



Bismuth surfactant growth of the dilute nitride $\text{GaN}_x\text{As}_{1-x}$

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Abstract

The presence of a bismuth surfactant is found to increase the nitrogen incorporation in the dilute nitride $\text{GaN}_x\text{As}_{1-x}$ by as much as 60% during growth by molecular beam epitaxy. Films with nitrogen concentrations in the 0.4–0.95% range were grown using an RF plasma source for nitrogen. The Bi surface coverage is inferred from reflection high-energy electron diffraction as a function of Bi flux and substrate temperature, and the nitrogen content is obtained by high-resolution X-ray diffraction. At constant substrate temperature the nitrogen content is found to increase with Bi coverage, which has the form of a Langmuir isotherm when plotted as a function of Bi flux.

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Recently it has been shown that the presence of a bismuth or antimony surfactant during molecular beam epitaxy (MBE) growth of dilute nitride semiconductors such as $\text{GaN}_x\text{As}_{1-x}$ dramatically reduces surface roughness, improves photoluminescence efficiency and increases the nitrogen incorporation efficiency [1–3]. In the case of III–V

semiconductor growth, large atoms such as In, Sb or Bi have a tendency to surface segregate and act as surfactants that modify surface phenomena during growth such as surface mobility. Although In and Sb incorporate to some extent into GaAs, under typical MBE growth temperatures and As overpressures, Bi does not incorporate even at the ppm level [1]. Being isoelectronic with As, even if trace amounts of Bi do incorporate into GaAs or other III–V semiconductor, substitutional Bi on a group V site is not expected to produce an

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electronically active defect. However, a surface layer of Bi could in principle have a profound effect on the processes which occur at the surface during epitaxial growth, as the interface energy between the Bi surfactant and the semiconductor surface is likely to be significantly lower than the energy of the semiconductor–vacuum interface. These ideas and the experimental results to date suggest that Bi surfactant growth is a promising new tool for extending the range of compositions and growth conditions that can be used to produce high-quality epitaxial semiconductor layers. In this letter, we describe the results of reflection high-energy electron diffraction (RHEED) measurements of Bi coverage on GaAs as a function of substrate temperature and Bi flux and show that the nitrogen incorporation during GaAsN growth increases linearly with Bi coverage with a maximum increase in nitrogen incorporation of approximately 60% when the surface is covered with a monolayer of Bi.

GaN_xAs_{1-x} films were grown on (001) GaAs substrates by MBE with a low-pressure rf plasma source for activated nitrogen. Standard solid source effusion cells were used for Ga and Bi and a two-zone cracker source for As₂. The growth chamber was equipped with a mass spectrometer with line of sight access to the substrate. The plasma source consisted of a helical resonator which could be cycled on and off without changing the flow of the high purity nitrogen. The substrates were cleaned by thermal desorption of the oxide at 615 °C, and then a GaAs buffer layer typically 200–300 nm thick was grown at 580 °C. The substrate temperature was then reduced to 400–460 °C for growth of the GaN_xAs_{1-x} layers. Substrate temperature was measured in-situ by bandgap thermometry. The group V/III ratio for each growth was maintained between 5 and 10, with growth rates between 10 and 12 nm/min as determined by RHEED with a high sensitivity CCD camera video recording system. The beam equivalent pressure of Bi was measured with a retractable ion gauge and varied from 10⁻⁸ to 10⁻⁵ Torr depending on the experiment. We expect a beam of approximately 50% Bi monomers and 50% Bi₂ dimers from the effusion cell at typical operating temperatures [4]. Nitrogen concentra-

tions in the grown films were determined by dynamical simulation of high-resolution X-ray diffraction measurements.

Bismuth surface coverage as a function of substrate temperature and Bi flux was inferred from RHEED during Bi adsorption and desorption experiments under constant As overpressure. The Bi flux caused a reconstruction change from the typical (4 × 2) pattern observed for GaAs at temperatures below 500 °C to a (3 × 1) reconstruction, consistent with a previous study [5]. This reconstruction change was accompanied by an increase in the RHEED specular beam intensity, which we assume to be proportional to the Bi surface coverage. At high Bi flux the specular beam intensity saturated, which we further assume to correspond to a Bi surface coverage of one monolayer. Under the growth conditions used in the present experiments, we saw no evidence for the formation of metallic Bi droplets on the surface.

