Strong band gap narrowing in quasi-binary \((\text{GaSb})_{1-x}(\text{InAs})_x\) crystals grown from melt

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Abstract

Large crystals of a quasi-binary semiconductor alloy \((\text{GaSb})_{1-x}(\text{InAs})_x\) with \(x = 0.02–0.05\) have been grown from melt for the first time. The family of quasi-binary crystals \((\text{GaSb})_{1-x}(\text{InAs})_x\) grown and reported here are different from the conventional \(\text{Ga}_{1-x}\text{In}_x\text{As}_y\text{Sb}_{1-y}\) quaternaries due to growth behavior and physical properties. Significant narrowing of the band gap was observed in these crystals compared to the conventional quaternary \(\text{Ga}_{1-x}\text{In}_x\text{As}_y\text{Sb}_{1-y}\) (with \(x = y\)). With an InAs content of about 2–5 at\%, band gaps in the range of 0.6–0.65 eV have been demonstrated. The possible origins of the band gap narrowing (i.e., high bowing parameter) include chemical and structural alterations in the grown crystals, resulting from the association of Ga–Sb and In–As in the melt.

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1. Introduction

The demand for bulk semiconductor crystals with band gap in the range of 0.45–0.60 eV is increasing for several applications involving low cost thermophotovoltaic generation of electricity [1]. This range of band gap can be realized in III–V ternary alloys like \(\text{In}_x\text{Ga}_{1-x}\text{Sb}\), \(\text{In}_x\text{Ga}_{1-x}\text{As}\) and \(\text{InAs}_y\text{P}_{1-y}\) [2]. The antimonide based system (In-GaSb) is preferred over the arsenic and phosphorus counterparts due to extremely low partial vapor pressure of antimony [3]. However, melt-grown InGaSb crystals exhibit a high density of cracks [4] due to: (i) large lattice mismatch between InSb and GaSb, and (ii) segregation of InSb during growth due to wide separation between the liquidus and solidus curves in the pseudo-binary phase diagram of the GaSb–InSb system [5]. These features make the growth of single crystals of ternary alloys from the melt extremely difficult. The lattice mismatch also hinders the use of binary seeds like GaSb, InAs, or InSb for single crystal growth. Lattice
matching to GaSb or InAs can be achieved by incorporating arsenic to form GaInAsSb quaternary alloys. However, miscibility gaps in the pseudo-quaternary systems and phase separation are the main obstacles for quaternary alloy solidification from melts [6—9]. These arise mainly from differences in chemical interaction between the constituent elements in the melt [8]. In the present studies, it has been experimentally demonstrated that bulk crystals of GaInAsSb, having high crystalline perfection, can be grown from the melt preferentially containing two binaries GaSb and InAs [10]. The family of quasi-binary crystals \((\text{GaSb})_{1-x}(\text{InAs})_x\) grown and reported here are different from the conventional \(\text{Ga}_1-x\text{In}_x\text{As}_y\text{Sb}_{1-y}\) quaternaries due to growth behavior and physical properties [10]. The reported experiments show a significant “band gap narrowing” in this melt-grown quasi-binary compared to any random quaternary having the same composition. In this letter, the focus is on the band gap narrowing phenomenon, which is postulated to arise from certain structural effects in the melt grown quasi-binary, different from that in the random quaternary alloys.

### 2. Experimental details

The quasi-binary \((\text{GaSb})_{1-x}(\text{InAs})_x\) alloys were synthesized from pre-compounded InAs and GaSb [10]. Synthesis was carried out in a multi-zone Mellen furnace [11] (vertical Bridgman set-up) in 20 and 32 mm diameter silica crucibles from pre-synthesized GaSb and InAs freshly etched with CP4 etchant \((\text{CH}_3\text{COOH} : \text{HF} : \text{HNO}_3 \text{ in } 3 : 3 : 5 \text{ by volume})\). Melt encapsulation was provided by boric oxide \((\text{B}_2\text{O}_3)\) or alkali halide salt eutectics \((\text{LiCl} – \text{KCl} \text{ and NaCl} – \text{KCl})\). Boric oxide encapsulation was found to be more satisfactory and suitable (due to extremely low vapor pressure and high viscosity) for inhibiting volatilization from the melt surface. The growth chamber was usually pressurized to slightly more than 1 atm by argon gas to prevent decomposition of the InAs. If the melt is not pressurized properly, the compounds decompose, and consequently form GaAs and InSb rich phases upon solidification. GaAs and InSb have a significantly different lattice constant. Therefore, the quality of the grown crystals will be poor. Synthesis was done at various temperatures in the range of 712–945°C, corresponding to the melting points of GaSb and InAs, respectively. After synthesis, the crucible was lowered at a constant rate of 3.3 mm/h through a temperature of 15–20 K/cm. At the end of solidification, the furnace was cooled down slowly to room temperature over a period of several hours. Crystal growth was performed without seed, either in flat bottom or conical tipped crucibles using the conventional vertical Bridgman technique [3,4].

