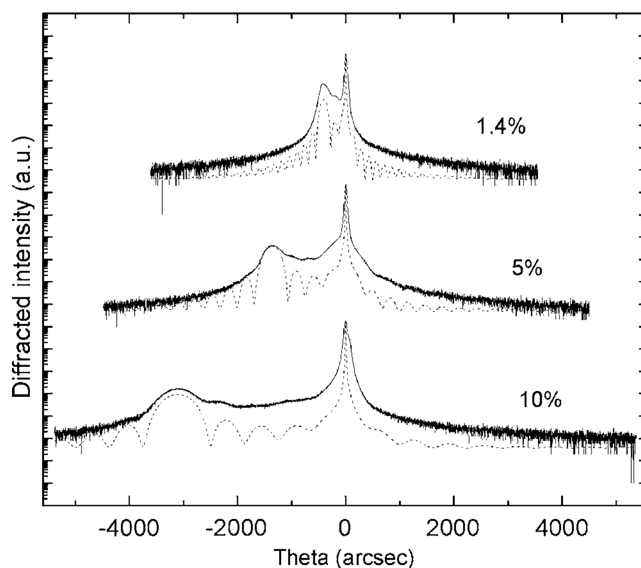

FIG. 1. High resolution x-ray [004] θ-2θ scans for $GaAs_{1-x}Bi_x$ epilayers with Bi content of 1.4%, 5%, and 10%. The corresponding sample thicknesses are 152, 56, and 30 nm, respectively. All samples show weak interference fringes.

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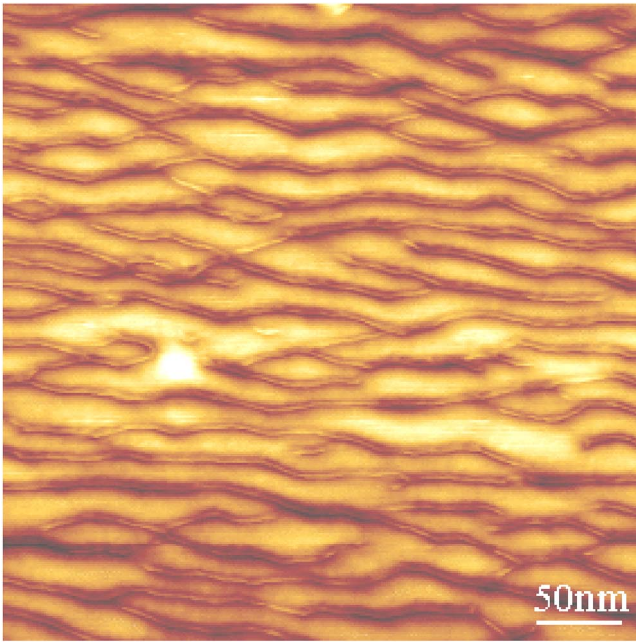

FIG. 2. (Color online) Typical AFM image of $GaAs_{1-x}Bi_x$ epilayer with Bi content of 3.6%. The sample is 30 nm thick. Image shows a 500×500 nm^2 scan. The rms roughness is 0.76 nm, with surface features elongated in the $[01\bar{1}]$ direction.