Fig. 1a shows the specular RHEED intensity as a function of time for different substrate temperatures with the Bi shutter kept open for 30 s and then closed, while maintaining a fixed Bi flux of 1.4 × 10⁻⁵ Torr, beam equivalent pressure. The exponential decay in the intensity when the shutter is closed is interpreted as due to thermal evaporation of the Bi from the surface. The decay rate of the RHEED intensity following the closure of the Bi shutter is plotted as a function of 1/T in the inset and has an activation energy of 1.34 eV. Fig. 1b is a plot of the specular RHEED intensity taken from data similar to Fig. 1a with the Bi shutter open, as a function of substrate temperature. The specular beam intensity decreases rapidly with substrate temperature above 500 °C, which we interpret as being due to a decrease in Bi coverage at high temperatures. Fig. 2 shows the specular beam intensity with the substrate temperature held constant at 460 °C, while the Bi flux is decreased by ramping the temperature of the Bi cell down linearly from 700 to 450 °C. In this case, there is a significant decrease in RHEED intensity for Bi fluxes below 1 × 10⁻⁶ Torr.

If we interpret the RHEED intensity as a measure of the Bi coverage then we can fit the RHEED data as a function of temperature and

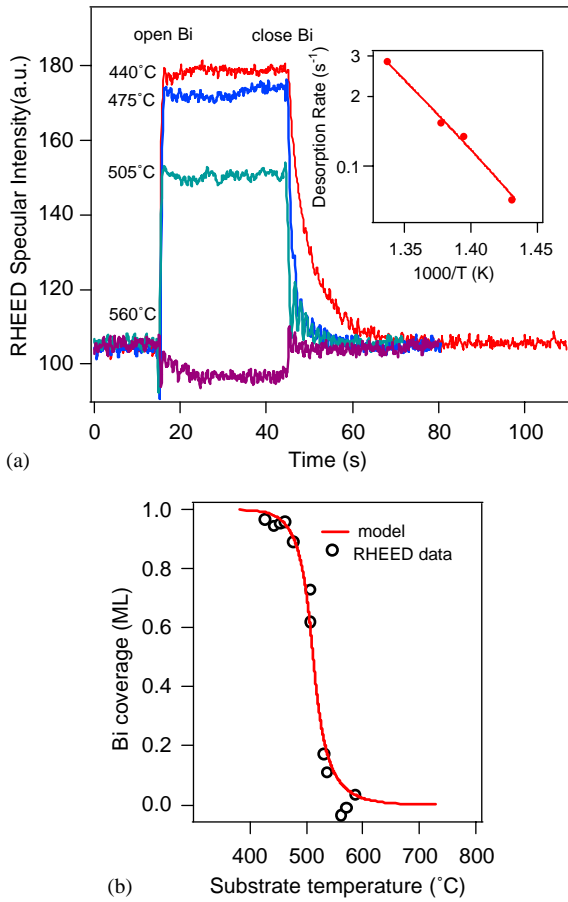


Fig. 1. (a) Change in RHEED specular intensity from GaAs substrate at different substrate temperatures when exposed to a Bi flux of 1.4×10^{-5} Torr, and decay in intensity when flux is removed. Inset shows desorption rate vs. inverse temperature. (b) Coverage vs. growth temperature as inferred from change in RHEED intensity, plotted with Langmuir model.

flux with a Langmuir adsorption isotherm. Assuming the adsorbed Bi is in thermal equilibrium with the vapour, the fraction of occupied surface sites, θ , is equal to

$$\theta = \frac{bP}{1 + bP}, \quad (1)$$

where P is the vapour pressure of Bi at the substrate surface due to the Bi source, and $b = b_0 \exp[U/k_b T]$, where b_0 is a constant and U is the activation energy for desorption, in the limit that the surface adsorbed Bi atoms do not interact with

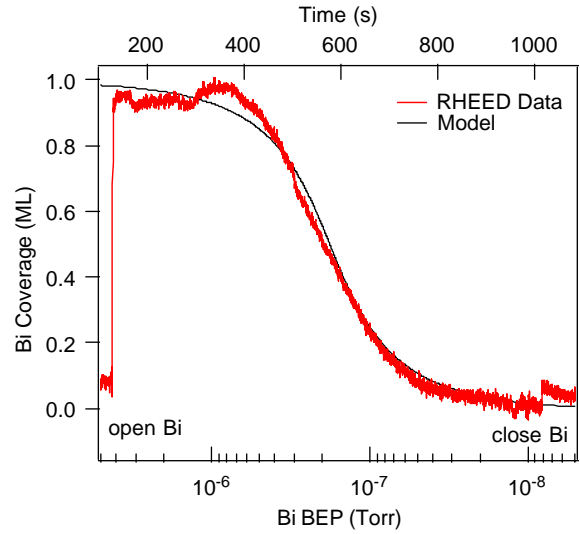


Fig. 2. Bi coverage at constant substrate temperature of 460 °C from RHEED specular intensity data vs. Bi flux as the Bi cell is ramped linearly from 700 to 450 °C. Solid line shows Langmuir model.

