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Surface morphology, electrical and optical properties of gallium antimonide layers grown by liquid phase epitaxy

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Abstract

Liquid phase epitaxial (LPE) growth of gallium antimonide has been carried out employing equilibrium cooling, step cooling, supercooling and two phase solution growth techniques. An optimum temperature range of 500–550°C was found to be suitable for the growth of high quality layers. The morphology of layers grown by the first three techniques improved with increase in layer thickness. In contrast, better morphology was obtained for thin layers when grown from the two phase solution technique. While the equilibrium cooling technique gave a diffuse substrate–epilayer interface, sharp interfaces were obtained by the step cooling, supercooling, and two phase solution growth techniques. Photoluminescence spectroscopy and current–voltage measurements carried out on the grown layers revealed that the layers grown from Ga-rich melts exhibit superior optical and electrical properties as compared to those grown from Sb-rich melts.

1. Introduction

Gallium antimonide (GaSb) based compound semiconductors have received increasing attention recently because the corresponding wavelengths of their alloys cover a wide spectral range from 1.24 μm (AlGaSb or AlGaAsSb) to 4.3 μm (InGaAsSb). Consequently, they have turned out to be promising candidates for the application in long wavelength lasers and photodetectors for fibre optic communication systems [1]. Though in general, the liquid phase epitaxial (LPE) technique has been found to be versatile and hence widely used for the growth of compound semiconductor based structures [2], fabrication of GaSb-based devices using LPE has been carried out by relatively few workers, see Ref. [1], and references therein. LPE growth of GaSb is impeded due to the wetting problem of the substrate resulting from the fast oxidation of the GaSb surface [3-5]. This leads to bad surface morphology of the grown layers and in turn poor interface quality of the devices grown on them. We have overcome this problem to a large extent by properly selecting the growth temperature and the mode of growth. In this paper, we present detailed studies on the morphology of LPE grown GaSb at various temperatures from both Ga-rich and Sb-rich melts. The equilibrium cooling, step cooling, supercooling and the two phase solution techniques have been employed for growth. The electrical and optical properties of the grown layers are also discussed.

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2. Experimental details

LPE growth was carried out in a single-zone isothermal furnace in hydrogen atmosphere using the horizontal sliding boat technique. The boat was made from high purity graphite. Epitaxial layers were grown mostly on the (100) surface and a surface 7° off (111). Layers were also grown on (110) oriented substrates. The substrates used in our studies were prepared from bulk single crystals grown in our laboratory by the vertical Bridgman technique [6,7]. The wafers were mechanically and chemically polished to mirror finish. Prior to placing in the slider, the substrates were degreased, etched using a solution of $HF:HNO_3:CH_3COOH$ (1:19:30), dipped in HCl and rinsed in methanol. The dip in HCl helps in removing the oxide layer usually found after etching the samples. Both gallium and antimony rich solutions were used for growth. Weighed quantities of charges were cleaned and placed in the bins. The solution was baked for 15 hours in ultra-pure hydrogen atmosphere at 700°C. After baking, the furnace was cooled down and the substrate was inserted in the slider. Then the solution temperature was increased above the growth temperature and allowed to homogenize for an optimum period of 4 hours. The cooling rate employed in all our growth experiments was 0.3°C/min. After the growth, the furnace was moved out from the boat region by sliding it on rails thereby facilitating the cooling of the system at a faster rate. Both pure and doped (Te and Zn) layers were grown. The thickness of the epitaxial layer was measured from the freshly cleaved cross section by staining it in a solution of $H_2O:KOH:K_3Fe(CN)_6$ (20:1:1) for 3 minutes. Other staining solutions like $H_2O:HF:H_2O_2$ (20:2:1) or $HF:HNO_3:H_2O$ (13:20:17) at 40°C could also be used. The thickness was also determined from the gain in weight after growth. The surface morphology of the layers were examined using the Leitz-Orthoplan microscope in reflection mode. For the electrical characterization, ohmic contacts to p and n regions were provided by thermal evaporation of Au–Zn (98:2) and Au–Ge (88:12) eutectic mixtures, respectively, at 10^{-6} Torr followed by annealing at 300°C for 2 minutes. Photoluminescence spectroscopy (PL) was used to evaluate the optical properties of the grown layers. The PL measurements were carried out using a MIDAC Fourier transform photoluminescence spectrometer at 4.2 K. A resolution of 0.5 meV was used in our measurements. An argon ion laser operating at 5145 Å was used as the excitation source. A liquid nitrogen cooled Ge photodetector was used for signal detection.