After the growth, the ingots were sliced parallel to the growth axis to evaluate the structural and compositional properties. The composition of the grown crystals \((\text{Ga, In, As, Sb})\) was evaluated by electron probe micro-analysis (EPMA) measurements in a JEOL 733 electron microprobe set-up. The standards used were InAs, GaAs, GaSb, and InSb single crystal substrates. Corrections for atomic number \((Z)\), self-absorption \((A)\) and fluorescence \((F)\) effects \((ZAF\) corrections) were performed by employing the commercial software SCOTT-I. Composition error was in the order of 2–3% of the measured values. For example, if the measured composition of indium is 5 at%, the error in determination is \(\sim 0.1\) at%. The microstructures of the crystals were studied through scanning electron microscopy (SEM) in the EPMA set-up. Room temperature fourier transform infrared spectroscopy (FTIR) measurements were carried out to determine the band gap energy. The resolution of the FTIR set-up was 0.5 meV.

### 3. Results and discussion

The grown crystals contained several large grains, were single phase in nature, and compositionally homogeneous. These quasi-binary crystals of \((\text{GaSb})_{1-x}(\text{InAs})_x\) have crystalline and chemical perfection significantly better (e.g., no cracks observed) than ternary crystals of \(\text{Ga}_1-x\text{In}_x\text{Sb}\) [10]. This result is obtained because the lattice mismatch of the two compounds (GaSb and InAs) which constitute the quasi-binary alloys is about 10 times smaller than lattice mismatch between the
compounds which constitute the ternaries (GaSb and InSb). Moreover, unlike the quaternary Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ crystals grown from various combinations of elemental and compounded sources, the quasi-binary crystals grown from GaSb and InAs showed no evidence of phase separation or multiple phase formation [10].

Fig. 1a and Fig. 1b, show the transmission spectra of typical quasi-binary samples with an InAs content of $\sim$3 and 5 at%, respectively. For comparison, the transmission spectrum of a pure GaSb crystal is shown in Fig. 1c.

Fig. 2a shows the room temperature band gap $E_g(x)$ of the quasi-binary crystals (full circles, measured using FTIR) along with published data Ref. [12] on Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ quaternary epi-layers lattice matched to GaSb (open squares). It is clearly evident from the figure that the present experimental data ($E_g$) of melt-grown quasi-binary significantly deviates from that expected in quaternary Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ with $x = y$. Several approaches were employed to theoretically estimate the band gap of the quasi-binary using existing schemes in the literature for quaternary alloys as discussed below.

The lowest direct band gap ($E_g$) in disordered isovalent ternary III–V alloys exhibits a deviation from linearity (bowing) as the composition is varied [13–15]:

\[ E_g(x) [\text{eV}] = xE_{1g} + (1-x)E_{2g} - bx(1-x), \]

where $E_{1g}$ is the band gap at $x = 1$, $E_{2g}$ is the band gap at $x = 0$ and the composition independent constant “$b$” is the bowing parameter accounting for

\[ \text{% } \text{Transmittance} \]

\[ \text{\lambda(\mu m)} \]

Fig. 1. FTIR of (a) Quasi-binary (GaSb)$_{0.97}$ (InAs)$_{0.03}$, (b) (GaSb)$_{0.95}$ (InAs)$_{0.05}$ and (c) GaSb crystals at 300 K. The samples thicknesses were $\sim$ 1 mm.
Fig. 2. (a) Band gap versus composition of quaternary Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ and quasi-binary (GaSb)$_{1-x}$(InAs)$_x$ at 300 K; (●) the experimental data of quasi-binary (GaSb)$_{1-x}$(InAs)$_x$; (○) the experimental data of DeWinter et al. [12] on quaternary Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$; (b) Various lines indicate: Eq. (2) for Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ latticed matched to GaSb, Eq. (3) for Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ lattice matched to InAs, and Eq. (4) for (GaSb)$_{1-x}$(InAs)$_x$ quasi-binary.

the nonlinearity. To reconstruct the energy band gap surface of quaternary alloys from the four ternary boundaries, various averaging schemes were proposed. These include: (a) Monte Carlo methods [16], (b) solution of Laplace's equation [17], and (c) geometrical averaging of the four ternary band gaps weighted by composition [18]. Moon et al. [19] proposed an approach based on combining the bowing caused by changes in the two sublattices (III and V). Their equation for quaternary $E_g(x,y)$ is a weighted average of binary $E_g$'s with two additional terms, each representing the average bowing, weighted by composition, on one of the sublattices. However, all the above approaches [16–19] were found to be inadequate to fit the complex quaternary band gap surface and could not provide a satisfactory agreement with the experimental data [12,20–27].

