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Kinetically limited growth of GaAsBi by molecular-beam epitaxy

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ABSTRACT

The growth of GaAsBi alloys is plagued by the appearance of Bi droplets due to excess Bi that accumulates during growth. Here we present an alternate growth regime that kinetically limits the amount of Bi on the surface, eliminating Bi droplets for a wide range of Bi compositions, while yielding atomically smooth surfaces. Growth rate plays a major role in the amount of Bi that accumulates on the surface, with high growth rates and low Bi fluxes leading to less surface Bi. A balance can be achieved between low Bi coverage, the resultant rough surfaces, and the excessive Bi coverage that leads to Bi droplets. Bi incorporation in this growth regime is linear with Bi flux and scales inversely with growth rate. Unlike previous studies, there is no sign of saturating Bi incorporation with increasing Bi flux, allowing for intuitive prediction and control of Bi content in this regime.

1. Introduction

GaAsBi has many possible technical applications, including solar cells [1], lasers [2], transistors [3] and spintronic devices [4], due to the unusual properties of this highly mismatched alloy. Unfortunately, growth of GaAsBi alloys by molecular-beam epitaxy (MBE) requires non-standard growth conditions compared to other III–V alloys. Bi only incorporates into GaAs at low growth temperatures and near-stoichiometric V/III ratios [5]. This indicates that either As atoms outcompete Bi atoms for incorporation sites or that Bi simply prefers, for energetic reasons, to be on the surface rather than in the bulk. Segregated Bi is a very effective surfactant, leading to much smoother surfaces at these unusually low growth temperatures and As fluxes than comparably grown GaAs without a Bi surfactant [6–9]. However, substantial unincorporated Bi on the surface leads to the formation of Bi droplets and an apparent limit to the maximum concentration of Bi that can be incorporated for a given set of growth conditions [9,10]. Balancing the amount of Bi on the surface ensures smooth layers while avoiding Bi droplets, but this balance has been difficult to achieve. In this paper, we describe a growth regime characterized by a kinetic limitation on the amount of Bi that accumulates on the surface. This regime, in contrast to previously published data [9], results in much less surface Bi, intuitive incorporation behavior in terms of fluxes and growth rates, and most importantly, a growth rate dependent Bi concentration window covering a large range of alloy compositions with extremely smooth surfaces and no Bi droplets.

2. Experimental procedures

GaAsBi samples were grown on undoped (100) GaAs substrates by solid-source MBE in an EPI930 growth chamber with a base pressure $\sim 1 \times 10^{-10}$ mbar. Conventional effusion cells supplied Ga and Bi fluxes and a cracker cell converted As_4 to As_2. Fluxes measured by the beam flux monitor were calibrated in the same way as previous reports by taking the mass, temperature, and ion gage sensitivity factor into account for each material [9,11,12]. The As/Ga flux ratio was maintained at 1.4. The growth rate is directly proportional to the Ga flux, as expected, so any change in growth rate requires a corresponding change in the As flux to maintain a constant As/Ga ratio. Substrate temperature was monitored using a k-Space Associates BandiT band-edge thermometry system and samples reported here were grown at 315 ± 5 °C. The Bi content [Bi] was calculated from either symmetric or asymmetric x-ray diffraction (XRD) scans using a Bede D1 high-resolution system and assuming a GaBi lattice constant of 6.33 Å [5]. Growth rates ranged from 0.16–2.0 μm/h as determined from growth times and dynamical thickness modeling of interference fringes in (004) XRD scans. Sample thicknesses were between 100 and 300 nm. We find that for a growth temperature of ~315 °C, relaxation of 100 nm thick films occurs above [Bi]~7%, but does not appear to play a role in any of the effects

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described below. Surface roughness was determined from the tapping mode atomic-force microscope (AFM) measurements.

3. Results and discussion

Fig. 1 shows [Bi] as a function of Bi flux for a number of GaAsBi samples grown at different rates. The trends are linear, with no signs of saturation. Similar data exist for 2.0 μm/h, the highest growth rate used in this study, but these data are omitted to facilitate the comparison of different fluxes and growth rates. Examination of Fig. 1 shows that changes in [Bi] are easily predictable for changes in both Bi flux and growth rate. This behavior is much like that of a unity-sticking-coefficient dopant, such as Si in GaAs. That is, doubling the Bi flux results in a doubling of [Bi], while doubling the growth rate halves [Bi]. The lack of any apparent saturation of [Bi] with increasing Bi flux in the data presented here is in contrast to a previously published growth model for Bi incorporation in GaAs that did show [Bi] saturation as the Bi/As flux ratio increased [9].

This growth model by Lu et al. [9] proposed two contributions to the Bi content in $GaAs_{1-x}Bi_x$: a term proportional to the Ga flux that leads to Bi incorporation, and a Ga–Bi bond-breaking term that causes Bi to be removed from the near-surface bulk and forced to the surface by an As atom:

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

where θ_{Bi} is the Bi surface coverage [8], F_{Ga} and F_{As} are the Ga and As fluxes, respectively, and a and U_1 are fitting parameters. Fig. 2 shows [Bi] for the set of GaAsBi epilayers from Fig. 1, plotted as a function of the Bi/As flux ratio, with the addition of the 2.0-μm/h data. The linear incorporation trend is again visible with increasing Bi flux, this time up to [Bi]~12%, and [Bi] shows no signs of saturation. These data clearly do not follow the Lu model, reproduced in Fig. 2 for reference [9]. It is, however, possible to fit the experimental data in Fig. 2 using the Lu model by either increasing the value of U_1, which is the activation energy for breaking a Ga–Bi bond and replacing it with a Ga–As bond, or decreasing the model growth temperature. Both of these have the effect of making Bi segregation negligible and freezing in the Bi. Altering the model temperature, but not changing U_1, requires an unrealistically low growth temperature ≤ 225 °C to fit the data. Comparing growth temperatures between laboratories is very difficult, but we note that temperatures in this paper are measured in the same way as those of Lu et al. (band-edge thermometry). Increasing U_1, which was a fit parameter in the Lu model, produces the same results. Instead of changing U_1, however, it is likely that the addition of another thermally activated process to the Lu model is necessary to fit our fundamentally different data, but that is not attempted here. Either way, the composition data are only successfully fit by assuming that the Bi atoms that reach the surface are all, or mostly all, incorporated into the layer as opposed to remaining on the surface.

