I. INTRODUCTION

The development of new semiconductor heterostructures with GaAsBi has attracted much scientific interest recently as it has potential applications such as lasers [1, 2], transistors [3], photo-detectors [4], spintronic devices [5], solar cells [6], because the energy gap of GaAsBi is much narrower than those of InGaAs, GaAsSb and various III–V compounds with the same strain due to lattice mismatch to GaAs. The band gap energy of GaAsBi alloy pseudomorphically grown on a GaAs(100) substrate is reduced at a rate of 86 meV/% with increasing the Bi composition in % [7], and also shows the temperature insensitivity [8, 9]. Increase of the valence band maxima of GaAsBi arises from an anti-crossing interaction between the valence band of GaAs and Bi resonant states which reduces the energy of the conduction band [10, 11]. The downward movement of the conduction band has also been demonstrated using room temperature photoreflectance spectra, which implies that GaAsBi/GaAs system has type I band configuration [12].

The growth of GaAsBi has proven complicated, requiring very low growth temperatures (\(< 400^\circ\text{C}\)) to incorporate significant fractions of Bi [7, 13]. The quality of GaAsBi is highly dependent on the Bi composition and the growth temperature. For particular growth condition, the flux also must be accurately controlled as a shortage of Bi may lead to surface roughness while excess Bi causes formation of Bi droplet [14]. Bismuth, which has an atomic mass number of 208, is the heaviest non-radioactive element in the periodic table. The Bi atom is approximately 25% larger in radius than Ga and As atoms, and tends to surface-segregate during growth [15], furthermore, improving the electronic properties of the material as a surfactant [16]. Hence, the composition of Bi in GaAs\(_{1-x}\)Bi\(_x\) is strongly dependent on the growth temperature and is determined by a more complicated mechanism than that of conventional III–V alloys, e.g., InGaAs or AlGaAs. In the growth of GaAsBi/GaAs/AlGaAs separate confinement heterostructures, the growth temperature of the top AlGaAs barrier is restricted by the growth of annealing temperature limits of the previous layers [17]. In this study, we grew GaAsBi/GaAs multi quantum wells (MQWs) sandwiched between AlGaAs layers by molecular beam epitaxy and investigated the dependence of x-ray diffraction spectrum and low temperature photoluminescence from MQWs on the growth temperature of GaAs layers with fixing the growth temperature of GaAsBi layers at 350°C.

II. EXPERIMENTAL

The GaAs substrate was etched by semico clean solution (Furuuchi Chemical Corp.) for 1 hr, transferred into an VG semicon V80H MK-III MBE system equipped with Ga, Al, As and Bi conventional K-cells. Beam equivalent pressures (BEPs) of Ga, Al, As and Bi were adjusted by an ion gauge as Ga flux 8.5 \(\times\) \(10^{-7}\) mbar, As4 flux 9.6 \(\times\) \(10^{-6}\) mbar, Bi flux 5.4 \(\times\) \(10^{-7}\) mbar and Al flux 1.9 \(\times\) \(10^{-7}\) mbar. The substrates were baked at a temperature of 400°C for 30 min, loaded into a growth chamber, and heated at 650°C for 5 min to remove the native surface oxide. A schematic illustration of the sample structure is shown in the Fig. 1. The samples comprise a 160 nm GaAs buffer grown at 580°C, followed by 112-nm AlGaAs layer grown at 640°C, 3 (3.5) alternating layers of 8.8-nm GaAs at \(T_{\text{GaAs}} = 350\) (450, 500, 550, and 600)°C and 5.6-nm GaAsBi at the growth temperature of GaAsBi, \(T_{\text{GaAsBi}} = 350\)°C, and 112-nm AlGaAs layers were stacked at 640°C with a 24-nm GaAs cap layer grown at 580°C. For the growth of the sample with 3.5 alternat-
FIG. 1. Schematic structure of GaAsBi/GaAs multi quantum well (MQW) sample.

FIG. 2. XRD spectra from (100) GaAs/GaAsBi MQW dependent on growth temperature of GaAs layers.

High-resolution x-ray diffraction (HRXRD) was measured by a Phillips X’Pert Pro Materials Research Diffractometer with an incident x-ray beam wavelength of CuK\(_\alpha\) (\(\lambda = 0.15406 \text{ nm}\)). The samples were mounted on a computer controlled goniometer stage. The XRD scans were then fitted using Epitaxy software to determine the Bi composition and the epilayer thicknesses assuming a GaBi lattice constant of 6.324 Å [18].

The optical properties of the sample were characterized by low-temperature (13 K) photoluminescence (PL) spectroscopy. The wavelength of an excitation laser was 442 nm (He-Cd laser, 10 mW) and focused on a sample surface area of about 200 \(\mu\)m diameter.

