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Atomically flat III-antimonide epilayers grown using liquid phase epitaxy

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ATOMICALLY FLAT III-ANTIMONIDE EPILAYERS GROWN USING LIQUID PHASE EPITAXY

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A novel process has been developed which allows the growth of device grade ultra-smooth epitaxial layers of antimonide based III-V compounds with a controlled thickness using Liquid Phase Epitaxy (LPE). GaSb epilayers (with thickness in the range of 20-50μm) on GaSb single crystalline substrates have been grown with a root mean square surface roughness of less than 1 nm over an area of 5 x 5μm.

Keywords: Liquid Phase Epitaxy, GaSb, surface morphology, atomically flat surfaces

1 Introduction

Device grade, single crystal substrates of only a few binary compounds (such as GaAs, GaSb, InP, CdTe) with discrete band gaps and lattice constants are commercially available. Ternary or quaternary based devices are fabricated on thin epitaxial layers grown on binary substrates. To grow these compound semiconductor epilayers, various epitaxial techniques such as molecular beam epitaxy (MBE), metalorganic chemical vapor deposition (MOCVD), and liquid phase epitaxy (LPE) have been in use. However for antimonide based materials, the extrinsic doping levels possible using MOCVD and MBE are in a limited range due to high concentrations of native defects in the material [1]. LPE growth takes place under near equilibrium conditions at low temperatures and therefore has low native defects enabling a wide range of doping levels. LPE also has an additional advantage of high growth rate compared to MOCVD and MBE. However, LPE suffers from the problems of non- uniform interface and rough morphology which limits it application as an industrial epitaxy technique for a large number of devices. In this paper, we have investigated the fundamental growth mechanism of the epilayers and engineered the growth process enabling ultra-smooth layers with predictable thicknesses. GaSb epi-growth on GaSb substrate has been used as a model material in this work. The process consists of isothermal growth following an initial supercooling. Data of surface roughness and layer morphology will be presented in this paper.

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2 Experimental details

LPE growth was carried out in a single-zone transparent vertical Bridgman furnace in hydrogen atmosphere using the dipping technique. The growth setup is shown in figure 1. A multi-bin crucible made from high purity graphite and a quartz wafer carrier was used.

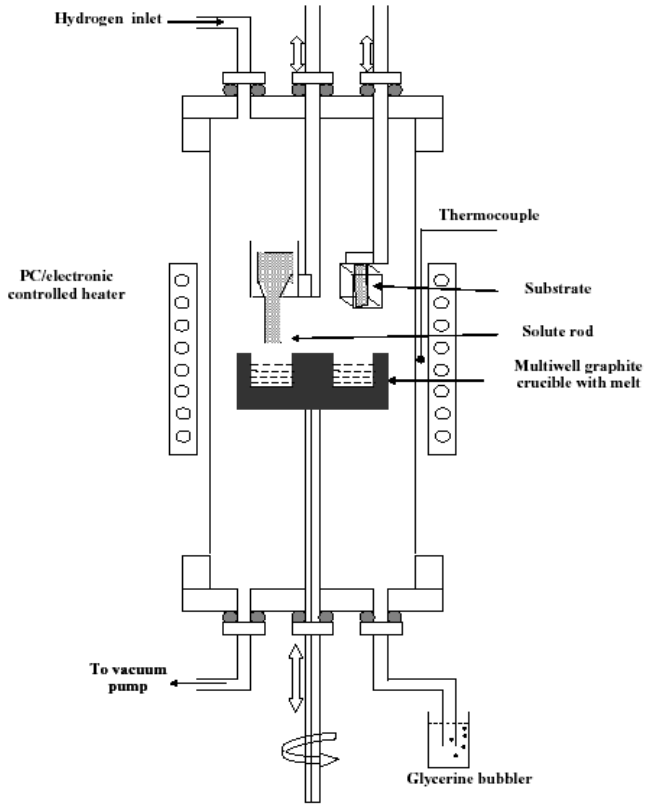

Figure 1: A schematic illustration of the epilayer growth setup.

Epitaxial layers were grown on the (100) surface of single crystalline Te-doped GaSb wafers from Wafer Tech. Corp. The wafers were degreased in warm xylene, acetone and methanol and the surface oxide was removed by a dip in HCl and a solution of Cr_2O_3:HF:H_2O (34gm:5ml:120ml). Gallium was used as the growth solution. Prior to growth, it was necessary to baked the gallium in ultra-pure hydrogen flow at 850 ^oC for 5-10 minutes in order to eliminate the oxide scum on the top of the melt. During this baking, the GaSb wafer and the GaSb solute rod (used for supersaturating the growth solution) were kept inside the growth chamber at about 200 ^oC. After the high temperature baking, the furnace was cooled to the growth temperature (in 30 minutes) and allowed to stabilize for 2-3 hours. The growth solution was prepared by dissolution

