KAPL-P-000010
(K95085)

CONF-9507247--

CHARACTERISTICS OF GaSb AND GaInSb LAYERS GROWN BY METALORGANIC VAPOR PHASE EPITAXY

H. Ehsani, I. Bhat, C. Hitchcock, J.Borrego, R. Gutmann
(Contact G. Nichols)

July 1995

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

NOTICE

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CHARACTERISTICS OF GaSb AND GaInSb LAYERS GROWN BY METALORGANIC VAPOR PHASE EPITAXY

H. Ehsani, I. Bhat, C. Hitchcock, J. Borrego and R. Gutmann
Center for Integrated Electronics and Electronics Manufacturing &
Department of Electrical, Computer and Systems Engineering
Rensselaer Polytechnic Institute, Troy, NY 12180-3590

ABSTRACT

GaInSb and GaSb layers have been grown on GaSb and GaAs substrates using metalorganic vapor phase epitaxy (MOVPE) with trimethylgallium, trimethylindium and trimethylantimony as the sources. As grown layers are p type with the carrier concentration in the mid 10^{16} cm^{-3} range. N type layers are grown using diethyltellurium as the Te source. Incorporation of Te in high concentration showed compensation and secondary ion mass spectrometry (SIMS) result showed that only 2.5% of Te are active when 2×10^{19} cm^{-3} of Te was incorporated. The carrier concentration measured in n type samples increases as the temperature is lowered. This is explained by the presence of second band close to the conduction band minima. Silane which is a common n type dopant in GaAs and other III-V systems is shown to behave like p type in GaInSb. P-n junction structures have been grown on GaSb substrates to fabricate TPV cells.

1. INTRODUCTION

There is both civilian and military interest in the use of cells for converting the energy of radiant heat sources, other than the sun, into useful electrical energy. In this application, the so-called thermophotovoltaic (TPV) cells use the same principle of operation as photovoltaic cells (PV), except that the radiant heat source is other than the sun. Since these heat sources are at a much lower temperature than the sun (generally in the range 900°C to 1500°C), different materials with much lower band gaps are required (1). Ternary compounds such as InGaAs or GaInSb are ideally suited for this purpose since their band gaps can be varied to match the radiant spectrum. However, epitaxial growth of these is difficult since suitable lattice matched substrates are not available. Hence, various dislocation reduction technique should be used to grow high quality layers. Epitaxial layers of InGaAs for TPV applications have been reported earlier and pilot production of TPV cells based on InGaAs materials are underway[1]. However, P- and As- based materials are expensive in the long run because one has to use large amount of dangerous gases such as arsine or phosphine during growth. The substrates used are also generally very expensive. Therefore, an alternative to InGaAs materials should be explored in order to reduce the cost of TPV cells.

In this work, we concentrate on GaInSb materials with energy gaps in the range from 0.5 eV to 0.75 eV grown on GaSb substrates. GaSb and $Ga_xIn_{1-x}Sb$ materials have received a considerable interest for applications as infrared detectors, in optoelectronics and high speed devices[2-6]. Unlike other commonly known III–V semiconductors such as GaAs and InP, the growth of Sb based materials is difficult because vapor pressure of Sb over GaSb is very low. Thus, only a narrow range of V/III ratios and growth temperatures can be used to grow a good quality layer. Beyond this narrow range, either Sb-droplets or Ga droplets are seen on the growth surface. Another difficulty is that the surface oxide can not be thermally removed by heating the wafer to high temperature prior to growth because the substrate will decompose.

This paper addresses the growth of high quality $Ga_xIn_{1-x}Sb$ on GaSb substrate. The effect of growth temperature, V/III ratio, and etching procedures on the quality of the layers was studied. P–type and n–type doping of $Ga_xIn_{1-x}Sb$ layers for TPV fabrication was also investigated.

2. EXPERIMENTAL PROCEDURE

The growth of $Ga_xIn_{1-x}Sb$ was carried out in a low pressure (100 Torr) horizontal MOVPE system with rf heating. Precursors for the growth of $Ga_xIn_{1-x}Sb$ were trimethylgallium (TMGa), trimethylindium (TMIn), and trimethylantimony (TMSb), each held in a temperature controlled bath at -10°C, at 20°C and at 5°C, respectively. Both GaAs and GaSb wafers were used as substrates. Since GaSb wafers are not available in semi-insulating form, GaAs wafers were used for making Hall Effect measurements. After cleaning the wafers in organic solvents, GaAs was etched in Caro's etch (solution containing $H_2SO_4:H_2O_2:H_2O$, 5:1:1 by volume) for 2 minutes and GaSb was etched in 1% Br-methanol solution for 30 seconds. Other etches such as Caro's etch and H_2O_2+acetic acid etch were also used.

Hall effect measurements were used for electrical characterization of the layers grown on GaAs substrates. Crystalline quality and the lattice parameter of the layers were determined by the double crystal x-ray diffraction. Fourier transform infrared (FTIR) spectrophotometer was used to measure the transmission spectra of layers grown on GaAs substrates from which the thickness and the approximate bandgap could be determined. The thickness of the layers grown on GaSb wafers was determined by measuring the change in the weight before and after the growth, and was generally found to be the same as that grown on GaAs. The FTIR spectra on GaSb wafers do not give thickness fringes since the refractive index of GaInSb and GaSb is very close.

