Growth of $In_xGa_{1-x}As$/GaAs heterostructures using Bi as a surfactant

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The effects of a bismuth surfactant layer on the molecular beam epitaxy of GaAs and $In_xGa_{1-x}As$ layers on GaAs (001) were studied. The $In_xGa_{1-x}As$ surface reconstruction changed from arsenic stabilized 2×4 to bismuth stabilized 1×3 for high enough bismuth fluxes and low enough substrate temperatures. Maintaining a bismuth stabilized surface during $In_xGa_{1-x}As$ growth resulted in a larger number of reflection high-energy electron diffraction (RHEED) oscillations. RHEED patterns were also streakier after $In_xGa_{1-x}As$ growth with Bi. Roughness measurements using atomic force microscopy showed reduced root mean square roughness with Bi, e.g., from 3.8 to 2.8 nm, for 4 nm thick $In_{0.3}Ga_{0.7}As$ layers. Simulations of x-ray diffraction results from 10 period $In_{0.5}Ga_{0.5}As$/GaAs superlattices showed that Bi reduced interface roughness from 1.1 to 0.5 nm and reduced interfacial broadening from 2.8 to 2.1 nm. The latter was attributed to reduced In segregation. $In_xGa_{1-x}As$/GaAs ($x=0.2-0.4$) multiple quantum wells grown with Bi exhibited photoluminescence peaks that were more intense than those grown without Bi. © *2000 American Vacuum Society.* [S0734-211X(00)12803-3]

I. INTRODUCTION

$In_xGa_{1-x}As$/GaAs heterostructures are used in high electron mobility transistors, microwave devices, and near infrared lasers.[1] However, the In content x and/or the thickness of the alloy layers are usually restricted to relatively low values. This is because the lattice mismatch strain, up to 7% for the case of pure InAs and GaAs, yields nonideal growth as the alloy layer relaxes by the formation of three-dimensional (3D) islands[2] or by the introduction of dislocations.[3] The ability to grow thicker alloy layers with higher strain would extend the wavelength range of devices based on InGaAs quantum wells, and allow higher mobilities in modulation-doped heterostructures. An additional nonideal feature of the InGaAs system is the tendency of In to surface segregate, which leads to interface broadening by $\approx1-3$ nm.[4]

The use of an adsorbed surface species, or surfactant, to modify strained-layer growth has been widely studied. Much of the work has been on GeSi/Si heteroepitaxy, where surfactants such as Sb and Bi have been shown to suppress roughening and Ge segregation.[5–7] Tellurium has been used as a surfactant during the growth of $In_xGa_{1-x}As$/GaAs heterostructures, and was shown to promote flatter interfaces.[8] However, residual Te incorporation leads to substantial donor doping. The use of a so-called ''virtual surfactant,'' where an excess of group-III element is maintained during growth, has also been shown to suppress roughening.[9] However, maintaining a group-III-stabilized surface without formation of group-III surface droplets requires exacting process control. Another possibility is the addition of a controlled amount of a group-V species. The effectiveness of this has been demonstrated in the AlGaAs/GaAs system,[10] where an adsorbed Sb surface layer was shown to improve reflection high-energy electron diffraction (RHEED) oscillations, indicating improved layer-by-layer growth, and yielded improved-quality photoluminescence peaks. Fundamental studies on metallic surfaces indicate that surfactants alter surface diffusion rates and step-attachment kinetics,[11] both of which have a strong influence on growth morphology and segregation. Bismuth is another potential group-V surfactant. It is known from prior studies that it is difficult to incorporate bismuth into III-V semiconductors during growth,[12] which is a key feature for a successful surfactant.

In this article, we describe the effects of a bismuth surfactant during the growth of $In_xGa_{1-x}As$/GaAs heterostructures by molecular beam epitaxy (MBE). Bi was chosen since it was expected to satisfy the key criteria for a good surfactant. As noted above, it should segregate to the growth surface rather than incorporating. Like Sb, Bi has the advantage that it is isoelectronic with group-V atoms, such that small amounts of incorporated Bi will not increase background doping levels. There are no previous studies, to our knowledge, of the effects of Bi as a surfactant in this system.