III. RESULTS AND DISCUSSION

Figure 2 shows the x-ray diffraction patterns of \(\theta-2\theta\) scans from reflection obtained from GaAsBi/GaAs MQWs grown at \(T_{\text{GaAs}} = 350 - 600^\circ\text{C}\). The sharp and largest peak located at 0 arcsec in each diffraction pattern corresponds to the diffraction from the GaAs buffer layer and substrate. The 2nd and 3rd largest peaks near -200 arcsec in diffraction patterns from MQW samples grown at \(T_{\text{GaAs}} = 350\) to 550°C is from the double AlGaAs epilayers and the two peaks are joined into a single peak in the diffraction patterns from MQWs grown at \(T_{\text{GaAs}} = 600^\circ\text{C}\) due to lateral fluctuation of the layer thickness caused by surface and interface roughness. Peaks from the GaAsBi/GaAs alternating layers are labeled by -3\(^\text{rd}\) to 1\(^\text{st}\), as usually done in x-ray diffraction patterns from a superlattice structures. The 0th peak labeled in the XRD spectra is a main peak and its diffraction angle position is determined by the average Bi composition of overall GaAsBi/GaAs layers. The others are satellite peaks and their angle position spacing is given by the period of the GaAsBi/GaAs alternating layers. A striking difference between diffraction patterns from samples grown at \(T_{\text{GaAs}} = 350^\circ\text{C}\) and 450°C is those peak positions and intensity. The -2\(^\text{nd}\), -1\(^\text{st}\), and 0th peak are observed at -3600, -2200, -800 arcsec in the diffraction pattern from the sample grown at \(T_{\text{GaAs}} = 350^\circ\text{C}\). For the sample at \(T_{\text{GaAs}} = 450^\circ\text{C}\), those peaks are shifted by 500 arcsec to the higher angle side, indicating reduction of the averaged Bi composition [7]. The diffraction pattern from the sample grown at \(T_{\text{GaAs}} = 500^\circ\text{C}\) is almost the same as that from the sample at \(T_{\text{GaAs}} = 450^\circ\text{C}\). For the sample grown at \(T_{\text{GaAs}} = 550^\circ\text{C}\), the satellite peaks are observed at 200 arcsec higher angles compared to the samples at \(T_{\text{GaAs}} = 450\) and 500°C. It shows 550°C sample has a slightly smaller Bi composition than 450 and 500°C samples. Although the sample grown at \(T_{\text{GaAs}} = 600^\circ\text{C}\) shows much smaller satellite peak intensity comparing to other patterns, their positions are almost the same as the sample grown at \(T_{\text{GaAs}} = 550^\circ\text{C}\) indicating the same Bi composition in the MQW.

Experimental and simulated curves of XRD for the sample grown at \(T_{\text{GaAs}} = 350^\circ\text{C}\) are shown Fig 3. In the simulation the Bi composition of the GaAsBi layers is 7% where it is assumed that all Bi atoms are uniformly contained in GaAsBi layers and there are no Bi atoms in GaAs layers. The simulated curve well reproduces the
The Bi composition of the GaAsBi layers is plotted in blue square as a function of the growth temperature of GaAs. The Bi Composition was determined by XRD simulation to reproduce the satellite peak position based on a structure where GaAsBi layers have all Bi atoms and uniform Bi composition. The beam equivalent pressure of Bi atoms supplied from the K-cell at 350 °C is \(1.0 \times 10^{-10}\) mbar and is smaller by 3 orders of magnitude than that at 610 °C \((5.4 \times 10^{-7}\) mbar\). It implies that 67% of Bi atoms were evaporated during growth of the GaAsBi layer at 350 °C were segregated and were incorporated into the successive GaAs layer grown at \(T_{GaAs} = 350^\circ C\). The vapor pressure of Bi from the K-cell is a good guide indicator to consider the evaporation of Bi atoms from the surface. The beam equivalent pressure of Bi atoms supplied from the K-cell at 350 °C is 1.0 \(\times\) 10^{-10} mbar and is smaller by 3 orders of magnitude than that at 610 °C \((5.4 \times 10^{-7}\) mbar\). It implies that 67% of Bi atoms were evaporated during growth of the GaAsBi layer at 350 °C were segregated and were incorporated into the successive GaAs layer grown at \(T_{GaAs} = 350^\circ C\). When the sample was grown at \(T_{GaAs} = 450\) or \(500^\circ C\), 50% of them evaporated and 17% were incorporated into GaAs. In the analysis, we consider the difference of the structure of samples. The result may suggest that substrate temperature range from 450 to 500 °C, Bi atoms bound to Ga atoms remain on the surface, while the Bi atoms bound to a Bi or As atoms are desorbed due to small bond strength. The Bi atoms bound to Ga atoms evaporate higher than 550 °C, all of segregated Bi atoms cannot remain on the surface. We also should consider interdiffusion of As and Bi atoms in the analysis. Makholoufi, however, reported that there is no out-diffusion of Bi atoms from GaAsBi layer to the GaAs layer up to 650°C [19].