3.RESULTS AND DISCUSSIONS

GaSb Layers

GaSb was first grown on GaSb and GaAs substrates in order to optimize the growth conditions for binary layer growth. The growth temperature was varied from 560°C to 630°C and the ratio of TMSb/TMGa partial pressure was varied from 1.1 to 4. The best layers were obtained at a substrate temperature of 600°C, with the TMSb/TMGa ratio between 1 and 2.5. The typical mole fraction of TMSb and TMGa were 2.2×10^{-4} and 1.3×10^{-4} respectively. The growth rate at lower temperature was slow and the morphology was poor. Figure 1 shows the growth rate of GaSb on GaSb as a function of the growth temperature. At higher temperature (<630C), the surface morphology was also poor, probably caused by the degradation of GaSb surface during heat up. The surface morphology of the GaSb layers on GaAs substrates were rough, except for the layers grown at 560°C and below.

GaInSb Layers

The growth of $Ga_xIn_{1-x}Sb$ was initiated by first growing a thin (about 1000Å) layer of GaSb. In some cases, step grading of the composition was carried out to accommodate the lattice mismatch between GaInSb top layer and the substrate. All the growth runs for GaInSb were carried out at 600°C and the ratio of TMSb/(TMGa + TMIn) partial pressure were kept between 1.2 and 2. Several etchants such as dilute Br_2-methanol, Caro's etch, and H_2O_2 + CH_3COOH were tried to etch GaSb wafers, but Br-methanol solution was found to be the best. The surface morphology of all the layers were mirror-like, but layers grown on Br-methanol etched wafers had better crystal quality as measured by the double crystal x-ray diffraction. Figure 2 represents the surface morphology of a 11 μm thick $Ga_{0.8}In_{0.2}Sb$ layer grown on GaSb substrate. The surface morphology is very smooth, except for the presence of a few hillocks. Since these hillocks have the same size and crystalline orientation, we believe that they originated at the interface. Better cleaning procedure or dust free surrounding may eliminate these hillocks.

The double crystal x-ray diffraction spectra of a 2 μm thick $Ga_{0.8}In_{0.2}Sb$ grown on GaSb substrate is shown in Fig. 3. The full width half maximum (FWHM) is about 450 arc-secs and is typical of layers grown on lattice mismatched substrates. Hall measurements showed that all the undoped materials (both GaSb and GaInSb) are p-type with the carrier concentrations in the mid 10^{16} cm^{-3} range at room temperature. Figure 4 shows the carrier concentration of a typical GaInSb layer grown on GaAs as a function of temperature. Figure 5 shows the mobility of this

layer as a function of temperature. Since the crystalline quality and the surface morphology of the layers grown on GaAs are poor, the value of mobility measured in these layers do not necessarily represents those of the layers grown on GaSb substrates.

Extrinsic Doping

Doping with Tellurium

For TPV cell fabrication, both n type and p type layers are necessary. We have investigated Te from diethyltellurium (DETe) as the n type dopant in $Ga_xIn_{1-x}Sb$. Figure 6 shows the carrier concentration at room temperature and at 77K as a function of the DETe flow rate. Two points should be noted here. First, the carrier concentration measured decreases as the DETe flow rate is increased. Second, the carrier concentration at 77K is higher than that at room temperature. Decrease of carrier concentration with the increase in DETe MF indicates compensation of Te-donors when incorporated in high concentration. This fact is supported by the fact that the Hall mobility decreased as the DETe mole fraction is increased (see Figure 7). SIMS measurement was carried out on a layer doped with $2.1x10^{-7}$ MF of DETe and the spectra is shown in figure 8. The Te concentration in this layer is about $2x10^{19}$ cm^{-3}, whereas the carrier concentration measured is about $5.3x10^{17}$ cm^{-3}, indicating that only 2.5% of Te is electrically active. The layer should be grown with lower DETe mole fraction than was used here. The system is being modified to deliver DETe in effuser mode so that the MF of DETe can be controlled in the low range.

The increase in the carrier concentration of n type GaInSb layer with the decrease in temperature cannot be explained by the simple impurity ionization model. This type of behavior is caused by the presence of a second conduction band minimum (L-minimum) very close to the minima at the center of the Brillouin zone (Γ). Carriers can be excited to the L band as the temperature is increased. Figure 9 shows the measured Hall coefficient as a function of temperature for a Te-doped GaInSb sample. Also shown is a first order theoretical curves of the Hall coefficient assuming two conduction band minima separated by an energy $\Delta E_{L\Gamma}$ of 80 meV. The curves has been calculated for mobility ratio of $\mu_\Gamma/\mu_L=10$ and density of states $N_L/N_\Gamma =11.4$ which corresponds to values of GaSb. Notice that the data can be better fitted when the energy separation between the L and the Γ band minima is 130eV. In InSb the calculated separation between the L and the Γ band minima is 0.78eV and in GaSb is 0.08eV. The separation of 0.13 eV corresponds to an In concentration of approximately 7%. X-ray measurements show the In concentration to be 15%. It should be mentioned that the theoretical curves drawn depend upon the mobility ratio and the density of states assumed.