II. EXPERIMENTAL PROCEDURE

All growths were carried out in a cryogenically pumped MBE chamber equipped with a 25 keV RHEED gun. El-

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emental gallium, indium, arsenic, and bismuth were used as source materials. Arsenic was sublimed as As_4. The films were deposited on epi-ready semi-insulating GaAs (001) singular substrates. Both the GaAs and the $In_xGa_{1-x}As$ layers were deposited at 520 °C. The substrates were degreased *ex situ* using acetone and methanol. After insertion into the chamber via a loadlock, the substrates were annealed *in situ* at 570 °C for 10–15 min to desorb any oxides. They were then cleaned using 1 keV Ar^+ ions impinging 15° from the surface plane for 15 min, a procedure that produces clean, flat, defect-free surfaces.[13] A 50 nm thick GaAs buffer layer was then grown on the cleaned surface at 570 °C.

Both single InGaAs ternary alloy layers and InGaAs/GaAs superlattice structures were grown on top of the GaAs buffer layer. The growth temperature for both the ternary alloy layers and superlattice structures was 520 °C throughout. The single layer ternary alloy structures were characterized *in situ* using RHEED and *ex situ* using atomic force microscopy (AFM). The superlattice structures had a period of approximately 12 nm, with the ternary layer 1–1.5 nm thick. Bi was deposited in the growth experiments by pre-deposition or co-deposition. In pre-deposition, Bi was first deposited and the Bi flux stopped prior to III-V growth. This approach was most useful for lower T_s and short depositions, where there was minimal Bi desorption, such that the Bi surface coverage remained essentially constant. In co-deposition, a Bi flux was maintained throughout heterostructure growth, at a value that gave a strong 1×3 surface reconstruction. This approach was necessary at higher substrate temperatures where Bi desorption was significant.

The superlattice structures were characterized by x-ray diffraction (XRD) and photoluminescence measurements (PL). $\theta-2\theta$ XRD scans using monochromatic Cu $K\alpha$ radiation were used to characterize the superlattice samples. A kinematical simulation, the details of which are described elsewhere,[14] was used to fit the experimental data. An exponential In composition profile was used in the simulations because of the segregation of In atoms to the surface during the growth of the InGaAs/GaAs heterostructures.[15] The simulation also accounted for both interfacial broadening and interfacial roughness. Experimental peak broadening was included by convoluting the XRD patterns with a Gaussian response function with a width corresponding to the resolution of the diffractometer. The best fit was determined by minimizing the difference between the data and the fit using a chi-squared (χ^2) minimization. This procedure is explained in detail in Ref. 14. The present fits represented clear minima in χ^2, with χ^2 typically ~1.

The photoluminescence measurements were carried out at 82 K. An Ar ion laser was used as a pump laser, with a wavelength of 514 nm. For the PL measurements in samples with $x=0.23$ and 0.3, the pump power was 40 mW. The pump beam was reflected using a dichroic beam splitter and focused through 50× Nikon objective lens. The emission from the sample was focused by the same objective into a Spex 500 m monochromator equipped with a liquid-nitrogen-cooled Advanced Detector Corp. Ge detector.

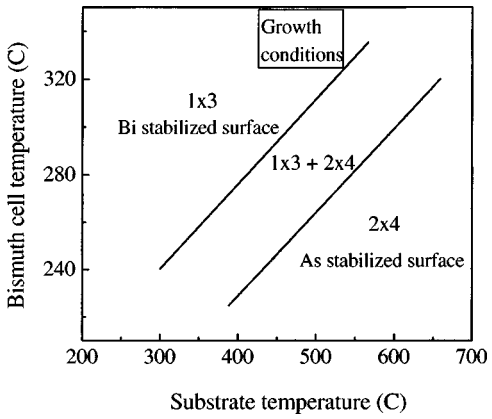

FIG. 1. Map of the surface reconstructions observed on GaAs (001) as a function of substrate temperature T_s and Bi cell temperature T_{Bi}.