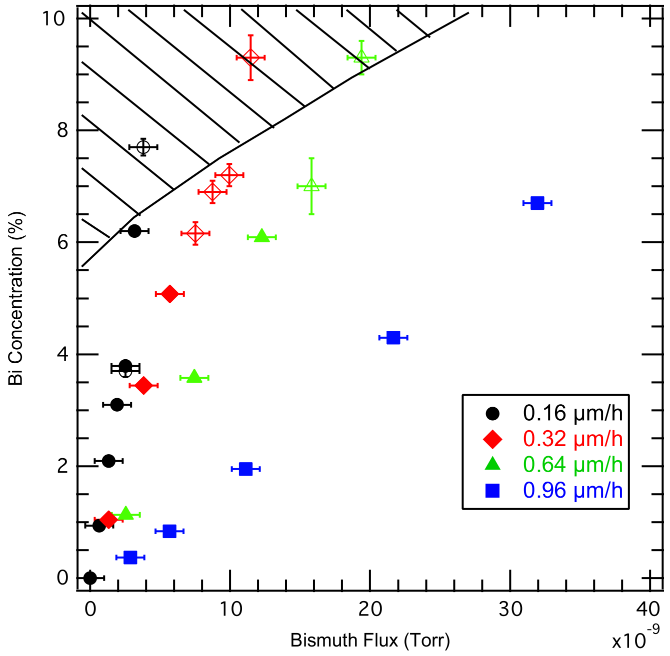

Fig. 1. [Bi] vs. Bi pressure for GaAsBi samples grown at 315 °C with growth rates from 0.16–0.96 μm/h. For the Bi pressure, the beam-equivalent pressure was corrected by taking the effusion cell temperature, Bi mass and ion gage sensitivity factor into account. Compositions are determined by symmetric (004) XRD scans (solid symbols) and asymmetric XRD scans or reciprocal space maps (open symbols). The hashed region denotes the approximate parameter space where Bi droplets are observed.

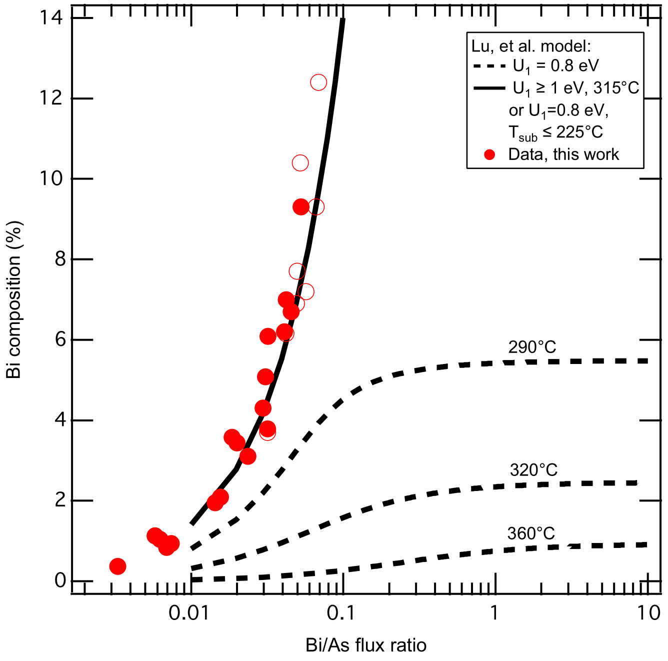

Fig. 2. [Bi] vs. Bi/As flux ratio for GaAsBi samples grown at 315 °C with growth rates from 0.16–2.0 μm/h. Compositions are determined as in Fig. 1. Dashed lines are generated from the model of Lu *et al.* [9] The solid line is a fit to the data using the same model with the parameters listed in the legend.

The boundary between the hashed and unhashed areas in the upper left part of Fig. 1 shows the approximate parameter space where Bi droplets begin to form for these samples. The shape of the droplet region in Fig. 1 is based on the droplet density, as determined by optical microscopy, for the various samples. For example, the [Bi]~9% sample at 0.64 μm/h has an extremely low droplet density ($<10^5$ cm^{-2}), whereas the same composition sample at 0.32 μm/h is completely covered with droplets ($\sim 4\times10^6$ cm^{-2}). Similar droplet counts were carried out for each sample to estimate the shape of the hashed region in Fig. 1. There is no sign at all of Bi droplets on samples outside the hashed region of Fig. 1. The samples in the Lu study were reported to be saturated with Bi and have Bi droplet densities $>10^7$ cm^{-2} for all alloy compositions [9]. There is a clear difference between material shown here and that of Lu et al. in terms of surface Bi coverage. The droplet area is dependent on both Bi flux and growth rate. Higher growth rates delay the onset of Bi droplets for a given [Bi]. We note that the growth rate used