of the GaSb solute rod in the Ga-liquid for 2-5 minutes at the final growth temperature. In initial growth runs, it was observed that during solute dissolution, an oxide scum was formed on the top of the solution that led to surface contamination of the wafer surface and inhibited proper nucleation during growth. Hence an oxide desorption Ga-solution was separately put in one of the graphite bins. Prior to dissolution, the surface of the GaSb rod was cleaned in the Ga-solution for 30-60 seconds. This process was also repeated for the actual growth wafer. Two separate oxide desorption solutions were used for the solute rod and the GaSb wafer to avoid cross contamination of the wafer surface with oxide scum. Without the surface oxide desorption process, the morphology of the GaSb epilayers were extremely rough and thicknesses inhomogeneous. After cleaning the GaSb wafer in a wafer oxide desorption melt, it was inserted in the growth solution. We have used two different temperature-time profiles for the epigrowth as shown in figure 2 and will be discussed in section 3. After the growth, the surfaces were cleaned using hot HCl to remove the excess gallium and the surface morphology of the layers were examined by a Nikon microscope and Scanning Electron Microscope (SEM). The root mean square roughnesses of the layers were analyzed using an Atomic Force microscope (AFM) and the layers were optically characterized by a Thermo-Nicolet Fourier Infra-red Transform. (FTIR) spectroscope. The thickness of the layers was measured by a profilometer.

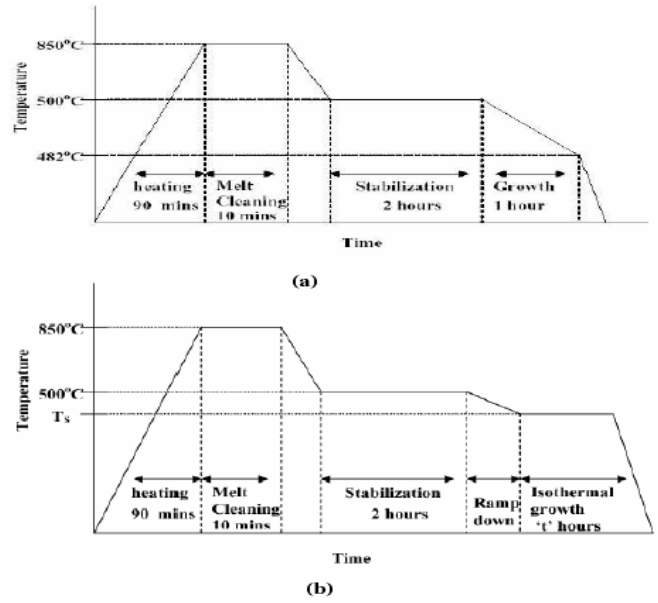

Figure 2 : The temperature-time profiles used for (a) 2-D epilayer growth using ramp- cooling and (b) isothermal growth with initial supercooling.

3 Results and Discussions

3.1 2-Dimensional Epilayer Growth using Ramp-cooling

The temperature profile shown in figure 2(a) was used in these experiments. To study the evolution of 2-D island growth, the duration of growth was varied from 30 minutes to 90 minutes, while the cooling rate of the growth solution was kept constant at 0.3 °C/min for all the experiments. It should be noted that the cooling rate used by us is much lower than that used in literature (e.g. 2-5 °C/min [3])[4,5,6]. This was intentionally done to enable the 2-D growth. The growth morphologies and SEM pictures can be seen in figure 3. Rectangular facets could be seen in all the layers.

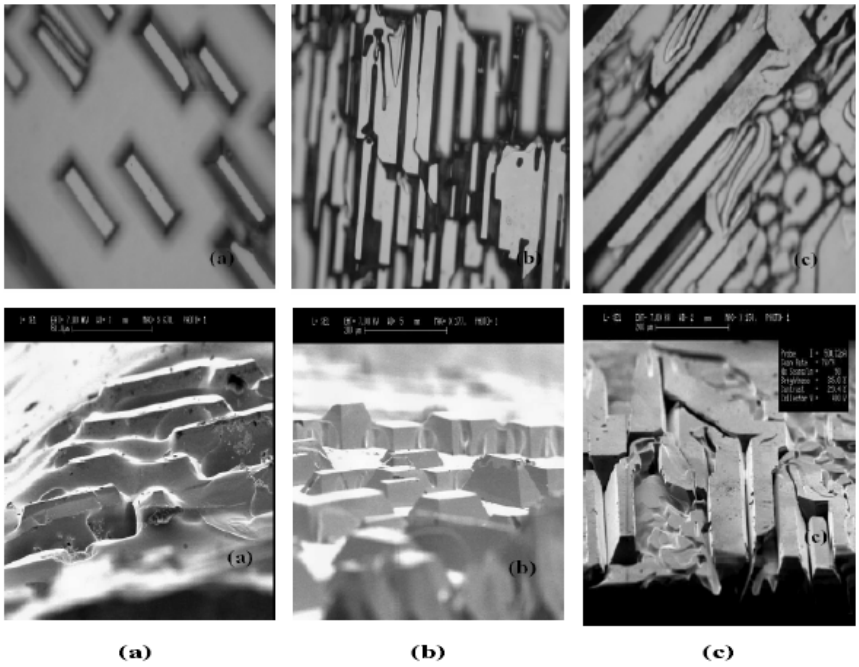

Figure 3: Optical and SEM micrographs of GaSb/GaSb layers grown with a cooling rate of 0.3°C/min for growth times of (a) 30 minutes (b) 45 minutes and (c) 60 minutes. The top row shows the optical micrographs (Magnification = 60X). The bottom row shows SEM pictures of corresponding samples.