Doping with silicon

Si is widely used for n-type doping in GaAs and GaInAs. It is an amphoteric dopant and its behavior depends on the growth methods and the growth conditions. In InSb, Si is known to behave as p type impurity[7]. Behavior of silicon in GaInSb has not been studied before. Since the control of p type doping level is necessary to fabricate TPV cells, we carried out extrinsic p type doping of GaInSb using silicon as the dopant. Silicon was supplied by 600 ppm silane in hydrogen. The GaInSb layers were grown at 600C on both GaSb and GaAs substrates. Hall

measurements showed that Si is p-type in $Ga_xIn_{1-x}Sb$. Figure 10 shows the measured carrier concentration as the silane mole fraction is increased. P type carrier concentration as high as $2x10^{18}$ cm^{-3} was achieved with silane doping. Similar to that of Te, the doping concentration decreases as the silane flow increased, indicating compensation.

Device Characteristics

A TPV device structure is grown on GaSb substrate using DETe for n type doping and silane for p type. The structure is shown schematically in figure 11. P-on-n devices have been fabricated in this structure and the results will be added in the final version of the paper.

4. CONCLUSIONS

GaInSb has been investigated as possible material system for TPV application. This material was grown on GaSb and GaAs substrates using OMVPE. As grown layers are p type with a carrier concentration in the mid $1 x 10^{16} cm^{-3}$ range. Extrinsically doped p type and n type layers have been grown using Te and Si as the dopants, respectively. Unlike other III-V system such as GaAs, silicon was found to behave as p type in GaInSb. The measured carrier concentration in n type layers increased as the temperature of measurement is decreased. This phenomena was attributed to the presence of second band very close to the conduction band minima in GaInSb. A first order simulation assuming two-band conduction adequately explains the behavior of n type GaInSb layers. TPV device structures have been grown on GaSb substrates and the results will be reported in the final version of the paper.