3. Results and discussion

3.1. Surface morphology

Since the morphology of the grown layers did not show any dependence on the type of dopants incorporated, no specific mention of the layer type is made in the text hereafter.

3.1.1. Equilibrium cooling technique

The initial growth runs for optimizing the growth parameters were carried out with the equilibrium cooling technique. In this technique, after homogenization, the substrate was brought in contact with the melt and the temperature was ramped down. Growth was terminated by removing the substrate from under the melt. Fig. 1a shows the photomicrograph of the layer grown on a 7° off (111) misoriented surface from a Ga-rich melt at 350°C. The morphology of the grown layer reflects the poor quality of the layer. This is essentially due to the wetting problem leading to discontinuous growth with a large number of islands. With increase in growth temperature, the layer quality improved. The temperature at which high quality surfaces are obtained with mirror finish was found to be around 550°C (see Fig. 1b). With the optimum growth temperature of 550°C, if the growth was carried out on a (100) or (110) surface, the quality of the grown layers was even better as can be seen from Fig. 1c. The orientation dependence of the layer morphology is understandable as the surface atomic arrangements are different. Usually lamellar growth occurs on the misoriented (111) surfaces [8]. The lamellae are believed to correspond to coalesced low-index growth steps and the shape and spacing of the lamellae are determined by the magnitude of the misorientation from the ⟨111⟩ polar axis.

Growth from Sb-rich melts resulted in inferior surface morphology to those grown by Ga-rich melts at all growth temperatures and irrespective of the substrate orientation. A large number of ridges and islands were