each other. The pre-exponential factor b_0 arises during the derivation of Eq. (1) by assigning 3 degrees of freedom to a Bi atom within the adsorbate layer; two translational within the site area, σ_0 , and one vibrational normal to the surface, and using the grand partition function to consider the occupancy of a single site. Thus the term b can be written explicitly as

$$b = \frac{1}{\hbar\omega_0} \sigma_0 \left(\frac{h^2}{2\pi m k_b T} \right)^{1/2} \exp \left[\frac{U + \varepsilon\theta}{k_b T} \right], \quad (2)$$

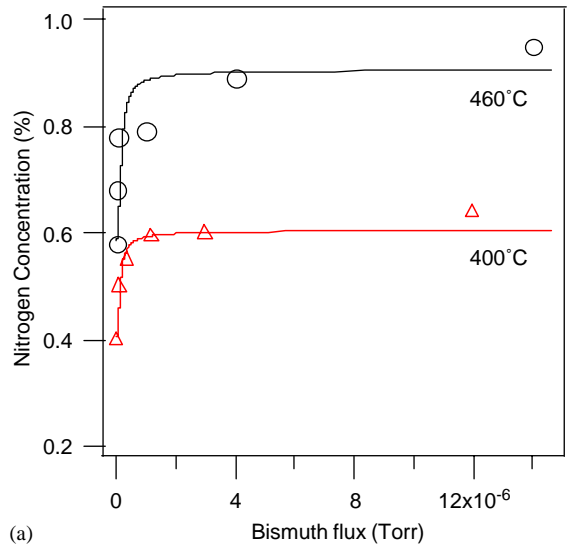
where ω_0 is the vibrational frequency of Bi on the surface and m is the mass of a Bi atom. An attractive Bi–Bi interaction is taken into account in the mean field approximation by the $\varepsilon\theta$ term in the exponent in Eq. (2) [6], where ε is the Bi–Bi interaction energy. The inclusion of the lateral interaction energy term $\varepsilon\theta$ causes a steeper transition from partial to full coverage as a function of pressure. The modified Langmuir model with $U = 1.8 \pm 0.4$ eV, $\varepsilon = 0.12$ eV and $\sigma_0 = 0.2$ nm² fits both the pressure and temperature dependence of the RHEED data, as indicated by the solid lines in Figs. 1b and 2. The adsorption

energy determined from the isotherm is in reasonable agreement with the activation energy determined from the temperature dependence of the Bi evaporation rate in Fig. 1a, and is also comparable with the activation energy of 1.7 eV for self-desorption of Bi [7]. We would expect the binding energy to be dependent on the Group V/III ratio, and to increase over the determined value for Group III-rich conditions. In fact Bi incorporation into the bulk crystal was observed when the V/III ratio was on the order of, or less than one [8].

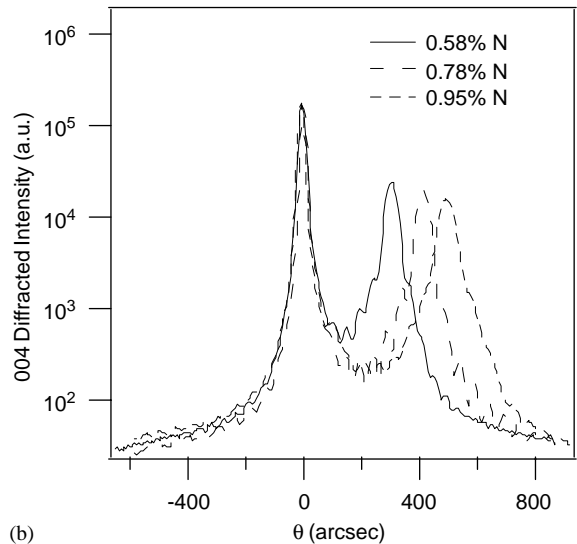
We observe an increase in the nitrogen content with Bi flux, in the case of $\text{GaN}_x\text{As}_{1-x}$ films grown with a Bi flux, as shown in Fig. 3 for films grown at 400 and 460 °C. A similar effect is observed in MBE growth of GaNAs with Sb [9], where the nitrogen incorporation is also enhanced by the presence of Sb, but the opposite behaviour is observed in GaNAs grown by organometallic vapour phase epitaxy (OMVPE), where a Bi surfactant results in a decrease in the nitrogen content of the layers [10]. The increase in N content with Bi flux closely parallels the Bi surface coverage and can be described by the same Langmuir isotherm as the RHEED data. In Fig. 3 the solid lines are given by $[\text{N}]_{\text{Bi}} = [\text{N}]_0(1 + .55\theta)$ where $[\text{N}]_0$ is the N concentration in the absence of Bi and θ is the Bi coverage from Eq. (1), are in good agreement with the N concentration data. This suggests that N incorporates 55% more efficiently on regions of the surface that are covered with Bi than those that are not.