5. ACKNOWLEDGEMENT

6. REFERENCES

1. R. Sharps et al., Proc. of first NREL conf. on TPV generation of electricity, AIP conf. Proec. V321, 194, 1994.
2. Y. Itani, H. Asahi, T. Kaneko, Y. Okuno and S. Gonda, J. Appl. Phys, 73, 1161-1167 (1993).
3. S. Iyer, S. Hegde, A. Abdul-Fadi, K.Bajaj and W. Mitchel, Phys. Rev. B, 47, 1329-1339, (1993).
4. L.J.G. Zaza,M.T.Montojo, J.L.Castano and J. Piqueras, J. Electrochem. Soc., 136, 1480-1484, (1989).
5. F. Karouta, A. Marbeuf, A. Joullie and J.H.Fan, J. Crystal Growth, 79, 445-450, (1986).
6. A.G.Milnes and A.Y. Polyakov, Solid State Electron., 36, 803-818, (1993).
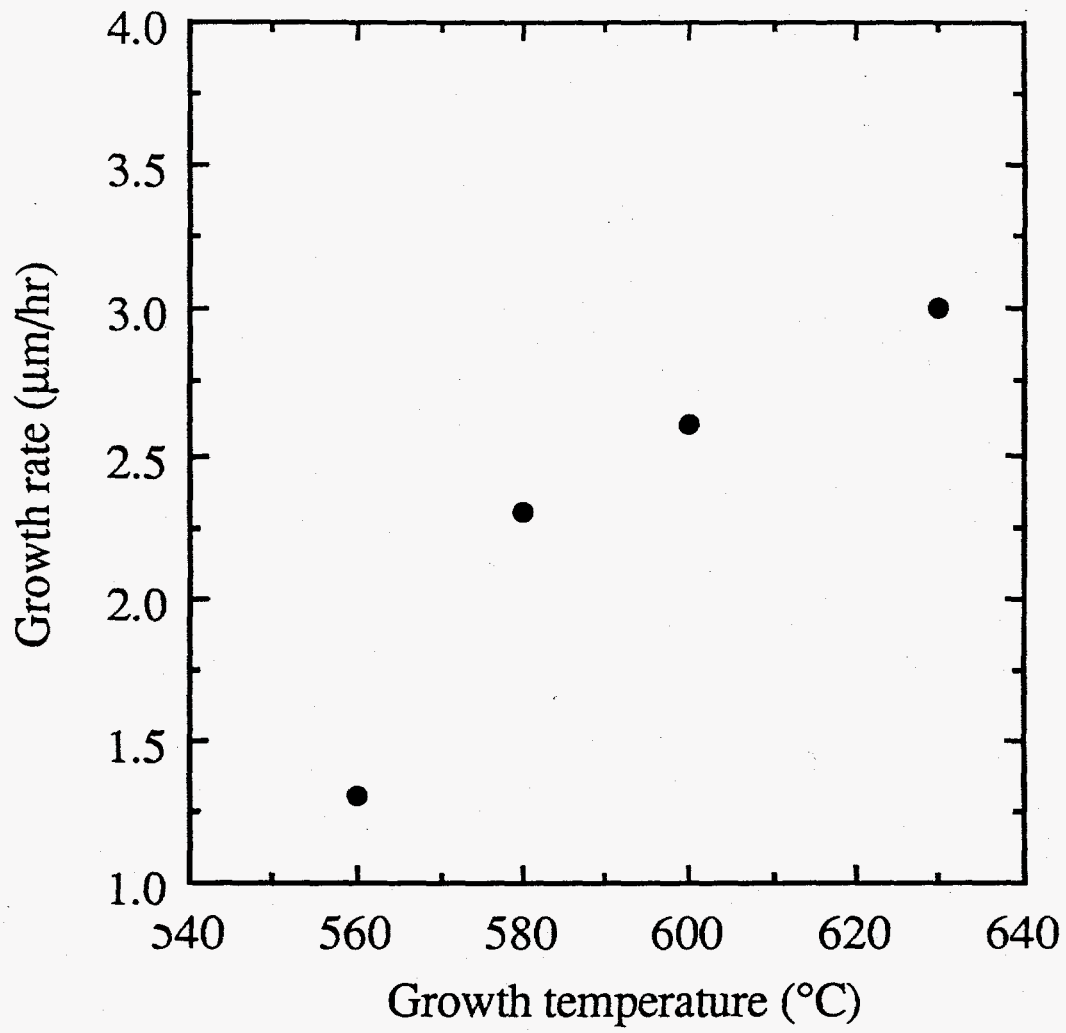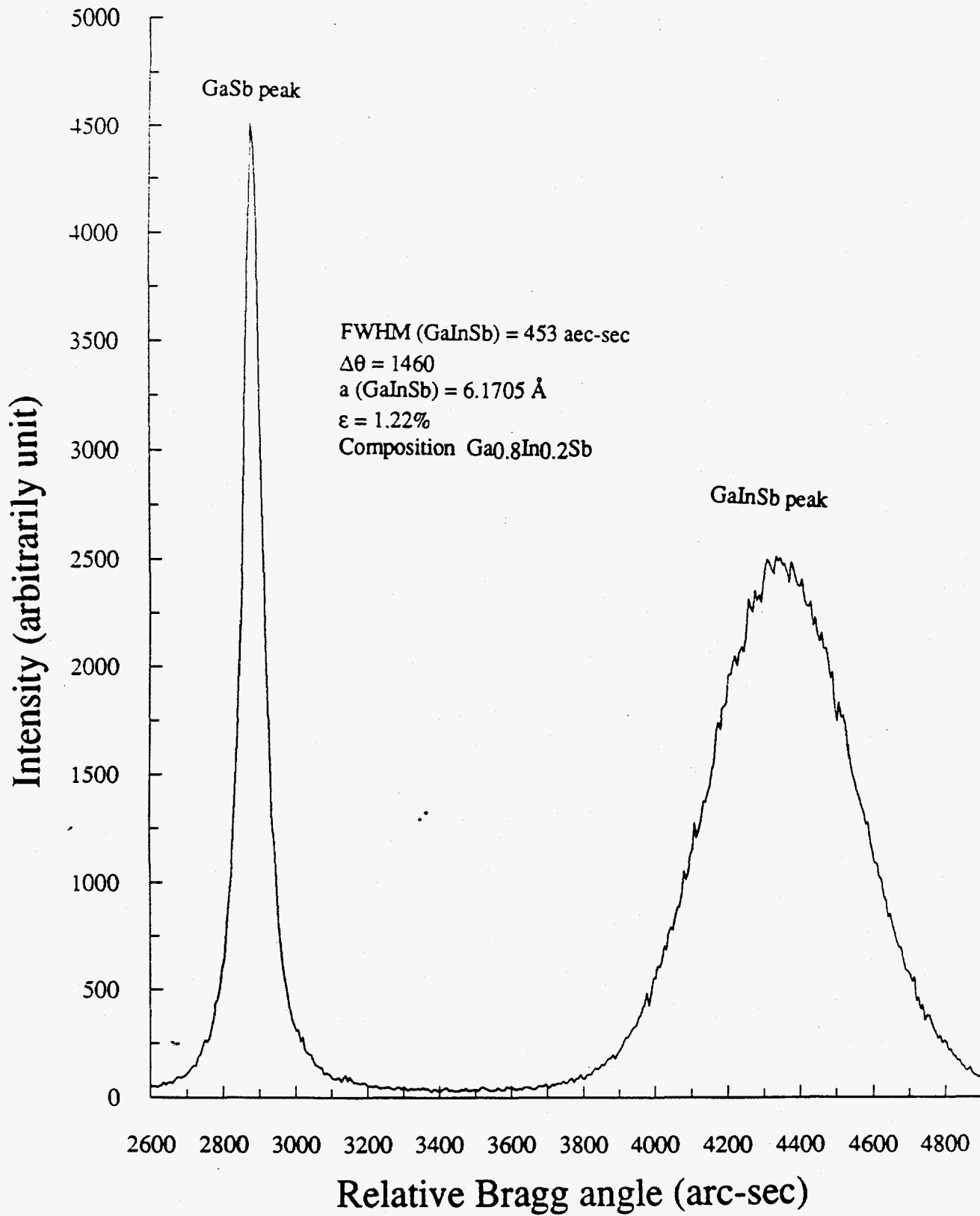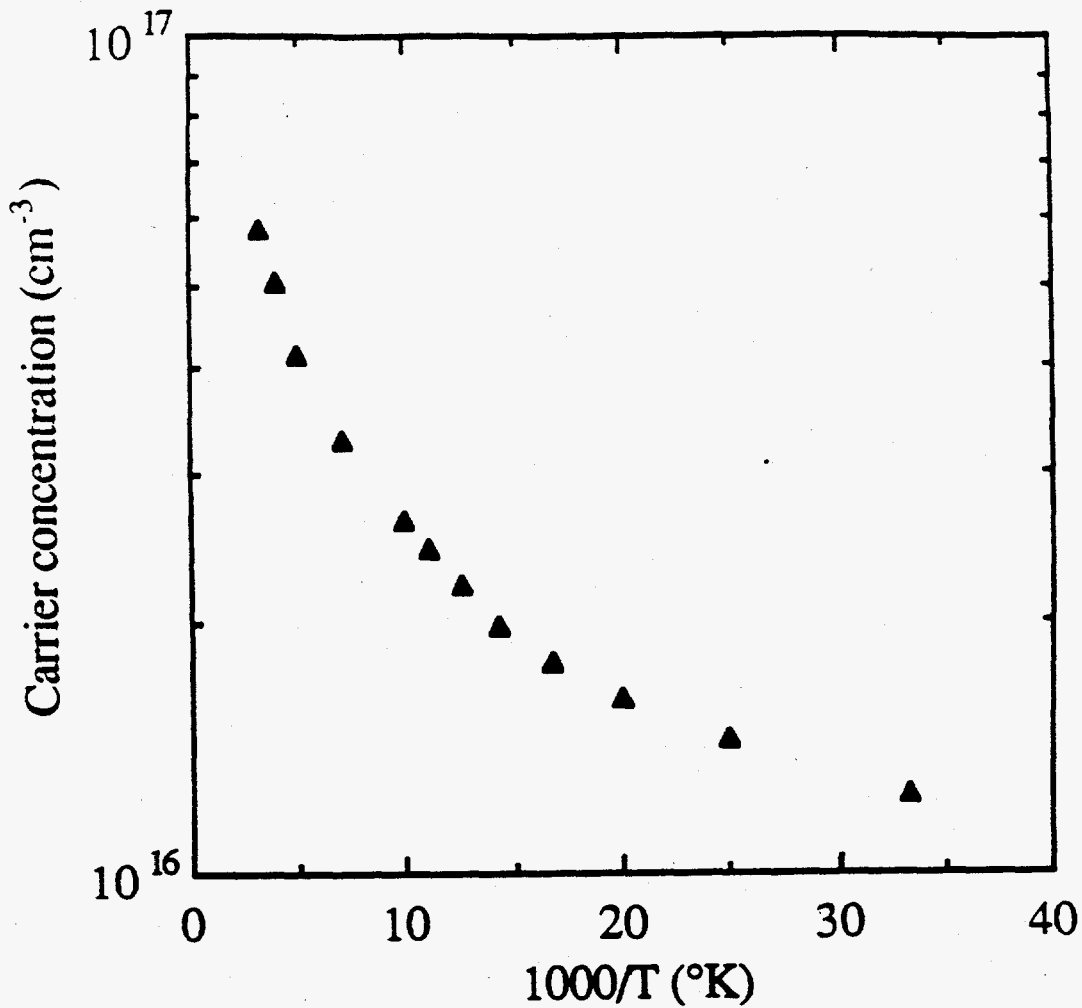7. P.Thompson et al., Mat. Res. Soc. Symp. PRoc. V216, 221 (1991).

