Liquid phase epitaxial growth of lattice mismatched InSb, GaInAs and GaInAsSb on GaAs substrates using a quaternary melt

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Abstract

We have developed and established a unique technique for growing highly lattice mismatched ternary and quaternary compounds on binary substrates using a quaternary melt thermo-chemistry. In this technique, growth is initiated from a pseudo-quaternary melt on compatible substrates. Growth of GaInAs, InAsSb, GaInAsSb and InSb epilayers on GaAs has been achieved using In–Ga–As–Sb melts. The grown epilayers have a uniform composition and are very thick (> 100 µm). Between the GaAs substrate and the uniform composition epilayer, there exists a graded composition quaternary which is found to be extremely beneficial in relieving misfit. No specific efforts were made to change growth conditions (during epi-growth) to compositionally grade the buffer layers. Hence, this growth scheme is extremely simple to implement and can be used for the growth of a variety of alloy semiconductors by appropriately selecting the growth temperature and melt composition. One of the key highlights of this work is the growth of In$_{x}$Ga$_{1-x}$As$_{y}$Sb$_{1-y}$ epilayers with cut-off wavelength of 10 µm on GaAs substrates. This paper will discuss the melt thermo-chemistries and the process for this new epilayer growth method.

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1. Introduction

Substrates of III–V compound semiconductors with variable band gaps and lattice constants are desirable to obtain high performance electronic and optoelectronic devices. Unfortunately at the present time, device grade, single crystal, substrates of only binary compounds (such as GaAs, InP, GaSb) with discrete energy band gaps and lattice constants are commercially available. Ternary and quaternary based devices are fabricated on thin epilayers grown by non-equilibrium techniques (from vapor or solid phases) on binary substrates using buffer layers [1–4]. A variety of techniques including step graded or linearly graded procedure and direct growth have been used for this purpose [1]. The first two approaches have two major disadvantages. First, these techniques produce a rough cross-hatched surface that is not suitable for submicron device fabrication. Second, these techniques are generally not suitable for material systems with lattice mismatch greater than 3% as the buffer layer thickness also increases proportionally. Direct growth has been investigated for systems with various amounts of lattice mismatches. For example, the InSb/GaAs system has a lattice mismatch of 14.6%. There have been reports of direct growth of InSb on GaAs by molecular beam epitaxy (MBE), chemical vapor deposition (CVD) and liquid phase epitaxy (LPE) [5] (and references therein). However, a large number of dislocation densities are observed in the grown layers (~10$^{12}$ cm$^{-2}$) [6]. Woodall et al. [7] observed that during MBE growth of these lattice mismatched compounds, a quaternary layer is produced in the interfacial region by a method similar to that in the LPE process.

Dutta and Miller [8] suggested quaternary isothermal phase diagrams for the Ga–In–As–Sb system. In this paper, we present the growth of InGaAs, InGaSb and InSb layers...
on GaAs using a buffer layer of the variable lattice parameter quaternary GaInAsSb using these phase diagrams. One of the interesting features observed in our growth experiments is the self-compositionally graded quaternary buffer layer between the substrate and the final layer of uniform composition. This growth process has many advantages: (a) the thickness of the layers is greater than 100 μm with high growth rates (~100 μm/h), which is impossible to obtain using MBE or MOCVD. This thickness is sufficient to eliminate the influence of the lattice mismatch leading to dislocation densities that are considerably lower than those observed in similar systems, (b) the cut-off wavelength of the layers does not change with thickness; i.e., the composition of the layers is constant in the growth direction, unlike in traditional solution based LPE grown layers and (c) using this technique the composition of the layers can be accurately controlled by choosing specific growth temperatures and melt compositions.

2. Experimental procedure

The growth setup used has been described in detail in previous papers [9,10]. Growth was initiated from a pseudo-quaternary melt comprising of binaries, InSb, GaSb and InAs on a binary substrate (GaAs in this case). For a desired epilayer composition, the growth temperature and starting melt compositions are determined using the quaternary phase diagrams [8,11]. The melt was homogenized for 3 h at the growth temperature using accelerated crucible rotation technique (ACRT) [13]. Growth was initiated by lowering the temperature of the melt at 1 °C/h for 1 h to crystallize approximately 100 μm thickness of the epilayer followed by rapid cooling to room temperature. An LiCl–KCl eutectic mixture was used as an encapsulant which also helps in desorbing oxide from the substrate and melt prior to growth [12]. During the entire growth process the melt was subjected to ACRT to prevent constitutional supercooling and the formation of inclusions at the growth interface. After the growth was completed, cross-sections were cut from the grown samples to observe the interface. Fig. 1(a) shows a schematic of the cross-section of the grown epilayers. The graded composition buffer layer is followed by a constant composition epilayer. The extra solidified melt is formed during the rapid cooling of the furnace at the end of the growth and can be removed by polishing. Several growth experiments were conducted using the same conditions to check the reproducibility of the composition in the uniform region of the epilayer. The Cameca SX-100 electron probe microanalysis (EPMA) instrument was used for the compositional analysis of the grown layers. The arrow in Fig. 1(a) shows the direction of a typical EPMA line scan. Point scans at random places in the epilayer were performed to confirm the compositional uniformity of the epilayer and for estimating the thickness of the uniform regions. The quantitative compositional analysis can be obtained with an accuracy of 0.01 wt%.

Beyond the uniform composition region, the EPMA scans were not continued since the growth was terminated and the melt rapidly cooled.

3. Results and discussion

Using a starting melt consisting of 80 mol% InSb and 15 mol% InAs, growth was performed at 800 °C. Fig. 1 shows the compositional profile of the epilayer grown along the growth direction. The composition of the final epilayer is In0.25Ga0.75As which remains constant for more than 100 μm. Between this thick epilayer of constant composition and the GaAs substrate, there exists a region of about 30 μm, where the composition slowly changes from GaAs to the final epilayer composition.