III. RESULTS AND DISCUSSION

A. Surface reconstruction

Surface reconstructions were observed using RHEED as a function of substrate temperature T_s and Bi cell temperature T_{Bi}. An As_4 flux with a beam equivalent pressure of $\sim6\times10^{-6}$ Torr, yielding a 2×4 GaAs reconstruction, was maintained throughout these measurements. Figure 1 shows the reconstructions observed versus T_s and T_{Bi}. The As-stabilized 2×4 pattern changed to a Bi-stabilized 1×3 pattern for high T_{Bi} and low T_s with an intermediate range where the 2×4 and 1×3 co-existed. Bismuth has been shown to modify the diffraction pattern of (001) InSb from C (8×2) to 1×3 in an earlier study.[16] An activation energy for Bi desorption of ~1.3 eV was obtained from the slope of the transitions. This is less than the activation energy for Bi evaporation from bulk Bi, 1.8 eV.[17] The box in Fig. 1 shows the conditions used for pre-depositing and co-depositing Bi on the growth surface in the experiments described below. When the Bi shutter was closed, the 1×3 reconstruction was retained for relatively long times, e.g., 50 s at 520 °C.

B. RHEED oscillations

Figure 2 shows a comparison of RHEED oscillations obtained during GaAs homoepitaxy with and without Bi pre-deposition, but under otherwise identical conditions. Bismuth pre-deposition caused a decrease in the specular beam intensity prior to growth. At the onset of growth, the intensity increased rapidly on the Bi-stabilized surface, in contrast to the rapid decrease observed without Bi. After the first monolayer of growth, the oscillations were similar in form, except that the amplitude of the intensity oscillations was larger on the Bi-stabilized surface. The damping of the oscillations was slower with Bi, suggesting that Bi helped to suppress the gradual roughening that generally occur during layer-by-layer growth. RHEED oscillations were also observed during heteroepitaxy of $In_{0.3}Ga_{0.7}As$ films on GaAs grown at 520 °C with and without Bi pre-deposition. Typical results are shown in Fig. 3. Again, bismuth had the same effect on the first monolayer of growth as that noted above.

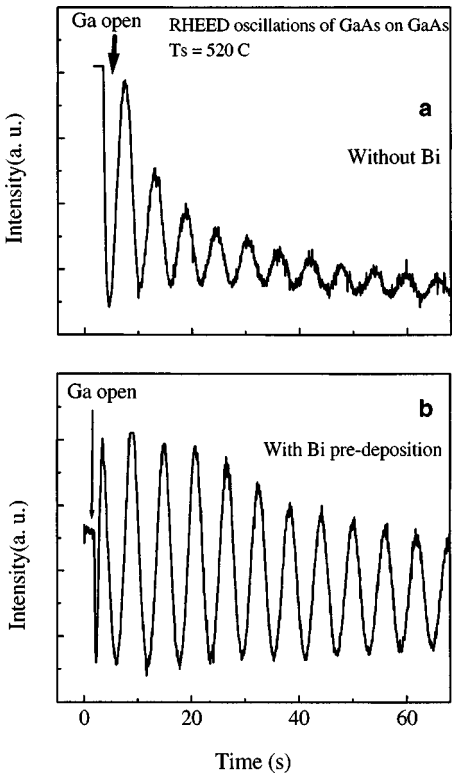

FIG. 2. RHEED oscillations observed during GaAs homoepitaxy at 520 °C (a) without Bi and (b) with Bi pre-deposition.