Fig 2   Surface Morphology Photographs

Double crystal x-ray diffraction data of GaInSb grown on GaSb substrate
Run # 35

Plot: Intensity (arbitrarily unit) vs. Relative Bragg angle (arc-sec)

GaSb peak

GaInSb peak

FWHM (GaInSb) = 453 aec-sec
$\Delta\theta = 1460$
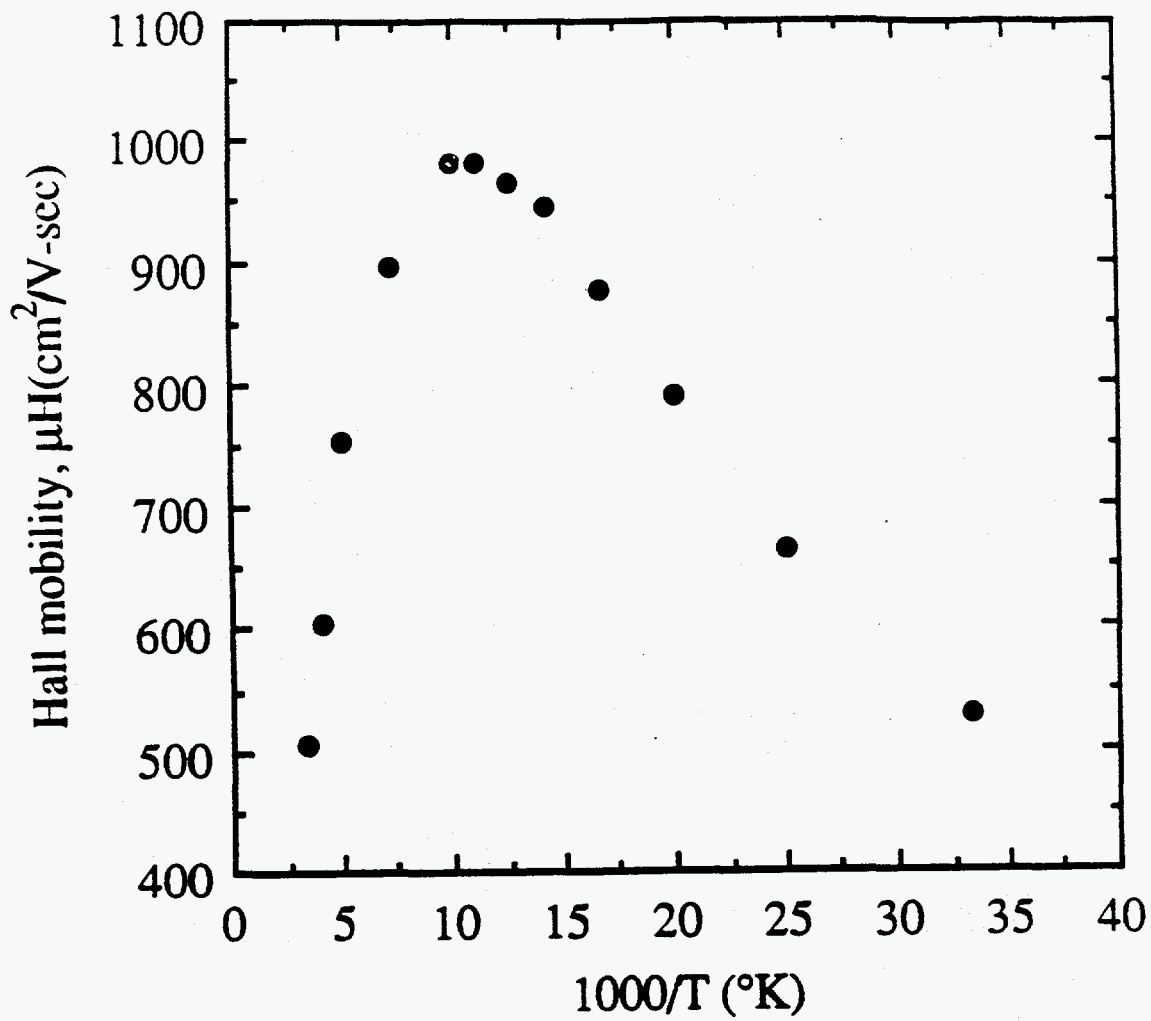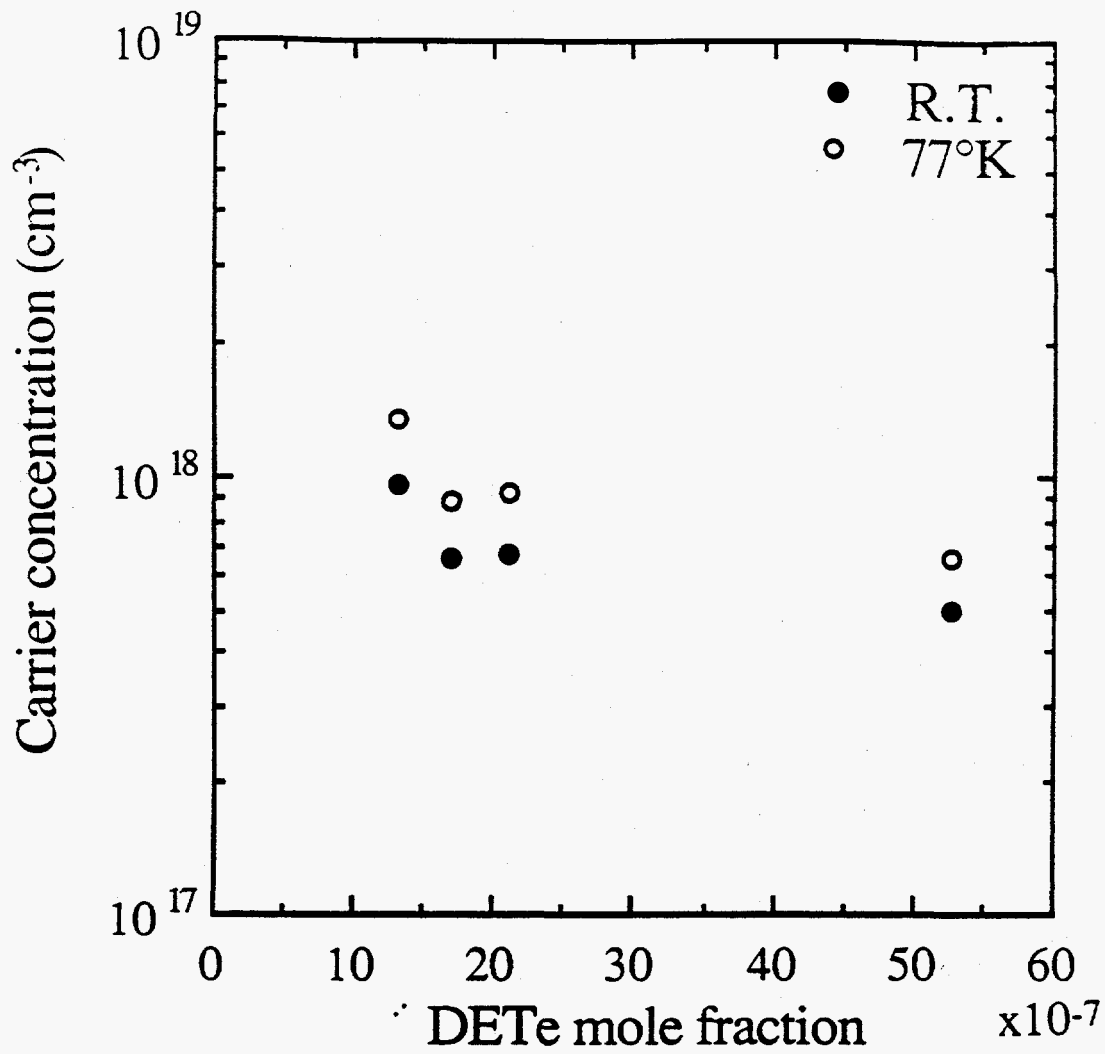a (GaInSb) = 6.1705 Å
$\varepsilon = 1.22\%$
Composition $Ga_{0.8}In_{0.2}Sb$

