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LPE growth of InGaAsP:InP high purity layers using rare earth elements

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Abstract. Use of rare earth (RE) elements has allowed the growth of high purity InGaAsP: InP layers in liquid phase epitaxial (LPE) systems. Experiments show that purification of material takes place on account of interaction between the RE and mainly group VI donor impurities.

Keywords. Liquid phase epitaxy; InGaAsP:InP; III–V compound semiconductors; rare earth elements.

1. Introduction

The necessity of working out a technology to grow high purity layers in the InGaAsP/InP-system has assumed urgency for fabricating high efficiency photodetectors required for fibre optic systems, transferred electron devices and buffer layers in FET structures. Growing high purity layers is a complex technological problem, since it is difficult to eliminate residual impurities which are present in source materials and containers used in liquid phase epitaxy (LPE). Normally, by using graphite boats a net residual donor concentration $\sim 10^{17}\,cm^{-3}$ is achieved. The main impurities consist of Si, C, O and S. In LPE various measures have been adopted to bring down the net carrier concentration: long term baking of melts (Cook *et al* 1982; Kuphal and Pocker 1982), introduction of water vapour in H_2 stream (Oliver and Eastman 1980), and high temperature-baking of indium in vacuum (Dentai *et al* 1981). Less effective methods to bring down the residual carrier concentration by compensating the material with shallow acceptors result in lower values of carrier mobilities (Yamazaki *et al* 1983; Rao 1985).

An alternative approach—baking the melts with rare earth elements (RE)—has produced more effective results, and allows much shorter baking times (Gatsoev *et al* 1985). Here, some results of the investigations carried out using RE-doped material are reported.

2. Experimental

Source materials for the melts, together with the RE, were baked in a graphite boat placed in a quartz reactor at 670°C. The RE was cleaned mechanically and weighed carefully, before loading into the graphite boat bin. These melts were used to grow epilayers on InP substrates. A typical temperature-time schedule is shown in figure 1. Normally, six InP substrates, each $10 \times 10\,mm^2$ in size were used in one experiment. A palladium diffuser acted as hydrogen purifier. For all the experiments

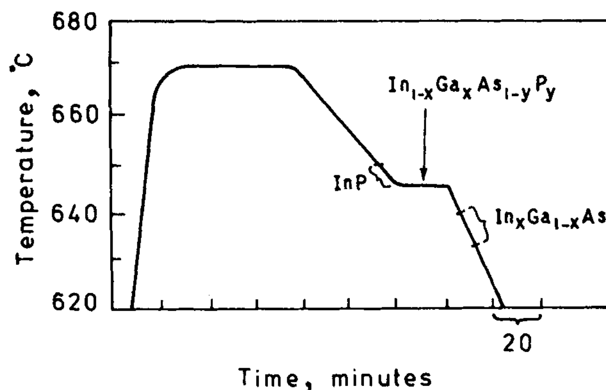

Figure 1. Temperature–time schedule for epitaxial growth.

conducted, the dew point was not more than -70°C. Other details are given elsewhere (Sarin 1987).

3. Results and discussion

It was possible to grow high purity layers with concentrations as low as 10^{13} cm^{-3} and carrier Hall mobilities as high as 70,000 cm^2/V.s (at 77°) for InP and InGaAs layers. The observed PL spectra were similar to those obtained for high quality layers (Di Forte Poisson *et al* 1985).

Rare earths when introduced into the melts actively interact with the residual impurities, mainly donors. To elucidate this, epilayers of InP doped with different donor species (Ge, Si, Sn, S, Te and Se) of carrier concentrations, $n_0 \simeq 5 \cdot 10^{18}$ cm^{-3} (an order greater than the normal residual carrier concentration) were grown. Different amounts of dysprosium (Dy) were added to these melts and these were then used to grow the epilayers. The results normalized with respect to n_0 are shown in figure 2. It is observed that the concentration of electrons (or donors) in epilayers, doped with the donors of group IV changes little. On the other hand, layers doped with the donors of VI group elements (Te, Se and S) show decrease in carrier concentration with the addition of RE. This decrease is more prominent for the layers doped with donors having lower atomic weight and higher chemical activity, e.g. S.

In figure 2, the curve represented by the sign (X) shows normalized concentrations in InP:Dy epilayers, grown without any intentional donor-doping. It may be observed that the points are well-matched to the curve obtained for the samples intentionally doped with sulphur. This shows that in the investigated layers, sulphur is the main residual donor impurity. Far infrared photoconductivity spectra have also shown that S and Si are the dominant impurities. This is consistent with the observations of Di Forte Poisson *et al* (1985) that S is the most common donor in epitaxial layers.

It was observed that with an increase in the amount of RE in melts, the concentration of donor (N_D) as well as that of acceptor (N_A) impurities fall (Sarin 1987). However the degree of compensation increases with this, i.e. the rate

of fall of N_D becomes more than that of N_A. This brings about an inversion in the type of conductivity in the layers as shown in figure 3.