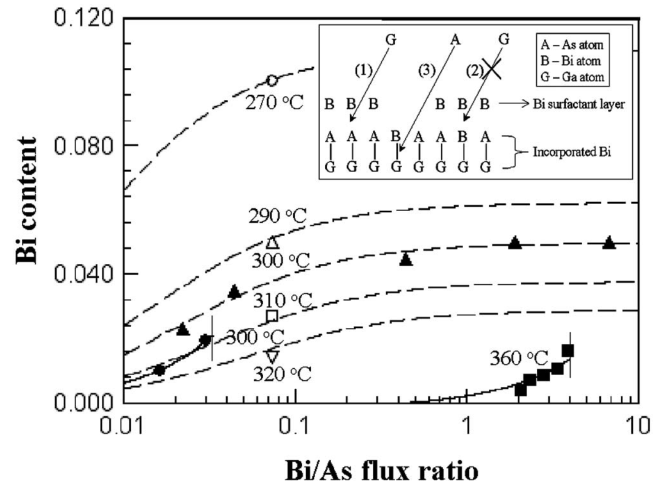

FIG. 3. The dependence of Bi content on growth conditions plotted as a function of the Bi/As flux ratio. The symbols represent the experimental data and the lines are fits based on the proposed model. The solid circles (with Bi flux of 0.05 $nm^{-2}\,s^{-2}$) and solid squares (with Bi flux of 15 $nm^{-2}\,s^{-1}$) correspond to two groups of samples grown at the same temperatures and Bi fluxes, but with varying As fluxes. The samples represented by the open symbols (with As flux of 2.2 $nm^{-2}\,s^{-1}$ and Bi flux of 0.16 $nm^{-2}\,s^{-1}$) and solid triangles (with As flux of 2.2 $nm^{-2}\,s^{-1}$) are all grown at the same As fluxes, but at different temperatures and Bi fluxes. The two solid lines cut off when the As/Ga flux ratio reaches unity. Further reduction in As flux will cause Ga droplets to form.

$[01\bar{1}]$ direction. Although this sample had a mirrorlike appearance to the eye, it also showed 0.3 μm diameter Bi droplets with the density of 1.5×10^7 cm^{-2}.

Figure 3 shows the Bi content of a number of films made under different growth conditions plotted as a function of the Bi/As flux ratio. The symbols represent the experimental data and the lines are fits to the model discussed below. The solid circles and squares correspond to two groups of samples grown at the same temperatures and Bi fluxes, but with varying As fluxes. These results show that the Bi concentration increases as the As flux decreases. The two groups of samples represented by the open symbols and solid triangles are all grown at the same As fluxes, but at different temperatures and Bi fluxes. The Bi content increases with decreasing temperature (open symbols), and increasing Bi flux (solid triangles). At large Bi fluxes, the concentration of Bi in the film saturates and Bi droplets eventually form on the surface during growth.

We have developed a model which provides a quantitative description of how the Bi content depends on the growth conditions. The model is intended to fit the data as a guide to future experiments and is based on the following simplified picture of the surface composition and structure during growth. Due to the strong tendency for Bi to surface segregate and the relatively low Bi vapor pressure at the growth temperatures of interest, a metallic Bi surface adlayer accumulates on the surface during growth. This is the primary source of Bi atoms for incorporation into the GaAs during film growth. The metallic Bi layer has a surface coverage equal to θ_{Bi} and lies on top of the $GaAs_{1-x}Bi_x$ film. Arsenic has a much higher vapor pressure than Bi and does not accumulate on the surface except insofar as it bonds to Ga. Since the As flux exceeds the Ga flux we expect that the film will be primarily As terminated under the Bi adatom layer.

Three processes can be identified that affect the Bi incorporation. These processes are schematically illustrated in the inset of Fig. 3. In the first process, a Ga atom may insert between the As-terminated surface of the film and a metallic Bi atom from the adatom layer, forming an As–Ga–Bi bond. Bismuth incorporation into the film is associated with the formation of Ga–Bi bonds. The rate of this process will be proportional to $\theta_{Bi}F_{Ga}(1-x)$, where F_{Ga} is the Ga flux. The factor $(1-x)$ means that we are excluding the second process in which a Ga atom inserts between a Bi atom bonded to the surface and a Bi atom in the surface adatom layer. A rationale for this assumption is that the large size of the Bi atoms does not favor the formation of next-neighbor Bi bonds of the form Bi–Ga–Bi. The third process involves the insertion of an As atom into a Ga–Bi bond, thereby displacing a Bi atom bonded to Ga, back into the surface wetting layer. Since a Ga–Bi bond is broken in this process, we assume that it is thermally activated with a rate proportional to $F_{As}e^{-U_1/kT}x$. Putting these processes together we obtain the following rate equation:

$$\frac{dx}{dt} \propto \theta_{Bi}F_{Ga}(1-x) - aF_{As}e^{-U_1/kT}x. \quad (1)$$

The constant a is a dimensionless fitting parameter that takes into account the relative cross sections for the Ga and As insertion reactions. In steady state, we have $dx/dt=0$. In this case the rate equation can be solved for x,

$$x = \frac{\theta_{Bi}e^{U_1/kT}F_{Ga}}{aF_{As} + \theta_{Bi}e^{U_1/kT}F_{Ga}}. \quad (2)$$