Karouta et al. [23] could fit the experimentally determined band gaps for Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ lattice matched to GaSb (see Fig. 2b) using the form of Eq. (1):

$$E_g(x) = 0.725(1 - x) + 0.290x - 0.6x(1 - x) \quad \text{at } 300 \, \text{K}. \quad (2)$$

Similar fit for Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$ lattice matched to InAs (Fig. 2b) was made by Voronina et al. [27]:

$$E_g(x) = 0.36x + 0.67(1 - x) - 0.54x(1 - x) \quad \text{at } 300 \, \text{K}. \quad (3)$$

Such an approach was also employed by Nahory et al. [28] for the GaInAsP system lattice matched to InP. Thus, one can conclude that any two points on the quaternary surface could be well fitted by a quadratic equation form (Eq. (1)). This approach has been employed in this work for the quasibinary GaSb–InAs system. As depicted in Fig. 2b, the $E_g(x)$ of quasi-binary could be fitted using the quadratic equation form:

$$E_g(x) = xE_g(\text{InAs}) + (1 - x)E_g(\text{GaSb}) - bx(1 - x) \quad \text{at } 300 \, \text{K}. \quad (4)$$

with a bowing parameter of $\sim 1.5$. The possible origin of such a strong and anomalous band gap narrowing (high bowing parameter) is discussed below.

The fact that quasi-binary crystals have band gaps significantly lower than the quaternaries
indicates that alterations in the band structure are produced as a result of solidification from the melt containing molecules of two binaries with similar lattice constant. The origin of these alterations causing high bowing is not well understood. The electronic structure of substitutionally random alloys is expected to be different from what a Virtual Crystal Approximation (VCA) would predict because of (1) a chemical perturbation, associated with an electronic mismatch between atoms, and (2) structural perturbation (positional relaxation) induced by a size mismatch between the atoms [29].

Band gap narrowing due to spontaneous long range ordering of the otherwise disordered isovalent semiconductor alloys has been recently observed in numerous III–V alloys systems exhibiting the CuAu–I, CuPt, and chalcopyrite structures [30–35]. The phenomenon of ordering readily occurs for alloys with composition ratios close to 50/50. Ordering has also been observed in dilute alloys of InAs$_{1-x}$Sb$_x$ grown by molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD) techniques [36]. Ordered domains (CuPt-type) in a disordered matrix are responsible for the band gap narrowing in the InAsSb dilute systems [36].

From transmission electron microscopy studies, no such ordering effects could be observed in the present quasi-binary crystals. On the other hand, the (GaSb)–(InAs) alloy system and the present preparation technique are unique in several ways, which tends to impose certain structural effects. The close lattice parameter between GaSb and InAs would imply no elastic driving force for ordering, while lowering the free energy to form a two phase mixture [35]. Because of the close physical properties (lattice parameter) of InAs and GaSb, even a two phase mixture will be homogeneous on a macroscopic scale. This is possible since the melt was experimentally monitored (in a careful fashion) to possess considerable association of Ga–Sb and In–As. Any breakage of bonds would result in a general random multiphase alloy as discussed earlier. The large bowing in the quasi-binary is probably due to alterations in the local bond structures between the Ga–Sb and In–As.

4. Conclusions

In conclusion, (GaSb)$_{1-x}$(InAs)$_x$ quasi-binary semiconductor bulk crystals with $x = 0.02–0.05$ having crystalline and chemical perfection comparable to binary III–V compounds were produced for the first time by melt solidification. Significant optical band gap narrowing was observed in these crystals than in conventional quaternary alloys (Ga–In–As–Sb). Due to the band gap narrowing effects, dilute alloys of quasi-binary can give the same band gap as the concentrated alloys of ternary. This is technologically important as the low solute content (in the quasi-binary) automatically leads to improvement in structural properties of the crystals and hence would improve the performances of devices fabricated on them.

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