This result is surprising since the presence of a non-incorporating group V surface layer might intuitively be expected to hinder the N incorporation, not increase it. Secondly at 500 °C and below the N incorporation is independent of temperature. This is most simply interpreted as a sign that all of the reactive nitrogen sticks to the surface. The fact that the N incorporation increases with Bi means that some of the reactive N does not incorporate in the absence of the surfactant.

Our results are in sharp contrast with the OMVPE results where high coverages of surfactant were found to completely suppress the N incorporation. The radical difference between the MBE and the OMVPE results may arise from differences in the adsorbing species on the surface.



(a)



(b)

Fig. 3. (a) Nitrogen concentration data for GaNAs samples grown at 400 and 460 °C with increasing Bi flux. Solid lines show $[\text{N}]_{\text{Bi}} = [\text{N}]_0(1 + .55\theta)$, where θ is coverage from the Langmuir model. (b) Sample of XRD (004) diffraction curves for GaNAs epilayers grown at 460 °C used to determine nitrogen content.

In OMVPE the dimethyl hydrazine does not completely decompose and the adsorbed species is expected to be a N–C or N–H complex [10]. These species may have rather different sticking characteristics than the active nitrogen produced in the N_2 plasma source.

The reason for the increased N incorporation is not known, however, a number of phenomena could contribute to the effect. Bi may displace As at the surface making it easier for the N to compete with As for Ga bonds. It is also possible that the Bi-induced surface reconstruction plays an important role. Reason et al. [11] find that a (2×1) reconstruction results in the highest substitutional N incorporation (for non-surfactant assisted growth by MBE), due to the higher number of available Group V sites, and Zhang and Zunger [12] use first principles calculations to show that the surface reconstruction may be responsible for the higher solubility of N on GaAs surfaces than in the bulk. In this case, the (3×1) reconstruction due to the large Bi atoms may locally alter the stress state of the surface, resulting in increased N solubility over that of an As-terminated surface. Finally, line of sight mass spectrometry shows that the formation of NAs is enhanced on Bi-covered GaAs surfaces. It is possible that NAs acts as an intermediary in the incorporation of N into GaAs.

In summary, we have measured the surface coverage of Bi surfactant during MBE growth of GaAs as a function of Bi flux and substrate temperature. The Bi coverage saturates at low temperature (450 °C) and high flux (10^{-6} Torr) and can be described by a Langmuir model with a surface binding energy for an isolated Bi atom of 1.8 ± 0.4 eV. The Bi surfactant increases the efficiency of N incorporation in $\text{GaN}_x\text{As}_{1-x}$ by up to

60%, thereby offering a new means of controlling N incorporation in dilute nitride semiconductors.

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References

- [1] S. Tixier, M. Adamczyk, E.C. Young, J.H. Schmid, T. Tiedje, *J. Crystal Growth* 251 (2003) 449.
- [2] W.N. Ha, V. Gambin, S. Bank, M. Wistey, H. Yuen, S. Kim, J.S. Harris, *IEEE J. Quant. Electron.* 38 (2002) 1260.
- [3] X. Yang, M.J. Jurkovic, J.B. Heroux, W.I. Wang, *Appl. Phys. Lett.* 75 (1999) 178.
- [4] A. Kawazu, T. Otsuki, G. Tominga, *Jpn. J. Appl. Phys.* 20 (1981) 553.
- [5] M.R. Pillai, S.-S. Kim, S.T. Ho, S.A. Barnett, *J. Vac. Sci. Technol. B* 18 (2000) 1232.
- [6] R.H. Fowler, E.A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, Cambridge, 1952.
- [7] G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*, D. Van Nostrand Company Inc., Princeton, NJ, 1950.
- [8] S. Tixier, M. Adamczyk, T. Tiedje, S. Francoeur, A. Mascarenhas, P. Wei, F. Schiettekatte, *Appl. Phys. Lett.* 82 (2003) 2245.
- [9] J.C. Hammand, G. Ungaro, L. Largeau, G. Le Roux, *Appl. Phys. Lett.* 77 (2000) 2482.
- [10] F. Dimroth, A. Howard, J.K. Shurtleff, G.B. Stringfellow, *J. Appl. Phys.* 90 (2002) 3687.
- [11] M. Reason, H.A. McKay, W. Ye, S. Hanson, R.S. Goldman, V. Rotberg, *Appl. Phys. Lett.* 85 (2004).
- [12] S.B. Zhang, A. Zunger, *Appl. Phys. Lett.* 71 (1997) 677.