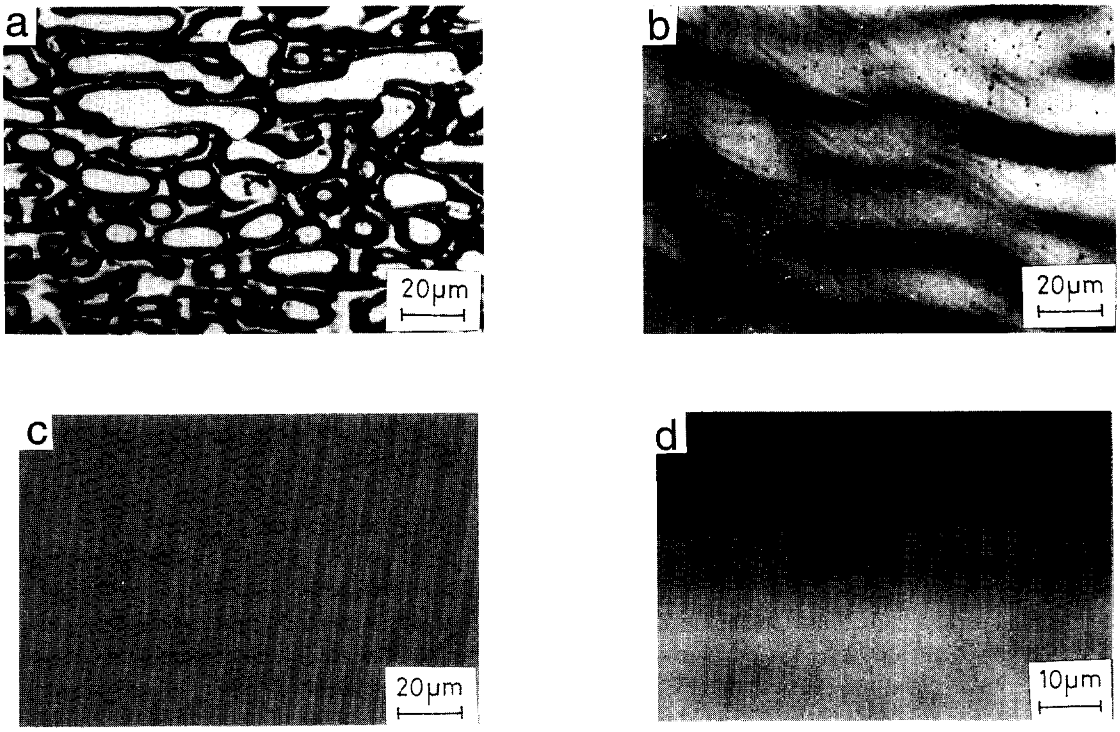

Fig. 1. (a)–(c). Surface morphologies of GaSb epilayers grown from Ga-rich melts by the equilibrium cooling technique. The layer thickness is given in square brackets. (a) 7° off (111) substrates at 350°C [12 μm]; (b) 7° off (111) substrates at 550°C [15 μm]; (c) (100) substrates at 550°C [12 μm]. (d) Typical substrate–epilayer interface for a layer grown by the equilibrium cooling technique.

seen. The poor quality of these layers is due to high precipitate formation and the sticking problem after growth. Growth beyond 680°C is not possible due to the softening of the substrate. Moreover, at these high temperatures, there is volatilization of antimony from the melt as well as from the substrate (prior to growth) which result in unevenly distributed patches. Woelk and Benz [3] have explained the high precipitate formation during growth from Sb-rich melts in terms of the slope of liquidus curve of the Ga–Sb phase diagram on the Sb-rich side. A high growth rate is expected as a result of this and hence uncontrolled growth occurs. To obtain layers with good morphology, the liquidus temperature should be known very accurately within ±0.1°C and the cooling rate should be extremely low compared to what is used for growth from Ga-rich solutions. Since in our case, the cooling rate was relatively high (0.3°C/min), the resulting layer morphology is expected to be poor as is observed.

Even though the layers grown from Ga-rich melts at 550°C (particularly on (100) or (110) orientations) were excellent, the substrate–epilayer interface was diffused in nature as shown in Fig. 1d. Also, thin continuous layers are difficult to obtain by this technique. The two techniques which have been found to be useful to obtain thin epilayers with sharp interface are the step and the supercooling techniques [2]. Accordingly, we carried out further growth experiments with the above mentioned techniques. The results are presented below.

3.1.2. Step cooling and supercooling techniques

In the step cooling technique, the solution is cooled to a fixed temperature below its liquidus temperature and then the substrate is brought into contact with the solution and kept at the same temperature until growth is terminated. In the supercooling technique, initially the solution is step cooled, then the substrate is brought into contact with the solution after which equilibrium cooling is followed. In our experiments, a supercooling of 5°C below the solution liquidus temperature was employed. Typical layer morphologies obtained by the