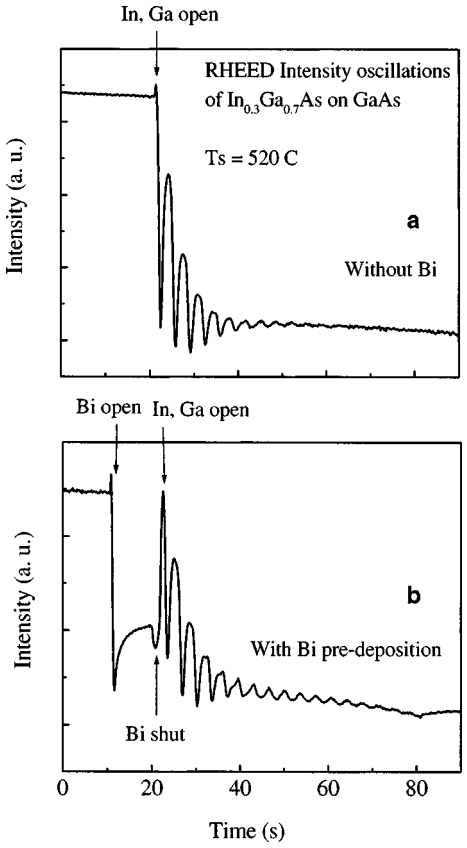

FIG. 3. RHEED oscillations observed during $In_{0.3}Ga_{0.7}As$ growth on GaAs at 520 °C (a) without Bi and (b) with Bi pre-deposition.

The InGaAs oscillations decayed more rapidly than for GaAs due to the lattice mismatch.[2] The weak oscillations were retained slightly longer with Bi pre-deposition and co-deposition compared to regular MBE, although the result is not as clear as in the GaAs case.

The present enhancement in GaAs oscillations is similar to that observed previously for AlGaAs/GaAs with Sb surfactant.[10] Recent data for metal epitaxy provide some insight into the mechanisms by which surfactants alter growth kinetics. Longer-lived RHEED oscillations generally indicate a greater tendency for each layer to be completed prior to nucleating two-dimensional (2D) islands on the next layer. Surfactants can cause this by increasing the energy barrier for attachment of the adatoms to islands and/or by reducing the Schwoebel barrier at descending steps.[18]

C. Surface morphology

RHEED patterns after the growth of GaAs remained streaky during regular and Bi mediated growth, as expected. However, RHEED patterns taken after growth of 4 nm thick $In_{0.3}Ga_{0.7}As$ alloy layers at 520 °C, shown in Fig. 4, were streakier with Bi pre-deposition. Similar improvements were seen when the alloy layers were grown with Bi co-deposition. In general, the addition of Bi to the surface increased the thickness to which streaky RHEED patterns were observed. In the best case, the thickness was increased by a factor of up to 3 times.

AFM images corroborated the RHEED results. Figure 5 shows typical AFM images from $In_{0.3}Ga_{0.7}As$ surfaces grown with and without Bi co-deposition. The main surface features were 3D islands. For growth without Bi, the circular islands were fairly uniform in size ($\approx$40 nm wide and $\approx$35 nm high), with a density of 4×10^{10} cm^{-2}. For growth with Bi, there was a smaller density ($\approx2\times10^{10}$ cm^{-2}) of larger ($\approx$70 nm wide and 35 nm high) islands. However, there was also a background of smaller height ($\approx$25 nm) islands that were elongated along the [100] direction. Root mean square (rms) roughness values taken from the AFM images showed a decrease from 3.8 nm for growth without Bi to 2.8 nm with Bi co-deposition. Bi pre-deposition results were similar to the co-deposition results. However, roughness values generally fell between the Bi-free and co-deposition results, which is not surprising given that the Bi coverage dropped gradually after pre-deposition.

D. Superlattice x-ray diffraction

Figure 6 compares $\theta-2\theta$ x-ray diffraction scans for typical $In_xGa_{1-x}As/GaAs$ ($x=0.4$) superlattices, grown with and without Bi co-deposition. The results are qualitatively similar for both superlattices, with a number of superlattice reflections observed. The x-ray simulation fits, also shown in Fig. 6, agreed well with the experimental data, and showed the following. First, the fit to the peak positions provides accurate information about lattice spacings. The spacings were identical for both superlattices, within experimental error. An error analysis indicates that $<1\%$ Bi was incorpo-