Fig 3

Temperature dependence of the carrier concentration of as grown layer of GaInSb grown on GaAs substrate.

= F.9 +
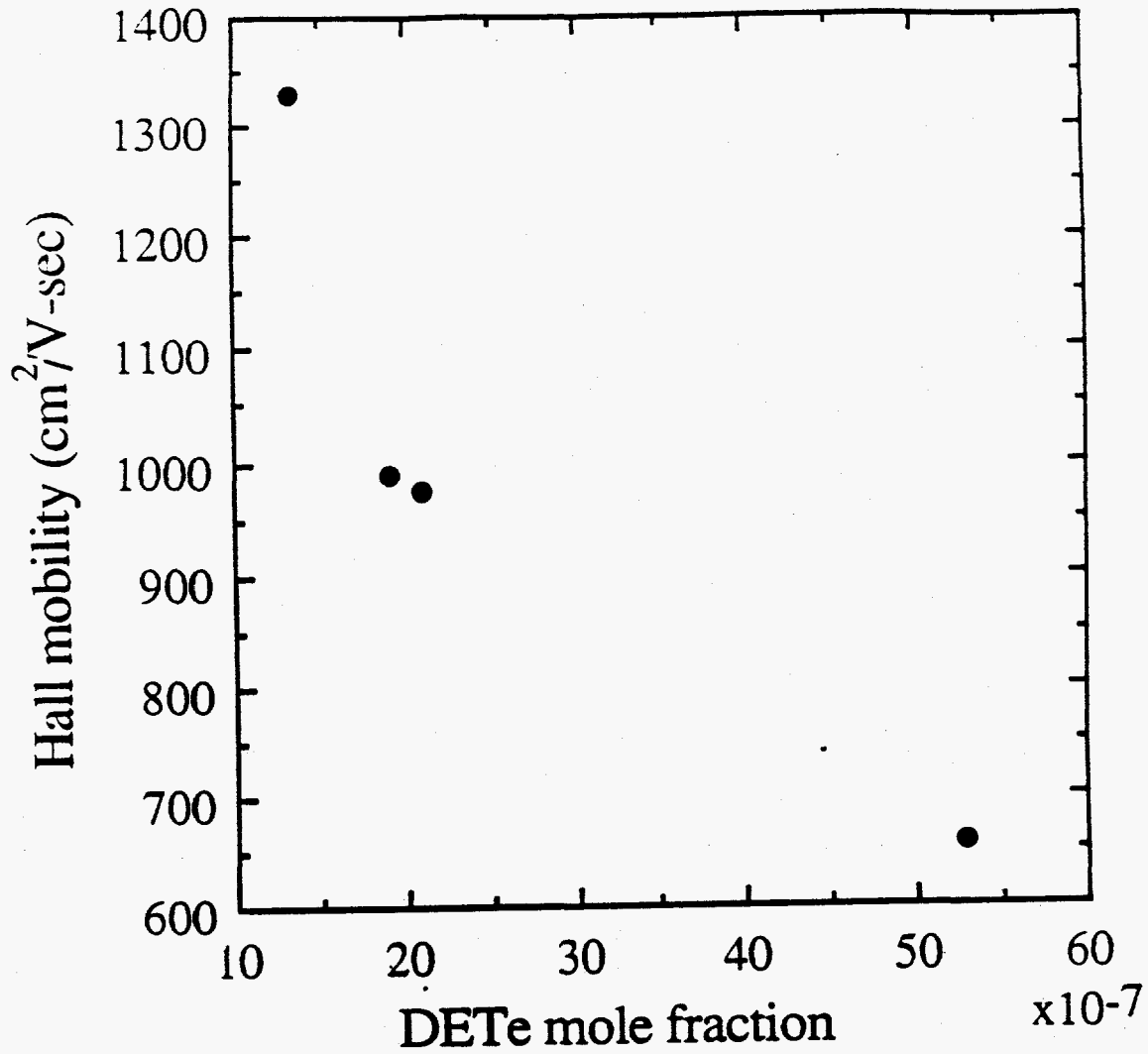
Temperature dependence of the Hall mobility of as grown layer of GaInSb grown on GaAs substrate.

