Molecular beam epitaxy growth of $GaAs_{1-x}Bi_x$

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$GaAs_{1-x}Bi_x$ epilayers with bismuth concentrations up to $x=3.1\%$ were grown on GaAs by molecular beam epitaxy. The Bi content in the films was measured by Rutherford backscattering spectroscopy. X-ray diffraction shows that GaAsBi is pseudomorphically strained to GaAs but that some structural disorder is present in the thick films. The extrapolation of the lattice constant of GaAsBi to the hypothetical zincblende GaBi alloy gives 6.33 ± 0.06 Å. Room-temperature photoluminescence of the GaAsBi epilayers is obtained and a significant redshift in the emission of GaAsBi of $\sim$84 meV per percent Bi is observed. © *2003 American Institute of Physics.*
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Materials for the active region of diode lasers and photodetectors operating in the infrared and near infrared are the subject of intense research.[1] Technology based on III–V substrates such as GaAs presents several advantages over competing technologies. Among these are the low cost of GaAs substrates and the availability of the low refractive index AlGaAs alloys, which are lattice matched to GaAs.

Material systems involving GaAs alloyed with nitrogen and antimony have been extensively studied whereas alloys with another element of the column V, bismuth, has received very little attention. GaBi has not been synthesized yet but is expected to be a semimetal.[2] Therefore, the introduction of Bi into GaAs should lead to a decrease in the band gap. Another interesting material is GaAs co-alloyed with nitrogen and bismuth.[3] Both N and Bi would lead to a reduction in the band gap, while the small atomic size of nitrogen compensate for the large size of the Bi atom, resulting in a low band gap alloy lattice matched to GaAs.

The molecular beam epitaxy (MBE) growth of most III–V alloys is rather well established whereas GaAsBi growth to date has only been reported using metalorganic vapor phase epitaxy (MOVPE).[4,5] Due to its large size, bismuth surface segregates and does not incorporate under typical MBE III–V growth conditions.

In this letter, we report on the epitaxial growth of GaAsBi by MBE. The lattice constant and the crystal quality of the layers are studied using x-ray diffraction. The Bi concentration is measured by Rutherford backscattering spectroscopy (RBS) and the energy of the band gap of the alloy is measured using room-temperature photoluminescence spectroscopy.

The samples were grown in a VG-V80H MBE deposition system, equipped with conventional Knudsen effusion cells for Ga, and Bi, and a two-zone cracker source for As_2. The substrate temperature is monitored throughout the growth using an optical band-gap thermometer with an accuracy of $\sim2.5\,°C$. The beam equivalent pressure (BEP) is measured using a retractable ion gauge. In order to incorporate Bi into the lattice, GaAsBi was grown at a low substrate temperature of 380 °C. In an earlier study, bismuth was used as a surfactant in the growth of dilute nitrides (GaNAs and InGaNAs) and it was found that for substrate temperatures higher than 450 °C and for arsenic flux larger than gallium flux, less than 2×10^{17} cm^{-3} of Bi is incorporated into the films as determined from secondary ion mass spectrometry.[6] As important as the substrate temperature, the arsenic to gallium flux ratio needs to be close to the stochiometric value in order for Bi to incorporate significantly. This may indicate that Bi and As compete for lattice sites, and we therefore assume that the Bi occupies As sites. Good control over the As_2 overpressure was achieved using a valve on the arsenic cracker. According to Farrow, the bismuth beam from a conventional Knudsen oven is composed of Bi and Bi_2 in comparable amounts.[7] In this work, the bismuth BEP ranged up to 10^{-7} Torr. Epiready (100)-oriented, on axis ($\pm0.5°$) GaAs substrates were used. The substrates were first ramped to $\sim615\,°C$ for 10 min to remove the native surface oxide. The GaAsBi growth rate was $\sim$12 nm/min. Each sample is composed of an $\sim$200 nm GaAs buffer layer and a 100–300 nm GaAsBi epilayer.

Figure 1 shows the Cu $K\alpha1$ x-ray diffraction patterns obtained from three $GaAs_{1-x}Bi_x$ epilayers. Diffraction from (004) planes is measured using θ–2θ scans. The angle $\Delta\theta$ relative to the diffraction peak of GaAs is used in the figure. The sharp peaks located at $\Delta\theta=0$ correspond to the diffraction from the GaAs buffer layer and substrate. The peak located on its left is from the GaAsBi epilayer.