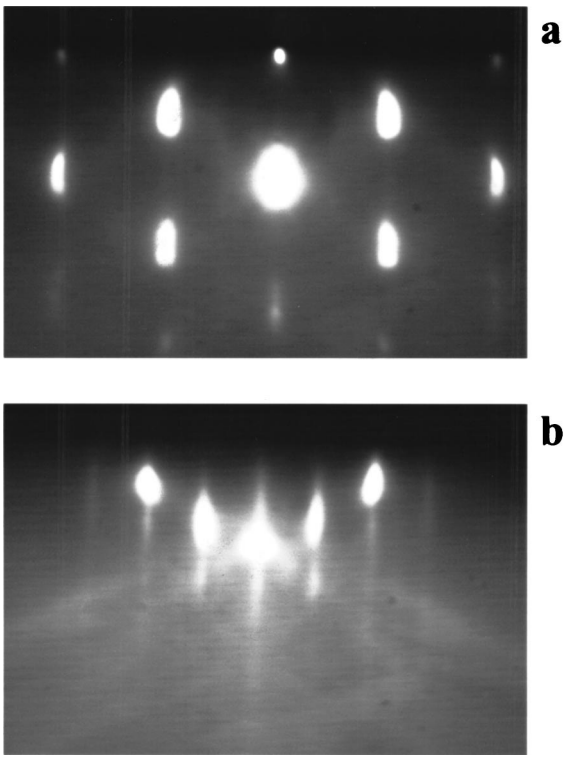

FIG. 4. RHEED patterns from 4 nm thick $In_{0.3}Ga_{0.7}As$ alloy layers grown on GaAs at 520 °C (a) without Bi and (b) with Bi pre-deposition.

rated into the film grown with Bi, assuming an InBi lattice spacing of 0.66 nm.[19] Second, the broadening of the satellite peaks provides information about the superlattice interface roughness.[14] The simulation results show a roughness de-

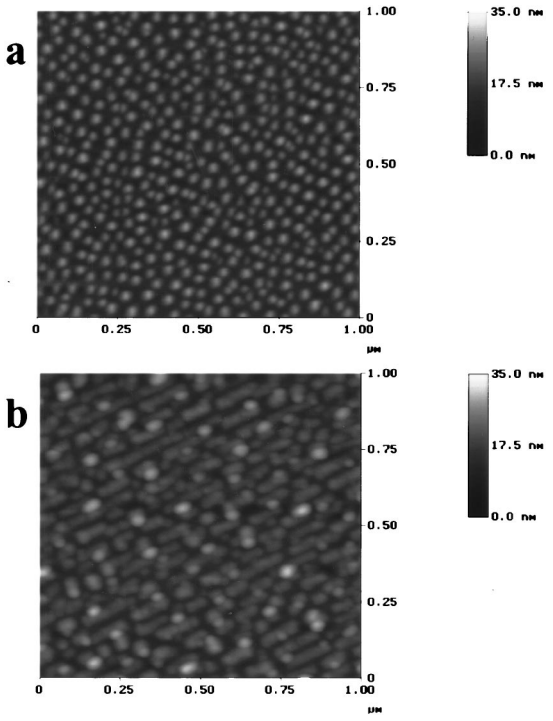

FIG. 5. AFM images from 4 nm thick $In_{0.3}Ga_{0.7}As$ alloy layers grown on GaAs at 520 °C (a) without Bi and (b) with Bi co-deposition.

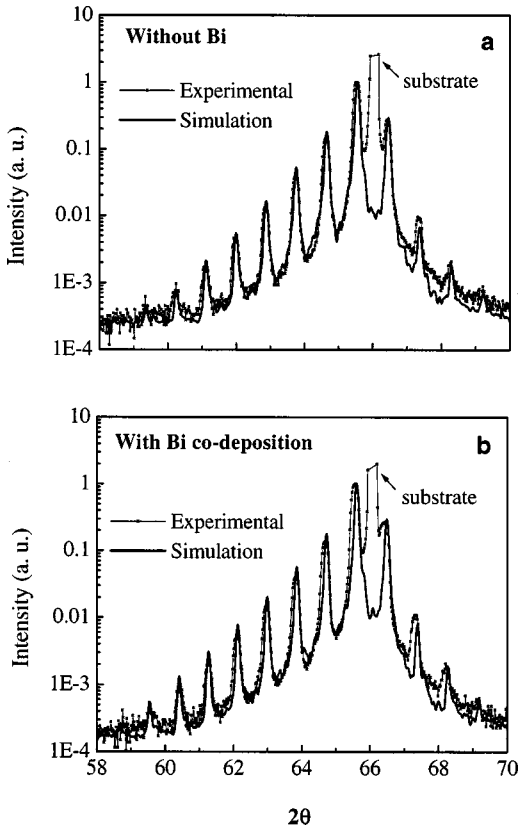

FIG. 6. XRD patterns and simulations from 10 period $In_{0.4}Ga_{0.6}As/GaAs$ superlattices, with periods of 12 nm and alloy layer thicknesses of 1.5 nm, grown (a) without Bi and (b) with Bi co-deposition.