Low temperature \((13\) K\) PL spectrum from each sample is shown in Fig. 5. The main peak of the PL spectra from the samples was observed from 1069 nm to 1116 nm and their full width at half maximum (FWHM) was 70 meV except for the sample \(T_{GaAs} = 600^\circ C\) (FWHM = 90 meV) [7]. The GaAsBi/GaAs MQW sample grown at \(T_{GaAs} = 550^\circ C\) has the longest PL peak wavelength and its value is \(\lambda = 1116\) nm (the value of photon energy is \(h\nu = 1.111\) eV). Even though the tremendous reduction of Bi incorporation into GaAs layers was observed due to increase of \(T_{GaAs}\), small change of the emission wavelength or red shift of the PL emission implies that the GaAsBi/GaAs MQW has the type II band configuration. The luminescence is generated by the recombination of the electrons and holes accumulated in different layers due to wavefunction penetration. If the GaAsBi/GaAs MQW has the type I band, reduction of Bi incorporation into the GaAs layer causes large blue shift in PL spectra.

Figure 6 shows a schematic illustration of band configuration of both samples grown at \(T_{GaAs} = 350^\circ C\) and at \(T_{GaAs} = 550^\circ C\). In the figure, we omit the GaAs layer between the GaAsBi layer and the AlGaAs layer for the sample grown at \(T_{GaAs} = 550^\circ C\) for the simplicity. A large valence band offset and small and negative conduction band offset are expected because a Bi atom has higher s-orbital and p-orbital energies than an As atom. Holes...
are confined in the GaAsBi layer, and electrons are in the GaAs layer. For the sample grown at $T_{GaAs} = 350^\circ C$, the 1st GaAs layer which is located in the substrate side does not have Bi atoms. On the other hand, 2nd and 3rd GaAs layers were grown after the growth of the 1st and 2nd GaAsBi layers, respectively. Therefore segregated Bi atoms are incorporated into 2nd and 3rd GaAs layers. The incorporation of Bi changes the bandgap energy and raises the energy level of conduction electron in the 2nd and 3rd GaAs layers. Origin of the two peaks observed in the PL spectrum from the sample grown at $T_{GaAs} = 350^\circ C$ in Fig. 5 is reasonably explained. The main peak comes from the transition between the electron states in the 1st GaAs layer to the hole states in the 1st GaAsBi layer. The small peak observed in the shorter wavelength side of the main PL peak corresponds to the transition from the ground state of electrons in the 2nd and 3rd GaAs layers to the ground state of holes in the GaAsBi layers. Small intensity of the shorter wavelength peak is due to the reduction of overlap between wavefunctions of the electrons and holes. On the other hand, the three GaAs layers of the sample grown at $T_{GaAs} = 550^\circ C$ do not contain Bi atoms and PL shows the single peak. This result indicates that we have realized GaAsBi/GaAs MQW without Bi incorporation into GaAs layers and with good optical quality. The band configuration of GaAsBi/GaAs is highly controversial. Tight binding band calculation of GaAsBi based on photoreflectance result suggests that GaAsBi/GaAs has the type I band configuration [20, 21]. Very short decay time (70 ps) obtained by time resolved PL for a single 7.5-nm-thick GaAsBi QW at RT implies that it may have the type I band configuration. In contrast to type-I semiconductor structures, the energy minima for electrons and holes lie in different layers in type II semiconductor structure. The defining feature of the type-II quantum well is the spatial separation of electron and hole confinement in the epitaxial growth direction at low temperatures. To determine the type of band configuration by PL measurement, photoexcited carrier densities of electrons and holes must be enough small to keep the flat band and also a sample must be at low temperature not to detect photons from the inner layer transition between thermally excited electron and holes. Actually the type II to type I transition was observed in GaAs/GaAsSb system with increasing photoexcitation power [22, 23]. On the other hand, there are reports which interpret that luminescence from a single GaAsBi/GaAs QW consists of lower energy photons due to localized electron hole pairs and higher energy photons from the band edge transition [24, 25]. For the evaluation of the band configuration of GaAsBi/GaAs, we prepared GaAsBi/GaAs MQW consisting of less than 10 nm thick layers and abrupt interface where electrostatic potential produced by charge separation and accumulation is not large and spatially separated electron and holes are recombined using the overlap of their wavefunctions which penetrate through interface and barrier potential. The GaAsBi/GaAs MQW grown by Authors has a suitable structure for determining band configuration and measurement of PL was carried out at low temperature (13 K) under a low power excitation (10 mW, 442 nm).

IV. CONCLUSIONS

Molecular beam epitaxial growth of GaAs$_{0.97}$Bi$_{0.03}$/GaAs (5.6 nm/8.8 nm) MQW on a (100) GaAs substrate with changing the growth temperature of the GaAs layer from $T_{GaAs} = 350$ to 600°C was investigated. The Bi atoms remain on the growing surface during growth of both GaAsBi and GaAs layers at a low temperature growth of 350°C. Analysis of the XRD spectrum of each sample revealed not only the amount of Bi atoms segregated during growth of GaAsBi at 350°C and also the amount of Bi atoms evaporated with increasing the substrate temperature prior to the growth of GaAs layer. We have realized the GaAsBi/GaAs MQW without incorporation of Bi into the GaAs layers and with good optical quality. It was confirmed that GaAsBi/GaAs has the type II band configuration.

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