The Bi surface coverage θ_{Bi} is needed before we can evaluate Eq. (2). The surface coverage has been measured on GaAs as a function of temperature and flux and found to obey a Langmuir isotherm with a surface binding energy of $U_0=1.8\pm 0.4$ eV.[8] Although the earlier studies were carried out at higher fluxes and higher temperatures (450–600 °C) than the present experiments, we expect the surface coverage

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to be described by a similar Langmuir model in our case. An important difference is that, in the present case, the surface of interest is on a growing film, which absorbs some of the Bi from the surface layer as it grows. Therefore, it is reasonable to replace the Bi flux (or pressure) in the expression for the Langmuir isotherm with the net flux, in which the incorporated Bi has been subtracted as follows:

$$\theta_{Bi} = \frac{b(F_{Bi} - xF_{Ga})e^{U_0/kT}}{1 + b(F_{Bi} - xF_{Ga})e^{U_0/kT}}. \tag{3}$$

When substituted into Eq. (2), this equilibrium expression for the surface coverage gives the correct low temperature limit for the Bi concentration, namely $x = F_{Bi}/F_{Ga}$, when all the incident Bi atoms incorporate into the film.

Equation (2) provides a good description for the concentration of incorporated Bi as a function of the growth conditions, as shown in Fig. 3. In this figure, the various solid and broken lines are computed from the model in Eq. (2), with $b = 8.5 \times 10^{-11}$ nm s, $a = 2.5 \times 10^8$, $U_0 = 1.3$ eV, and $U_1 = 0.8$ eV. The surface binding energy (1.3 eV) is similar to the value reported earlier $(1.8 \pm 0.4$ eV) if the experimental uncertainties are taken into account. The solid lines in Fig. 3 show that the Bi content increases with decreasing As flux, when the Bi flux and the substrate temperature are held constant, in agreement with the model. The broken lines show the dependence on Bi pressure and substrate temperature, with the As flux held constant. In particular, the broken line at 300 °C shows that the Bi content saturates at high Bi flux in the model, when other growth parameters are kept fixed, in agreement with the measurements.

In Eqs. (2) and (3), the Ga flux, which is proportional to the growth rate, enters only as a ratio with the Bi and As fluxes. This means that if all three fluxes are scaled by the same parameter, the Bi content will remain the same. One could conclude that the growth rate is not a critical factor in Bi incorporation. However, it turns out that the growth rate is important in controlling the formation of Bi droplets. Bi atoms incident on the sample surface can do one of three things: incorporate into the film, evaporate back into the vapor or attach to a Bi droplet on the surface. In order to prevent formation of Bi droplets, the flux of deposited Bi atoms must be less than the sum of the rates of evaporation and incorporation or

$$0 < F_{Bi} - xF_{Ga} < E_{Bi}. \tag{4}$$

The evaporation rate θ_{Bi} is controlled by the substrate temperature and the Bi surface coverage θ_{Bi} which is typically close to one, in the growth of high Bi concentration films. If the inequality in Eq. (4) is violated, that is if the Bi flux exceeds the incorporation rate by more than the rate of Bi evaporation, then droplets will form. As the data in Fig. 3 show, in order to achieve a high Bi content, a low growth temperature is required. At low temperatures, the Bi evaporation rate will also be low. This means that, for low temperature growths, the Bi flux must be rather precisely controlled to match the incorporation rate, as the excess Bi has a low evaporation rate. The ratio of the Bi evaporation rate to the Bi incorporation rate can be viewed as a measure of the process latitude. The process latitude can be maximized by slowly growing, so that any excess Bi has a chance to evaporate. In this case, the Bi flux does not have to be as accurately matched to the incorporation rate. By reducing the growth rate to 0.07 μm/h, we have been able to grow mirrorlike films with Bi concentrations as high as 10%, and a reduced density of Bi droplets $(1.7 \times 10^6$ cm^{-2}).

In conclusion, we have explored the effect of the growth conditions on the Bi concentration in $GaAs_{1-x}Bi_x$ grown by MBE. A model has been developed that describes the measured Bi content as a function of the Bi and As fluxes and the substrate temperature. We find that low growth rates facilitate the growth of films with high Bi concentrations and low Bi droplet density.

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