crease from 1.1 to 0.5 nm due to Bi co-deposition with $x=0.48$. This result is consistent with the RHEED and AFM results above. Third, the envelope function of the satellite intensities provides information on interface broadening. Interfaces in InGaAs/GaAs superlattices are broadened due to In segregation.[15] The resulting exponential composition variations have a $1/e$ length γ, i.e., γ provides a measure of the interface width. The simulations incorporated exponential In composition profiles, and showed a decrease in γ due to Bi co-deposition, as shown in Fig. 7. While these effects were small, they were reproducibly observed in samples with different x values and were greater than experimental run-to-run variations. This shows that Bi suppressed In segregation slightly, in agreement with results for Bi and Sb surfactants that suppressed Ge segregation during Ge–Si growth.[5–7]

E. Multiquantum well photoluminescence

Photoluminescence spectra were measured from $In_xGa_{1-x}As/GaAs$ superlattice multiquantum wells (MQWs) with $x=0.23$ and 0.3, grown with and without Bi co-deposition. Figure 8 shows the spectra. Strong MQW emission peaks were observed near the positions expected for $In_xGa_{1-x}As$ alloys of these compositions.[20–22] The broaden-

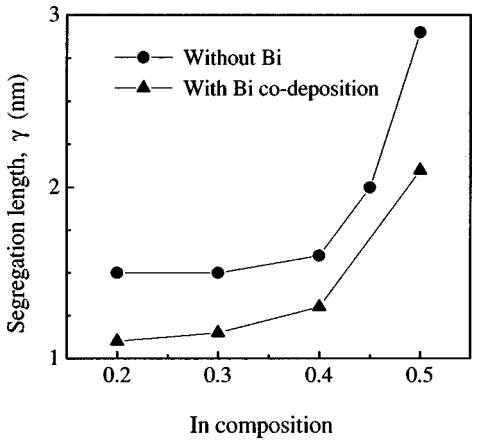

FIG. 7. In segregation length γ during growth of $In_xGa_{1-x}AsAs/GaAs$ superlattices for x ranging from 0.2 to 0.5. Results are shown both for conventional MBE films and films grown with Bi co-deposition.

ing of the peaks, which was similar for Bi and non-Bi MQWs, can be attributed to nonuniform quantum-well thickness due to nonideal growth.[23] While the above RHEED, AFM, and XRD simulation results showed reduced InGaAs layer roughness due to Bi, the reduction was apparently insufficient to significantly sharpen the PL peaks. PL intensities generally increased due to the presence of Bi by a factor ranging from 1.5 to 8 in the present data. While PL intensity comparisons are generally qualitative, the results indicate that any residual Bi incorporated did not deleteriously affect the optical properties. Indeed, they suggest an improvement in the quality of the layers. An increase in PL intensity was also observed in the case of an AlGaAs/GaAs system using Sb as a surfactant,[10] which was attributed to Sb incorporation at defects, thereby eliminating traps. Another possibility is that the Bi-covered surface was less reactive with MBE chamber background contaminants, thereby reducing the background impurity concentration.

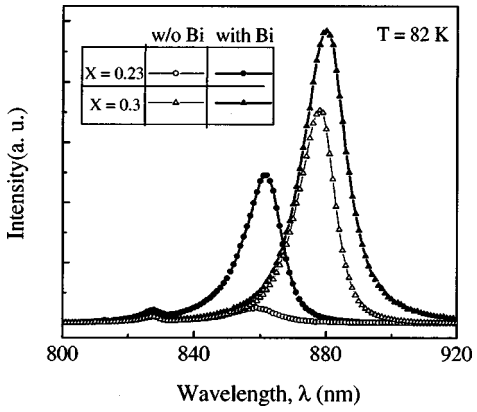

FIG. 8. PL spectra from $In_xGa_{1-x}As/GaAs$ superlattices with $x=0.23$ and 0.3 for growth (a) without Bi and (b) with Bi co-deposition.

