CHAPTER 8
Conclusion

8.1 Importance of epitaxial growth

Single crystals of semiconductors and optical materials have an enormous importance in much of today’s advanced technology. Virtually all electronics and optoelectronic devices are made out of single crystals. At present, the quality of the crystals used by semiconductor industry is far below the theoretical limit of perfection. The gap between theory and experiments is still unbridged due to the complexity of the growth process. This is a great driving force for laboratories and research institutions to put their ultimate efforts in order to overcome the problems arising during the fabrication of more complicated devices.

Epitaxial growth has been found to be the best way for growing thin single crystal layers of semiconductor and their heterojunctions for device applications. The multidisciplinary nature of the technology of crystal and epilayer fabrication, the complex multiparameter process – where two or more growth parameters have to be compromised and optimized, and also the scaling problem have made this field really challenging. The growth process must be able to accurately calibrate and control doping levels and thickness, alloy compositions, interfaces and junction formations. Of the important epitaxial growth techniques, such as, liquid phase epitaxy (LPE), vapor phase epitaxy (VPE), metalorganic vapor phase epitaxy (MOVPE), and molecular beam epitaxy (MBE), the LPE technique is the simplest and flexible method for growing a variety of III-V, II-VI and IV-VI compound layers for applications in optoelectronic devices.

The present work is dedicated to the epitaxial growth of III-V compound semiconductor layers, mainly InGaP and dilute GaAsN, employing the LPE technique. Epitaxial layer properties are optimized through suitable modification of the growth
8.2 Summary of the work

This work is devoted to the growth and characterization of two technologically important III-V compound semiconductors, InGaP and dilute GaAsN, pseudomorphically grown on \(<100>\) semiinsulating or \(n^+\) GaAs substrates. The layers for the study were grown by our in-house horizontal liquid phase epitaxy (LPE) system employing sliding boat technique. Growth was done under an ambient of ultrapure hydrogen. In order to characterize the layers using optical techniques like photocapacitance and photoconductivity measurements, evaporated gold Schottky barrier diodes were formed on the surface of the layer with alloyed In-Sn ohmic contacts. A major part of the study concerns characterization of various deep levels in the material, either present in-situ or generated during growth and processing of the materials.

The first part of the thesis includes studies on Fe- and Er-doped LPE InGaP. Lattice-matched \(\text{In}_{0.5}\text{Ga}_{0.5}\text{P}\) on GaAs substrates, is an important material for high-speed electronic devices as well as for fabricating efficient light emitters for the visible range of the spectrum. The features that give InGaP/GaAs system an edge over hitherto used AlGaAs/GaAs system are low recombination velocities, high doping capability without creating deep levels (like DX centers), high immunity against oxidation of the surface and a large direct bandgap upto 2.26 eV for \(x=0.74\). The LPE InGaP layers of 3-4 \(\mu m\) thickness were grown in our laboratory using a growth melt of prebaked In, polycrystalline GaP and InP, at 740-742°C under a melt supersaturation of 8-10°C and a cooling ramp of 0.3-0.4°C/min.

Doping of III-V compounds with transition metals like Fe, Cr, Ni, Co etc. are usually done to get high resistivity and semiinsulating layers which act as isolation regions (i.e. Current blocking layers) between devices fabricated on a single substrate. Further Cr-doped GaAs and Fe-doped InP semiinsulating substrates are used for optoelectronic and electronic devices and integrated circuits fabrication. In all cases
transition metals in III-V compounds produces a deep acceptor level which then act as a trapping and recombination center and hence compensates for the shallow background donors, present in nominally undoped material. InGaP layers were doped with varying amounts of Fe by directly adding 99.9999% Fe to the growth melt. The deep levels in the material were studied by photocapacitance and photoconductivity techniques. Similar experiments were done on an undoped sample for comparison. In all the samples we observed an initial rise in photocapacitance, which we attributed to a 0.54 eV electron trap commonly observed in MBE and MOCVD InGaP. In the InGaP layer grown from low (0.02 wt%) Fe containing melt, we detected two electrons traps of energies a 0.95 and 1.0 eV. In the layers, grown with a higher Fe content (0.08 wt%), the concentration of the 1.0 eV hole trap was found to be increased. Similar results were obtained from 10K photoemission measurements done on the same material. From these results we suggested that the particular 1.0eV trap is the compensating center in Fe doped InGaP.

Growth of epitaxial layers from melts, treated with minute quantities of rare earth metals like Er, Gd and Yb is an established technique to get high purity bulk crystals and epitaxial layers. The rare earth elements form insoluble stable complexes with the residual impurities in the growth melt and the grown crystal comes out with greatly reduced background impurity concentration. We have studied the LPE growth of InGaP layers using melts treated with upto 0.2% Er and explored the possibility of reducing the background impurities in the grown layer.

Van der Pauw Hall measurements on the material showed an increase in 300K and 77K Hall mobilities and decrease in carrier concentration, indicating impurity reduction by Er. This directly gave an evidence of impurity gettering action of Er in InGaP. Double Crystal X-ray Diffraction (DCXRD) measurements showed that the lattice-substrate mismatch increased as Er content in the melt increased. It is suggested that part of Er combined with phosphorous to form ErP thereby depleting phosphorous in the growth melt with a corresponding change in alloy composition and lattice constant. The deep levels in the material were studied by low temperature photocapacitance experiments. The main feature of the photocapacitance spectrum was the presence of a 0.66 eV electron trap and a hole trap at 0.95-0.98 eV which are not observed in layers grown without Er. The origin of the 0.66 eV trap is not clear. Comparing the
photocapacitance results with that obtained on InGaP:Fe, we see that the 0.95 eV hole trap is a characteristic of both Er and Fe doped InGaP. The trap is thought to be the same as the hole trap HP1 with an activation energy of 0.90 ± 0.05 eV, reported by other workers and was related to phosphorous vacancy related complexes.