As expected, increasing the Bi content of the epilayer increases the lattice constant and shifts the diffraction peak

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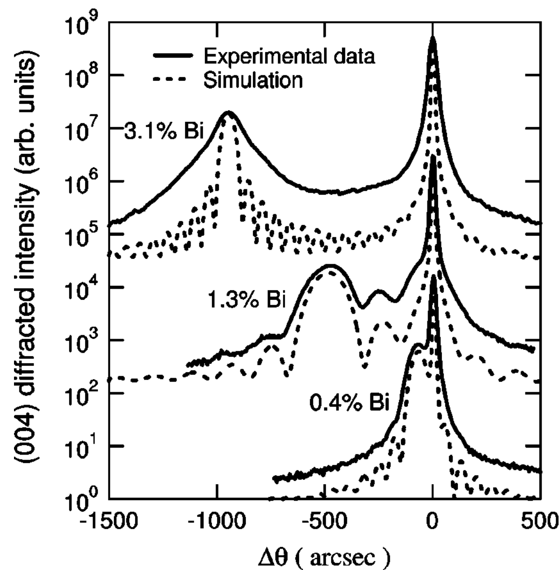

FIG. 1. X-ray θ–2θ diffraction pattern from (004) lattice planes of GaAsBi epilayers on GaAs. The dotted lines are simulations using the dynamical theory.

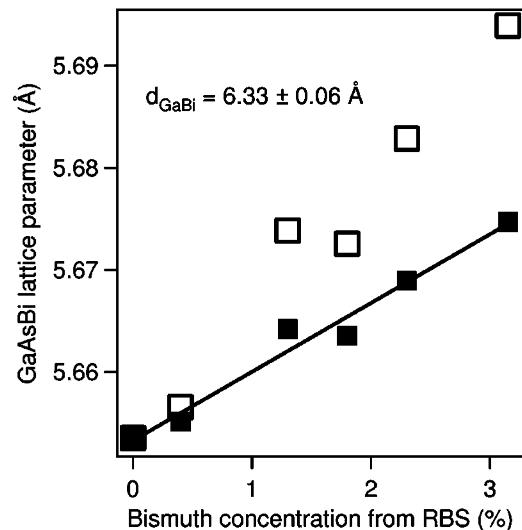

FIG. 2. Lattice parameter of the pseudomorphic (open square) and free standing (filled square) GaAsBi alloys as a function of the Bi concentration. The lattice parameters are from x-ray measurements and the Bi concentrations are from RBS. The solid line is a linear fit. The extrapolated lattice parameter for GaBi (d_{GaBi}) is indicated.

to lower diffraction angles. Asymmetric k-space maps were performed to study the strain state of the epilayers. The three samples shown in Fig. 1 were found to be pseudomorphic.

Since the lattice constant of cubic GaBi is unknown, the Bi concentration cannot be obtained from the lattice constant, as is routinely done for ternary semiconductor alloys. Bi concentrations were measured with RBS, the results of which are discussed below. We find that the Bi concentration in the samples are $x=0.4\%$, 1.3%, and 3.1% (see Fig. 1). The epilayer thicknesses as obtained by x-ray diffraction simulations and RBS profiles are $\sim$270, 110, and 270 nm for the sample with 0.4%, 1.3%, and 3.1% Bi, respectively. The dotted lines in Fig. 1 are simulations of the x-ray patterns using the dynamical theory. The tetragonal distortion induced by the epitaxy is taken into account using the elastic constants of GaAs. We find that there is a good agreement between experimental and simulated patterns, especially for the sample with 1.3% Bi. The diffraction pattern for this sample shows well defined thickness fringes, indicating the presence of a smooth and coherent interface. The sample with 0.4% Bi shows very weak interference fringes most likely due to roughening of the surface. It appears that as the growth proceeds, the surface roughness increases. In the case of the 3.1% Bi sample, no interference fringes can be observed and the diffraction peak sits on a wide diffuse scattering peak. This is an indication that structural disorder and/or Bi concentration inhomogeneity are present in this sample. It is possible that plastic deformation started to occur in this sample and that inhomogeneous strain associated with misfit dislocations may explain the broadening of the x-ray peak. The lattice mismatch with GaAs of the $GaAs_{1-x}Bi_x$ epilayer with $x=3.1\%$ Bi is 0.37%. Critical thickness reported for the formation of misfit dislocations of InGaAs on GaAs with a similar lattice mismatch is $\sim$60 nm, which is significantly less than the 270 nm of the present sample.[8]

The lattice parameter for the pseudomorphic and free standing GaAsBi alloys is shown as a function of the Bi concentration in Fig. 2. The lattice parameters were measured by x-ray diffraction while the Bi concentrations were obtained using RBS. The parameters for the pseudomorphic GaAsBi films are obtained from the raw x-ray data and represent the lattice parameters in the growth direction. The parameters for the free standing films are obtained by correcting the x-ray data for the tetragonal distortion using the elastic constants of GaAs. The lattice parameters show a linear trend with the Bi concentration in accordance with Vegard's law. By extrapolating the trend for the free standing films to the binary GaBi, a lattice parameter of 6.33 $\pm$0.06 Å is obtained. This is higher than the value of 6.192 Å extrapolated by Oe from MOVPE GaAsBi grown epilayers,[5] but is in very good agreement with the calculated value of 6.324 Å using the local density approximation in the density-functional formalism.[2]