IV. SUMMARY AND CONCLUSIONS

The present results show that a Bi surface layer causes useful modifications of the growth of GaAs and $In_xGa_{1-x}As$ layers on GaAs. The bismuth incorporation was too small to be detected by x-ray diffraction. Any bismuth incorporation did not deleteriously affect the properties, since the photoluminescence peaks were always stronger with Bi. The structural results clearly show that Bi reduces interface roughness in single layers and multiple quantum wells. In addition, Bi caused a slight reduction in interface widths, suggesting that In segregation was reduced. Overall, the use of a Bi surfactant is a simple means for improving the structural and optical quality of InGaAs/GaAs structures. Based on these results, further work with this technique is merited that should include both optimization of growth conditions and observations of the effect of Bi on device performance.

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[1]S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981).
[2]J. M. Millunchick and S. A. Barnett, Appl. Phys. Lett. **65**, 1136 (1994), and references therein.
[3]J. W. Matthews and A. E. Blakeslee, J. Cryst. Growth **32**, 265 (1976).
[4]K. R. Evans, R. Kaspi, J. E. Ehret, M. Skowronski, and C. R. Jones, J. Vac. Sci. Technol. B **13**, 1820 (1995).
[5]M. Copel, M. C. Reuter, M. Horn von Hoegen, and R. M. Tromp, Phys. Rev. B **42**, 11682 (1990).
[6]K. Sakamoto, K. Miki, T. Sakamoto, H. Yamaguchi, H. Oyanagi, H. Matsuhata, and K. Kyoya, Thin Solid Films **222**, 112 (1992).
[7]K. Sakamoto, H. Matsuhata, K. Kyoya, K. Miki, and T. Sakamoto, Jpn. J. Appl. Phys., Part 1 **33**, 2307 (1994).
[8]J. Massies, N. Grandjean, and V. H. Etgens, Appl. Phys. Lett. **61**, 99 (1992).
[9]E. Tournie and K. H. Ploog, Thin Solid Films **231**, 43 (1993).
[10]R. Kaspi, K. R. Evans, D. C. Reynolds, J. Brown, and M. Skowronski, Mater. Res. Soc. Symp. Proc. **379**, 79 (1995).
[11]D. Kandel and E. Kaxiras, Phys. Rev. Lett. **75**, 2742 (1995).
[12]K. Sakamoto, K. Kyoya, K. Miki, H. Matsuhata, and T. Sakamoto, Jpn. J. Appl. Phys., Part 2 **32**, L204 (1993).
[13]J. G. C. Labanda, L. Hultman, and S. A. Barnett, Appl. Phys. Lett. **63**, 3114 (1995).
[14]A. Madan, P. Yashar, M. Shinn, and S. A. Barnett, Thin Solid Films **302**, 147 (1997).
[15]P. Yashar, Manoj R. Pillai, J. M. Millunchick, and S. A. Barnett, J. Appl. Phys. **83**, 2010 (1998).
[16]A. J. Noreika, W. J. Takei, M. H. Francombe, and C. E. C. Wood, J. Appl. Phys. **53**, 4932 (1982).
[17]J. L. Zilko and J. E. Greene, J. Appl. Phys. **51**, 1549 (1980).
[18]I. Markov, Phys. Rev. B **50**, 11271 (1994).
[19]S. A. Barnett, J. Vac. Sci. Technol. A **5**, 2845 (1987).
[20]J. Pamulapati, P. Bhattacharya, R. L. Tober, J. P. Loehr, and J. Singh, J. Appl. Phys. **71**, 4487 (1992).
[21]N. G. Anderson, W. D. Laidig, R. M. Kolbas, and Y. C. Lo, J. Appl. Phys. **60**, 2361 (1986).
[22]N. G. Anderson, W. D. Laidig, and Y. F. Lin, J. Electron. Mater. **14**, 187 (1985).
[23]E. Tournie, O. Brandt, and K. Ploog, Appl. Phys. Lett. **60**, 2877 (1992).