The top faces of the facets were extremely smooth. An increase in the time of growth leads to a steady increase in the lateral dimensions of the facets implying different growth rates along different directions. The heights of the facets are approximately 50 μm for the layers grown for 45 minutes. AFM measurements show a root mean square roughness of the surface of these facets to be an average of 0.9 nm for a scan of 5 x 5 μm^2 area. After a growth time of 90 minutes, the facets merge. However, complete

coverage of the substrate is not achieved at the same time. The occurrence of these facets can be explained by the fact that {100} and {111} planes have interfacial energy densities which are the highest and the lowest respectively[7]. Hence the {100} plane will tend to breakdown and produce {111} planes. This leads to the formation of facets instead of uniform terraces under non-equilibrium conditions.

3.2 Isothermal growth with initial supercooling

Even though the above process gave extremely flat layers, complete coverage of the substrate by the individual islands *at the same time* could not be controlled.

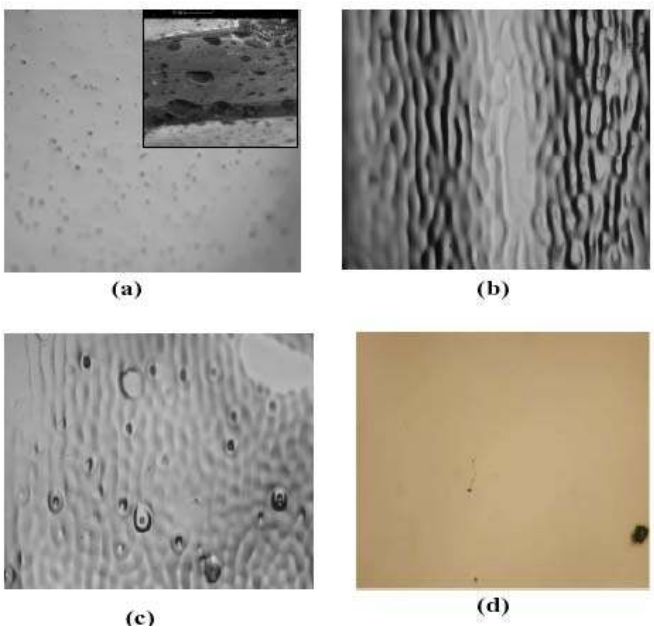

Figure 4: Optical micrographs of GaSb/GaSb layers grown for (a)T_S = 2°C, ramp rate = 0.3°C/min, t= 2 hours; (inset)SEM picture of the layer (b)Ts = 4°C, ramp rate = 0.3°C/min t= 2 hours (c) T_S = 2°C, ramp rate = 0.3°C/min, t= 4 hours (d) Ts = 2°C, ramp rate = 0.1°C/min , t= 2 hours; (Magnification = 60X)

Due to the fact that upon supersaturation, the solute takes time to diffuse through the boundary layer before it can attach to the substrate, it is intuitive that a very low supersaturation coupled with long growth duration is required to achieve a uniformly thick layer using LPE [2]. Hence, a new temperature profile as shown in figure 2(b) was used in subsequent experiments. In this process, the growth melt was cooled by an amount T_S = 2-4°C from the saturation temperature at a rate of 0.1-0.3 °C/min followed by an isothermal growth time, t= 2-4 hours. The growth wafer was inserted in the melt prior to the cooling cycle and removed at the end of the isothermal growth period. Continuous layers with complete substrate coverage could be grown using this strategy.

It was observed that for a higher cooling rate, lots of pin holes were present in the layer (see Figure 4a). By decreasing the cooling rate, pinholes were eliminated (as shown in figure 4(d)). AFM measurements show that the rms roughness of the surface in figure 4(d) is 0.88 nm. For comparison, the rms roughness of a typical GaSb starting substrate is in the range of 0.3-0.5 nm. Achievement of atomically flat surfaces (contrary to what is expected in LPE grown layers) is due to the etch-back and re-growth process as a result of the long isothermal sequence used in our temperature-time profile during growth. It should be noted that the initial surface oxide desorption process is crucial in ensuring uniform nucleation during growth. It is possible that during the oxide desorption process in gallium solution, etch pits get exposed which could form nucleation centers for the 2-D islands. The transition from 2-D faceted growth to a continuous layer takes place by a continuous etch-back and re-growth mechanism.

4 Conclusion

A new 2-D island dissolution and re-growth process has been shown to result in atomically flat epilayers by liquid phase epitaxy under isothermal growth conditions. Extremely smooth layers over large area up to 1 x 1 cm^2 have been obtained. Using this process, it is anticipated that epilayers with controlled thicknesses could be grown by changing the initial supercooling level in the solution and the growth times.

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