Photoluminescence (PL) spectra from the three samples presented in Fig. 1 are shown in Fig. 3. These spectra were recorded at room temperature. GaBi is believed to be a semimetal. Its estimated band gap is approximately -1.45 eV.[2] As expected, the PL peak energy decreases with increasing Bi content. The peak energies are 1.4, 1.28, and 1.16 eV for the samples with 0.4%, 1.3%, and 3.1% Bi, respectively. Note that the energy measured from photoluminescence is in agreement with the energy of the heavy-hole to conduction band transition measured from modulated electroreflectance.[9] The band gap change is $\sim$84 meV/% Bi, which is significant when compared to the band gap variation of other III–V alloys with similar alloying ratios (i.e., 16 meV/% In, 21 meV/% Sb, and $\sim$125 meV/% N for InGaAs, GaAsSb, and GaNAs, respectively). This dependence is significantly larger than the $\sim$46 meV/% reported earlier by Oe.[5] The reason for this discrepancy is not known. Our data provide evidence for an abnormally large decrease in the band gap compared to that expected from linear interpolation.

The full width at half maximum (FWHM) of the PL increases with Bi concentration. In order of increasing concentration, the values are $\sim$50, 89, and 106 meV. The broad-

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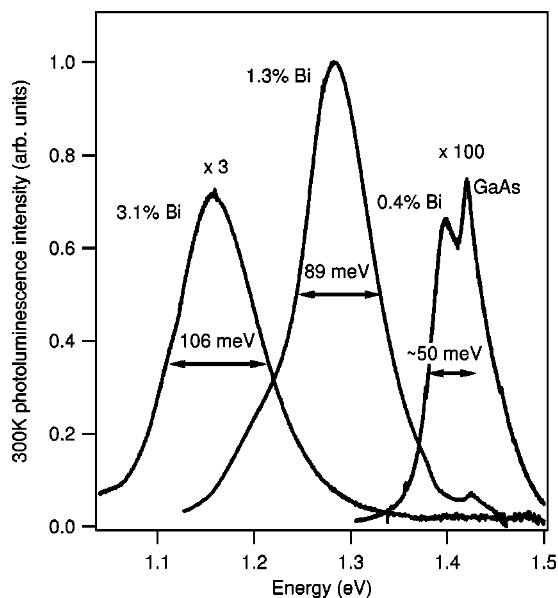

FIG. 3. Room-temperature photoluminescence from GaAsBi epilayers with 0.4%, 1.3%, and 3.1% Bi.

ening is relatively large. The photoluminescence width of InGaAs at 1 eV is typically under 40 meV. The photoluminescence intensity is greater for the thinner sample with 1.3% Bi content. This is consistent with the thicker sample with large Bi content being partially relaxed and containing misfit dislocations. The weak PL intensity of the sample with low Bi could be the result of the small electronic confinement at the epilayer/buffer interface, which leads to higher probabilities of radiative recombination in the buffer layer and nonradiative recombination at the buffer/substrate interface. The peaks at 1.42 eV in the 1.3% and 3.1% Bi samples are due to the GaAs buffer layer.

The relatively large peak width of the photoluminescence could be attributed to the structural disorder caused by the low growth temperature and low As_2 overpressure. Films with high structural quality are usually obtained by increasing the surface and bulk atom diffusion, that is by increasing the growth temperature and the arsenic flux. However, the mismatch between GaAs and the extrapolated value of cubic GaBi is very large, approximately 12%. Therefore, the strain energy in the GaAsBi epilayers with large Bi concentrations likely contributes to the deterioration of the crystalline quality of the samples and to the increase in the FWHM of the photoluminescence. Optimization of the growth conditions and/or restriction of the growth to quantum well type thicknesses may solve this problem.

$GaAs_{1-x}Bi_x$ epilayers with Bi content up to $x=3.1\%$ were grown on GaAs substrates by molecular beam epitaxy. Good structural properties and room-temperature photoluminescence were obtained. However, the presence of some structural disorder or plastic relaxation is evidenced by the relatively large width of the photoluminescence spectra, and further optimization of the growth conditions is possible. The extrapolation of RBS and x-ray diffraction data to the GaBi alloy gives a lattice parameter of 6.33 ± 0.06 Å. GaAsBi is a promising new materials system for long wavelengths devices.

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