As seen above (figure 2) the concentration of layers, simultaneously doped with donors of group IV and RE, does not change significantly. This fact allows us to work out a method of controlling the residual carrier in the layers by doping the melts with RE and Sn (figure 4). This is important from the device-fabrication point of view.

Depth distribution of donors was measured with the help of a Polaron profilometer. Results for an epilayer doped with Ho (0·03 at%) and Sn (0·01 at%) are shown in figure 5. This indicates that the layers grown are homogeneous.

4. Conclusion

Rare earth metals have been used to grow high purity InGaAsP: InP layers in LPE systems. Investigations confirm that sulphur is the dominant impurity. Purification of material takes place on account of high temperature compounds formed by the interaction of residual donors of group VI with the RE which form slags. It is

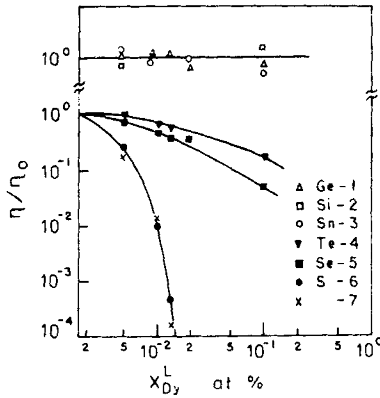

Figure 2. Normalized electron-concentration in InP layers doped with donors of group IV (1-Ge, 2-Si, 3-Sn) and of group VI (4-Te, 5-Se, 6-S) as a function of dysprosium concentration in melts (7-unintentionally doped with donors).

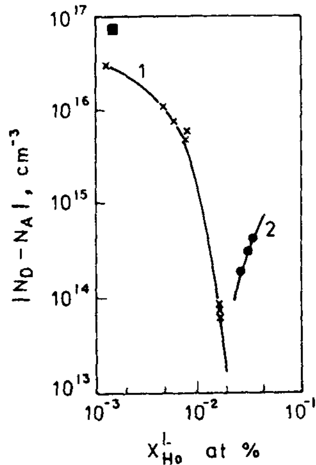

Figure 3. Carrier-concentration of InP-epilayers as a function of the amount of RE in liquid phase; (1) *n*-type, (2) *p*-type.

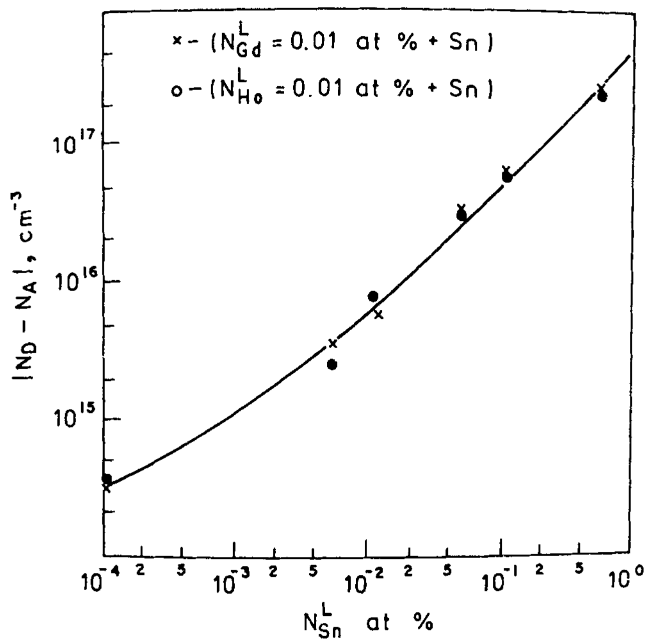

Figure 4. Carrier-concentration dependence of InGaAs-epilayers as a function of Sn and Gd (or Ho) concentrations in melts.

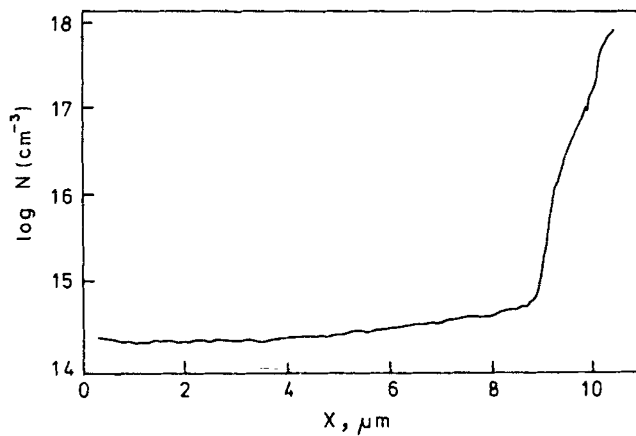

Figure 5. Depth distribution of electrons in InGaAs: (Ho + Sn) epilayers.

possible to control the residual carrier concentration of the layers by doping the melts with RE and donors of group IV simultaneously.

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