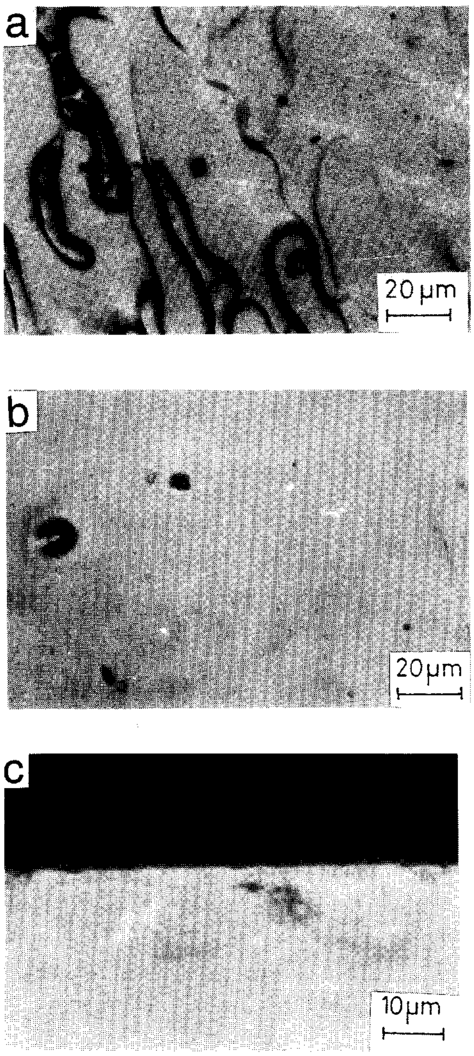

Fig. 2. (a),(b) Surface morphologies of GaSb epilayers grown on (100) substrates by the step cooling technique for a layer thickness of 4 and 9 μm, respectively. (c) Typical substrate–epilayer interface for a layer grown by the step cooling technique.

step cooling technique on (100) oriented substrates at 550°C with Ga-rich melts are shown in Figs. 2a and 2b. The morphology of the thin layers (Fig. 2a) exhibited large terraces, ridges and islands. With increase in layer thickness, the quality improved and above 5–7 μm, layers with mirror finish could be obtained (Fig. 2b). This is mainly due to the fact that initially when the growth starts, there is non-uniform nucleation on the substrate caused by the supercooled melt. With increase in layer thickness, nucleation occurs throughout the substrate and a smooth uniform layer is obtained. The layer morphology from both step cooling and supercooling techniques was found to be similar. As regards to the epilayer–substrate interface, a marked improvement in terms of the sharpness was seen in the layers grown by these techniques. A typical substrate–epilayer interface is shown in Fig. 2c.

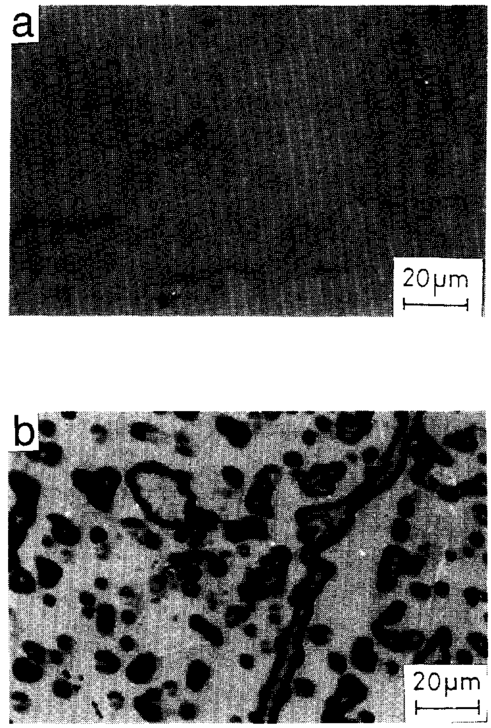

Fig. 3. Surface morphologies of GaSb epilayers grown on (100) substrates by the two phase solution growth technique. (a) Layer thickness 1 μm. (b) Layer thickness 3 μm.

3.1.3. Two-phase-solution technique

The two phase solution technique has been used to grow ultra-thin layers [2] and hence was also adopted here to grow thin epilayers. This technique is similar to the supercooling technique, but in this case a source substrate covers the whole solution. Growth takes place on the seed and on the source substrate simultaneously and hence the thickness of the layers grown is reduced. In our experiments, thin layers of approximately 1 μm were obtained by this technique. The photomicrographs of the layers are shown in Fig. 3. It can be seen that in contrast to the step or supercooling techniques, the layer morphology was better for the thin layers (Fig. 3a) than for the thicker ones (Fig. 3b). This is essentially because of the fact that during the growth of thicker layers, high precipitation in the solution and at the growth interface occurs leading to poor surface morphology. This does not happen in the short period during which thin layers are grown.