In the second part of the thesis we studied the LPE growth and characterization of dilute GaAsN layers. Dilute III-V nitrides have emerged as a kind of material where the bandgap of the parent III-V semiconductor is substantially reduced by the incorporation of very little amounts of nitrogen. Such behavior indicates that the material has a large bowing parameter and has been a subject of intensive theoretical investigation. From the application point of view, dilute nitrides show the promise of their use in the fabrication of long wavelength lasers with suitably tailored wavelengths.

We have grown dilute GaAsN layers by LPE technique and important trapping properties were investigated. The growth melt was composed of Ga metal and polycrystalline GaAs to which precisely weighted polycrystalline GaN powder was been added as the source of nitrogen. Since nitrogen has the tendency to outdiffuse at high temperatures, temperature of growth was kept low. Layers were typically grown at 730 – 740 °C for 10-15 min under a melt supersaturation of 8-10 °C and a cooling ramp of 0.4-0.5 °C. The grown layers were shining and free from any macroscopic surface defects. From Hall measurements we obtained an average mobility of around 5000 cm²/V.sec for our samples with carrier concentrations in the mid 10¹⁶ cm⁻³.

Form high resolution X-ray diffraction measurements, the presence of nitrogen in the layers is verified. In the high resolution X-ray rocking curve two separate peaks, one for the LPE-grown GaAsN layer and other due to the GaAs substrate were clearly observed. Further, the presence of nitrogen in the grown layers was confirmed by a nitrogen related shoulder at 471 cm⁻¹ obtained in the Fourier transform infrared absorption spectrum. A resultant bandgap reduction of 100 meV was measured by optical transmission, room temperature photocurrent technique, and 20K PL measurements in a layer grown from a melt containing 1wt% GaN. From this data, a nitrogen content of 0.5% is calculated in the material. On increasing the nitrogen content to 2wt% in the growth melt, the same in the layer is enhanced to about 0.7%. The full-width-at-half-
maximum (FWHM) values for PI peaks were in the range of 4-5 meV, which indicated good crystallinity of the material.

Low temperature photocurrent and photocapacitance measurements revealed the presence of an electron trap with ionization energy in the range 0.65 – 0.67 eV in the as grown layers. The apparent concentration of this trap was found to increase with that of GaN, added to the growth melt. Comparing with the data for the same material grown by other techniques, we tentatively assigned the trap to an interstitial \((N-N)_{As}\) defect. Annealing of the material at 750°C for 1hr greatly reduced this trap and new electron traps with activation energies of 0.8 and 0.9 eV are generated. It is suggested that, during annealing process, \((N-N)_{As}\) defects, due to their lower energy of formation, are converted to more thermally stable \((As_{Ga-N}_{As})\) or \((AsN)_{As}\) defects which might be the source of the new electron traps. Photocurrent experiment on the annealed samples indicated the presence of the same electron traps. In order to further substantiate the results, about 0.1 wt% Er along with 2 wt% GaN was added to the GaAsN growth melt and baked at 750°C for 3 hrs. PL data for the layers grown from this melt indicated total absence of nitrogen and photocapacitance and photocurrent measurements did not reveal any electron trap. We suggest that Er in the growth melt removed nitrogen by forming ErN which resulted in the absence of any nitrogen in the grown layer and removal of the nitrogen related traps.

8.3 Important results

The important results derived from the overall study are the following

1. Deep levels in Fe doped InGaP layers grown by LPE technique have been studied. A particular 1.0 eV deep hole trap was detected in the Fe-doped layer only and its concentration increased with that of Fe. We suggested that this particular trap might be the compensating center in Fe-doped InGaP.

2. Purification of InGaP layers by rare earth gettering of residual impurities in the LPE growth melt is explored. Increased layer-substrate mismatch, as a result of Er addition due to the formation of ErP in the growth melt and change in alloy composition is revealed. Also impurity reduction effect in presence of Er is observed. Occurrence of a 0.9 eV hole trap is detected in Er
doped material, which is also detected in InGaP:Fe, and is attributed to phosphorous vacancy.

3. The growth of dilute GaAsN layers by LPE, using polycrystalline GaN as the source of nitrogen, is reported. A band gap bowing of 100meV is measured which corresponds to a little more than 0.5% substitutional nitrogen in the layer. Doubling the GaN content in the growth melt did not substantially decrease the band gap of the LPE grown samples, which is suggested to be due to nitrogen related interstitial defects.

4. An electron trap with ionization energy in the range, 0.65-0.67eV is detected in the as-grown GaAsN layers, whose concentration is directly linked to that of nitrogen in the melt. The trap annealed out at high temperature and new electron traps at 0.8 and 0.9 eV were generated. Considering the energy of formation of various nitrogen related defects in GaAsN, it is suggested that the 0.65-0.67 eV electron trap in the as-grown material is related to interstitial (N-N)$_{As}$ defects which, after high temperature annealing, are converted to more thermally stable (As$_{Ga}$-N$_{As}$) or (AsN)$_{As}$ defects. These defects are believed to be the origin of the new electron traps. High temperature treatment of the growth melt with Er is found to remove nitrogen in the layer as well as the electron traps and we suggested that this is due to the removal of nitrogen from the melt by Er.