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Near infrared photoluminescence observed in dilute GaSbBi alloys grown by liquid phase epitaxy

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ABSTRACT

We report the first observation of photoluminescence (PL) from the dilute bismide alloy GaSbBi. Epitaxial layers are grown by liquid phase epitaxy technique onto GaSb (1 0 0) substrates and PL is obtained in the near infrared spectral range ($\lambda \sim 1.6$ μm). Incorporation of 0.2, 0.3 and 0.4 at% Bi to the layer results in a decrease of band gap energy up to 40 meV as well as an increase of luminescence from the sample. Structural analysis confirms the successful incorporation of Bi consistent with an increase in lattice parameter. Raman spectroscopy measurements indicate vibrational modes due to GaBi as well as to free Bi atoms residing at interstitial spaces.

1. Introduction

Bismide semiconductors such as $GaSb_{1-x}Bi_x$ are formed by the introduction of small quantities ($x \sim 0.01$) of Bi into the parent III–V lattice, resulting in a large reduction in the band gap [1]. These materials are potentially important for the development of infrared sources and photodetectors operating in the technologically important near and mid-infrared spectral range. The bismides are similar to the well known dilute III–V-nitrides [2]. However, there are some important differences between these two material systems [3,4]. In case of dilute nitrides, nitrogen forms an isolated impurity level within the conduction band which is resonant with the bottom of the conduction band together with a number of N–N pair states. The resonant interaction of the nitrogen level with the conduction band minimum introduces large band gap bowing and a lowering of the conduction band minimum [5]. In a similar way, it has been theoretically predicted [3] and experimentally found [6] that Bi forms an isolated energy level which is resonant with the valence band maximum resulting in an upward movement of the same. Although the band gap reduction of GaAs due to Bi is reported to be smaller (88 meV/% Bi) than that due to nitrogen (about 200 meV/% N), bismides potentially offer two distinct advantages over dilute nitrides. One is a relatively temperature independent band gap [7] which offers the possibility of developing laser diodes with temperature insensitive emission wavelengths. The other is that in contrast to dilute nitrides, where the electron mobility of the material is greatly degraded by N, the degradation of mobility with Bi addition is only marginal [8]. Most research to date has concerned GaAsBi which has been grown by molecular beam epitaxy (MBE) [9–13] and metalorganic vapor phase epitaxy (MOVPE) [7,14,15] for applications in near and mid-infrared light emitters. Growth of InAsBi [16] and InSbBi [17] by MOVPE has been reported for longer wavelength applications. Feng et al. [18] reported the growth of InGaAsBi lattice-matched to InP substrates by MBE for the fabrication of temperature-insensitive lasers for fiber-optic communications. Yoshimoto et al. [19] used co-doping to obtain GaNAsBi alloys, grown on GaAs substrates. However, to our knowledge there are no reports of the epitaxial growth of GaSbBi. Although the growth of dilute bismides has so far been realized by using either MBE or MOVPE, the simpler liquid phase epitaxy (LPE) technique is an attractive alternative. In this work we report on the near infrared photoluminescence of as-grown GaSbBi layers containing up to 0.4 at% Bi and which exhibit a bandgap reduction of 40 meV.

2. Growth of GaSbBi layers

The GaSbBi epitaxial layers were grown in a horizontal sliding boat LPE reactor using a high purity graphite boat and a semi-transparent gold furnace. Pure Ga (99.9999%) was loaded into the boat and baked at 800 °C for 10 h under Pd-diffused hydrogen flow to reduce any oxides and other volatile impurities in the metal. The purified Ga solution was then saturated with Sb by placing it in contact with an undoped GaSb sacrificial substrate wafer for 1 h

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at 500 °C. The resulting growth solution was then subjected to a further bake at 750 °C for 4 h. Prior to growth, the required amount of pure Bi (99.9999% granules obtained from Azelis France), was added to the growth melt. The addition of Bi was found to increase the liquidus temperature of the melt which was determined by visual observation through the semi-transparent shield of the gold furnace. After loading the GaSb substrate the temperature of the melt was raised to 20 °C above the saturation temperature and held there for 15 min for homogenisation. The temperature of the melt was then reduced at 0.4 °C/min until the liquidus temperature was reached and then the cooling rate was reduced to 0.2 °C/min. Growth was carried out for 5–10 min using a supercooling of 5–6 °C. Bi contents of up to 0.8 at% in the melt were used. A GaSb control sample (produced without any Bi in the melt) was grown at 490 °C for 8 min for comparison.

3. Characterization

The thickness of the resulting GaSbBi epitaxial layers was in the range 4–5 μm as measured from cleaved cross-section using a Nomarski phase contrast microscope with a calibrated eyepiece. The layers exhibited abrupt planar interfaces and apart from a few Ga inclusions, the surfaces were mirror-smooth and shiny in appearance. The presence of Bi in the grown layers was confirmed by energy dispersive X-ray (EDX) measurements using a scanning electron microscope. High resolution X-ray diffraction (HRXRD) measurements were done in a PANanalytical X-Pert Pro diffractometer using Cu Kα radiation. Photoluminescence (PL) measurements were done on each of the layers in the range 4–300 K using a continuous flow He cryostat. An Ar^+ ion laser was used for excitation (20 W/cm^2 at the sample) and the luminescence was analyzed through a 0.3 m monochromator and detected with a 77 K InSb detector and a lock-in-amplifier. Raman spectroscopy measurements were done on the GaSbBi samples at Indian Institute of Technology, Kharagpur using a Horiba Jobin Yvon micro Raman spectroscopy unit with a 1024 × 256 pixel CCD detector and a single monochromator.