The results of various growth experiments carried out with optimized growth parameters are summarized in Table 1 for the purpose of comparison. From our results, it can be inferred that in device applications like LEDs, wherein thick layers are needed and the interface quality is not a stringent condition, the equilibrium cooling technique can be advantageously used. On the other hand, for thin layers with sharp interfaces, the two phase solution growth technique should be employed. Both the step cooling and supercooling techniques can be used for applications where thick layers with abrupt interfaces are necessary.

3.2. Electrical and optical characterization of the grown epilayers

The effect of interface sharpness on the I–V characteristics of the p–n junctions made from our epilayers is shown in Fig. 4. It is clear from the figure that with an abrupt interface, the reverse leakage current reduces and the breakdown is much sharper. This is highly desirable for better device performance. Further, a detailed investigation on the influence of temperature and junction area on the I–V characteristics has been carried out. For the diffuse p–n junctions it was found that with increase in junction area, the reverse current in the low voltage regime increased, indicating the contribution from interface leakage (similar to surface leakage at the metal-semiconductor junction). Furthermore, this leakage current component was found to persist at all temperatures. In the medium and high voltage regimes, tunneling and avalanche breakdown dominate, respectively. The contribution of the tunneling current is large even in the forward characteristics for the diffused p–n junctions. However, the p–n junctions with abrupt interface showed reduced contribution from tunneling and interface leakage.

Fig. 5 shows the PL spectra of undoped p-GaSb layers grown at various temperatures from Ga-rich as well as Sb-rich melts. In general, the PL yield of the layers grown from Ga-rich melts is much higher than

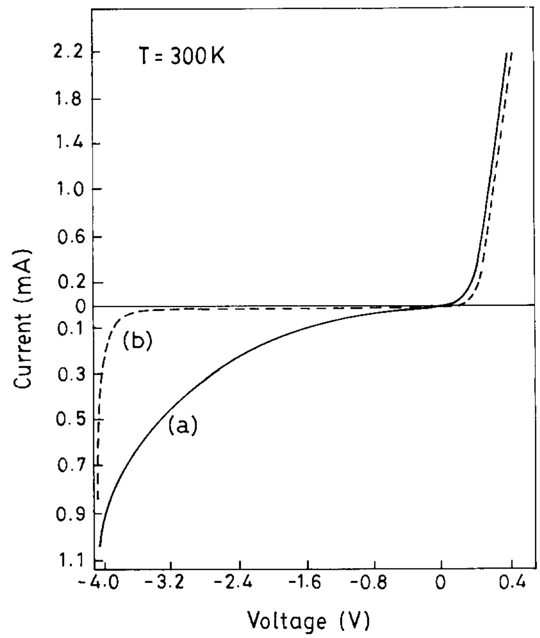

Fig. 4. Current–voltage (I–V) characteristics of GaSb p–n junctions. Epilayers grown by (a) the equilibrium cooling technique (b) the two phase solution growth technique.

that grown from Sb-rich melts. Also, all the spectral lines are broadened in the case of layers grown from Sb-rich melts. This is attributed to increased contamination with impurities and poor surface morphology which result from higher growth rates in case of Sb-rich solutions. The dominant transition in case of layers grown from Ga-rich solutions at and above 500°C is at 777 meV which is attributed to the native acceptors V_{Ga} and Ga_{Sb} [9]. Apart from this, several transitions at 710, 746, 792, 797, 801 and 810 meV appear with different relative intensities in various samples. The origins of these transitions have been discussed in detail elsewhere [10,11]. As can be seen from the figure, the relative intensity of the 777 meV peak decreases with decrease in growth temperature. Also, the layers grown from Sb-rich melts exhibit reduced relative intensity of this transition. This clearly indicates that the 777 meV transition is related to the deficiency of Sb in the crystal. However, the defect centre cannot be a vacant antimony site (V_{Sb}) as it would lead to n-type layers. Nevertheless, the formation of the defect complex like V_{Ga}–Ga_{Sb} can in turn be related to the presence of antimony vacancies [12,13].