Growth of the quaternary transition region followed by the thick uniform composition epilayer can be modeled using the calculated phase diagram at 800 °C (Fig. 2) and the fact that this is an equilibrium growth technique. At the growth temperature, InSb melts to form a layer of melt on top of the substrate. At any given instant of time, there is a thin interfacial liquid region which is always in equilibrium with the substrate. This interfacial liquid is formed by the dissolution of Ga and As from the substrate. The composition of this liquid may be represented as point A.
on the phase diagram. This leads to the growth of a solid $A'$. However, due to mechanical mixing, this interfacial liquid is continuously diluted with In and Sb from the bulk. Hence, the composition of the interfacial liquid can be modeled to change continuously from $A$ to $B$ leading to the growth of a solid whose composition changes continuously from $A'$ to $B'$. At the same time, the InAs added to the melt also contributes to increasing the amount of As in the melt. This gradually changes the composition of the interfacial liquid to a point that lies at $C$ (for example) resulting in a change in the solid composition to $C'$. This process continues until the entire melt is well mixed and is in equilibrium with the substrate (of the last to freeze composition). This equilibrium composition may be represented by a point $D$. Melt with composition $D$ is in equilibrium with a solid of composition $D'$ and liquid of composition $D^*$. As growth continues, the solid composition remains at $D'$ and the liquidus composition moves along the tie line from point $D$ towards point $D^*$ until the melt composition reaches $D^*$ after which the growth stops. Hence, a epilayer of constant composition $D'$ is formed.

**Fig. 2** Calculated phase diagram of In–Ga–As–Sb system at 800 °C [8]. The dash-dotted tie lines ending in filled circles are experimental tie lines of Nakajima et al. [15].

**Fig. 3.** EPMA compositional profile of sample with In-rich epilayer composition $\text{In}_{0.8}\text{Ga}_{0.2}\text{As}_{0.12}\text{Sb}_{0.88}$ grown at 800 °C using a starting melt composition of 75 mol% InSb and 20 mol% InAs.

**Fig. 4.** EPMA compositional profile of sample with epilayer composition $\text{In}_{0.4}\text{Ga}_{0.6}\text{As}_{0.9}\text{Sb}_{0.1}$ grown at 600 °C using a starting melt of 100% InSb. This epilayer is found to have band gap and lattice parameter close to GaSb and InP, respectively.

Using similar thermo-chemistries and different growth temperatures and starting melt compositions, we can obtain a wide range of epilayer compositions. For example, using a growth temperature of 600 °C and a starting melt comprised of 100% InSb, a 60 μm constant composition...
epilayer of In$_{0.4}$Ga$_{0.6}$As$_{0.9}$Sb$_{0.1}$ with a graded composition quaternary buffer layer of 10 μm was obtained (Fig. 4). It should be noted that this epilayer has a band gap of 0.731 eV which closely matches the band gap of GaSb ($E_g = 0.726$ eV) and the lattice constant is found to be 5.859 Å, which is extremely close to that of InP ($a = 5.868$ Å).

Using a starting melt comprised of only InSb, at a growth temperature of 560 °C, a 100 μm epilayer of composition In$_{0.88}$Ga$_{0.12}$As$_{0.3}$Sb$_{0.7}$ was obtained (Fig. 5). The graded composition quaternary was only 10 μm thick. This epilayer has a band gap of 0.116 eV (corresponding to a cut-off wavelength of 10.7 μm). We have previously demonstrated the growth of similar long wavelength material at 540 °C with extremely low dislocation densities ~10$^5$ cm$^{-2}$ [10]. These long wavelength materials are suitable for use in infra-red (IR) optoelectronic, high speed electronic, and galvano-magnetic devices.

Our growth technique has been found to have various advantages over conventional epitaxy. The thicknesses of the epilayers grown using this technique are approximately 100 μm. This thickness of the epilayers is found to be sufficient to eliminate the influence of the lattice mismatch leading to dislocation densities that are considerably lower than those observed in similar systems. In our experiments, growth typically occurs during the first few hours of the temperature ramp down. After this the solvent becomes InSb rich due to the preferential segregation of the solute into the solid phase. Since, the thicknesses of our epilayers are greater than 100 μm, this implies that typical growth rates of the order of 0.1 mm/h. These growth rates are extremely high compared to the growth rates encountered in conventional epitaxial techniques like MBE and MOCVD and is also higher than that encountered during LPE (typical growth rates ~50–60 μm/h). Another advantage of our growth technique is that the cut-off wavelength of the epilayer does not change with thickness i.e., the composition of the epilayer remains constant in the growth direction. This is in contrast to LPE where growth is initiated from a supersaturated liquid of an element (Ga, In, Sn, etc.) and hence the composition changes continuously due to segregation.

4. Conclusions

We have developed and established a unique technique for growing highly lattice mismatched ternary and quaternary compounds on binary substrates using a new melt thermo-chemistry. In this technique, growth is initiated from a pseudo-quaternary melt on compatible substrates and can be used for the growth of a variety of alloy semiconductors by appropriately selecting the growth temperature and melt composition. Various compositions ranging from Ga-rich to In-rich Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ have been demonstrated. The grown epilayers have a uniform composition and are very thick (>100 μm). Between the GaAs substrate and the uniform composition epilayer, there exists a graded composition quaternary which is found to be extremely beneficial in relieving misfit. No specific efforts were made to change growth conditions (during epi-growth) to compositionally grade the buffer layers. Hence, this growth scheme is extremely simple to implement and can be used for the growth of a variety of alloy semiconductors by appropriately selecting the growth temperature and melt composition.

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