4. Results and discussions

Fig. 1 shows the EDX spectrum from a bulk GaSbBi epitaxial layer obtained using 0.8 at% Bi in the growth solution. Distinct peaks due to Ga, Sb and Bi are clearly observed in the spectrum confirming the incorporation of Bi in the layer. The HRXRD curve for one of the GaSbBi samples (GSBI5B) is shown in Fig. 2 and

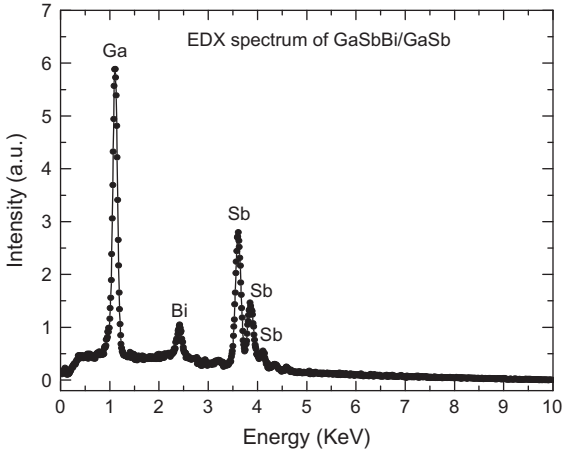

Fig. 1. EDX spectrum for LPE GaSbBi.

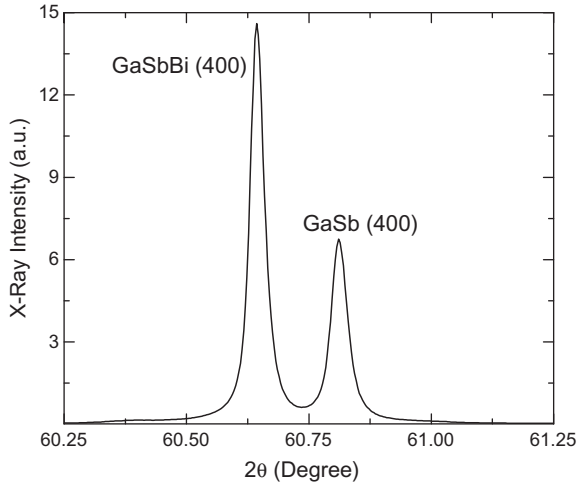

Fig. 2. HRXRD rocking curve for LPE GaSbBi on GaSb substrate.

exhibits two sharp peaks corresponding to lattice constants of 6.0953 Å and 6.1107 Å associated with the substrate and the GaSbBi epitaxial layer respectively and corresponding to a net lattice mismatch of 0.25%. The composition was determined as $GaSb_{0.996}Bi_{0.004}$ assuming Vegard's law is valid over the composition range of interest. The diffraction peak from the GaSbBi epitaxial layer is as sharp as the substrate peak and is narrower compared to MBE and MOVPE grown III–V-bismides [12,15,20] indicating that LPE grown GaSbBi has good crystalline perfection.

Fig. 3 shows the 4 K PL spectra for three GaSbBi samples as-grown from melts containing 0.2, 0.5 and 0.8 at% Bi. (Corresponding to 0.2, 0.3 and 0.4 at% Bi in the solid alloy respectively). Each epitaxial layer had a mirror-like surface and a thickness ~5 μm. PL from a GaSb control sample grown without any Bi is also shown for comparison. The as-grown GaSb exhibits a single peak labelled 'A' at 0.794 eV which is characteristic of near band edge (bound exciton) recombination [21]. GaSbBi layers grown with 0.2 and 0.5 at% Bi in the melt, exhibit a lower energy peak 'B' in addition to the band edge emission peak A which shifted to lower energies with increase of Bi in the growth melt. A further increase of Bi in the melt to 0.8 at% produced a single broad peak which has been resolved into individual peaks A and B by Gaussian deconvolution. The resolved peak A appears at an energy of 0.754 eV corresponding to a band gap reduction of 40 meV. Fig. 4 illustrates the varia-

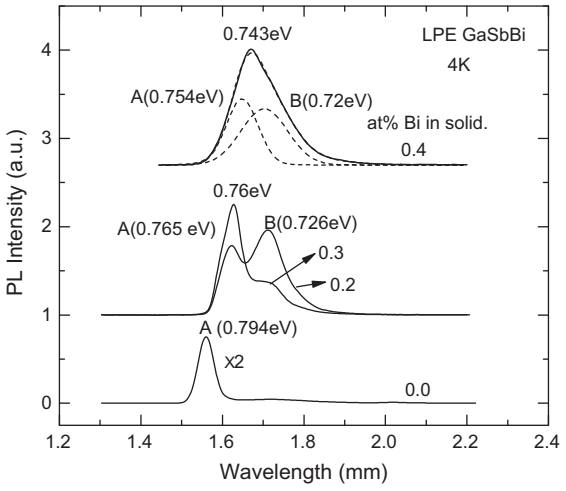

Fig. 3. 4 K PL spectrum for GaSb and GaSbBi with Bi content of 0.2, 0.3 and 0.4 at.%.