Table 1
Comparison of morphology and interface quality of epilayers grown by various techniques under optimized growth conditions (growth temperature: 550°C, substrate orientation: (100), Ga-rich melt)

Growth technique	Duration of growth (min)	Average layer thickness (μm)	Remarks
Equilibrium cooling	1	5	Patchy, non-uniform layer with irregular interface
Equilibrium cooling	4	12	Smooth layer with mirror finish but wavy interface
Step cooling	2	4	Layer with sharp interface but non-uniform thickness and poor morphology
Step cooling	5	9	Layer with sharp interface and excellent surface morphology
Two phase solution	1	1	Layer with abrupt interface and mirror finish
Two phase solution	4	3	Layer with abrupt interface but poor surface structure

The results for the supercooling technique are similar to those of step cooling.

It is interesting to note from the figure that the best PL spectrum with well resolved peaks and with extremely small "full width at half maximum" (FWHM) of 1 meV for the 777 meV transition were obtained

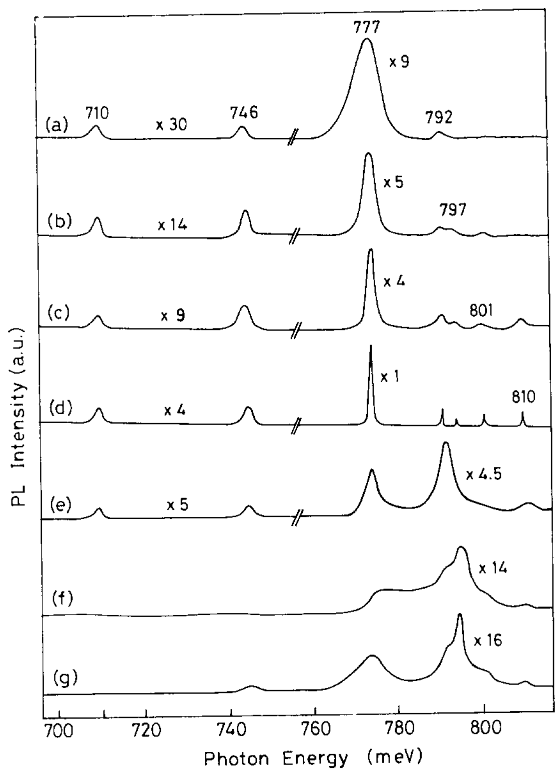

Fig. 5. PL spectra of undoped p-GaSb at 4.2 K for (a) bulk substrate, (b)–(e) epilayers grown from Ga-rich melts, (f),(g) epilayers grown from Sb-rich melts. The growth temperatures are (b) 580°C, (c) 550°C, (d) 500°C, (e) 450°C, (f) 600°C, and (g) 630°C.

from Ga-rich melts at 500°C. Purely from morphological considerations, one would expect the PL spectrum to be the best for the layers grown at ~ 550°C. This difference is probably because of the fact that the reduction in the background native defect concentration resulting from the reduced growth temperature more than compensates for the *slight* deterioration of the surface morphology of the layers grown at this temperature, thus leading to well resolved peaks. For growth temperatures below 500°C, even though the relative peak intensity of the 777 meV transition decreased with decrease in growth temperature, the peak width broadened due to further degradation of the layer morphology. Hence there exists a trade-off between the best layer morphology and the best optical quality. Thus the temperature regime in which high quality layers can be obtained lies in the range 500–550°C.

4. Conclusions

Our results show that the surface morphology of GaSb epilayers grown by LPE is strongly influenced by the condition of growth solution at the time of its initial contact with the substrate. A marked improvement in substrate–epilayer interface sharpness is achieved by introducing appropriate supercooling in the solution. The morphological, electrical and optical properties of the epilayers grown from Ga-rich melts are superior compared to those grown from Sb-rich melts.

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