Carrier concentration vs DETe mole fraction of GaInSb grown on GaAs substrate.

Fig C

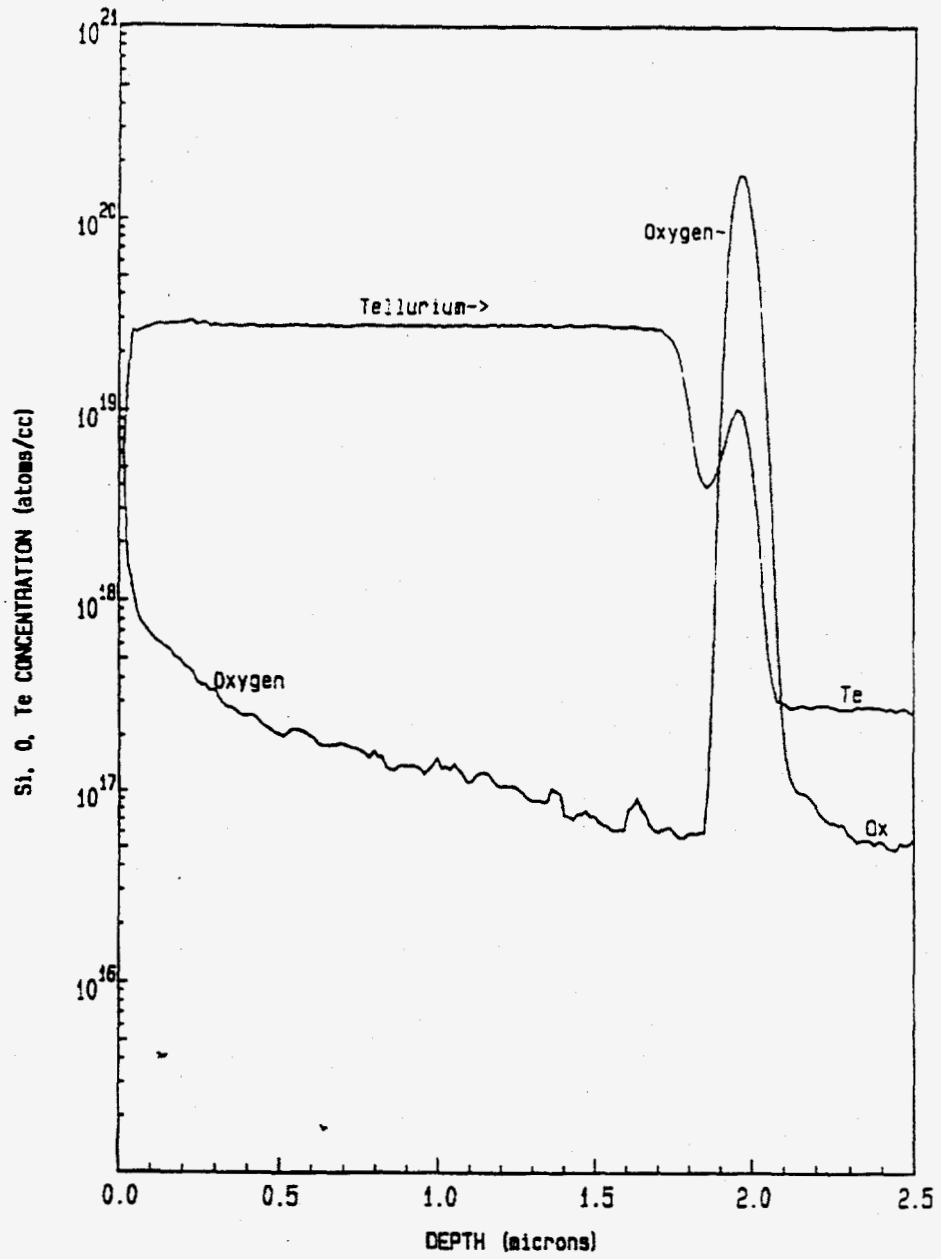Hall mobility vs DETe mole fraction of GaInSb grown on GaAs substrate.

Fig 8

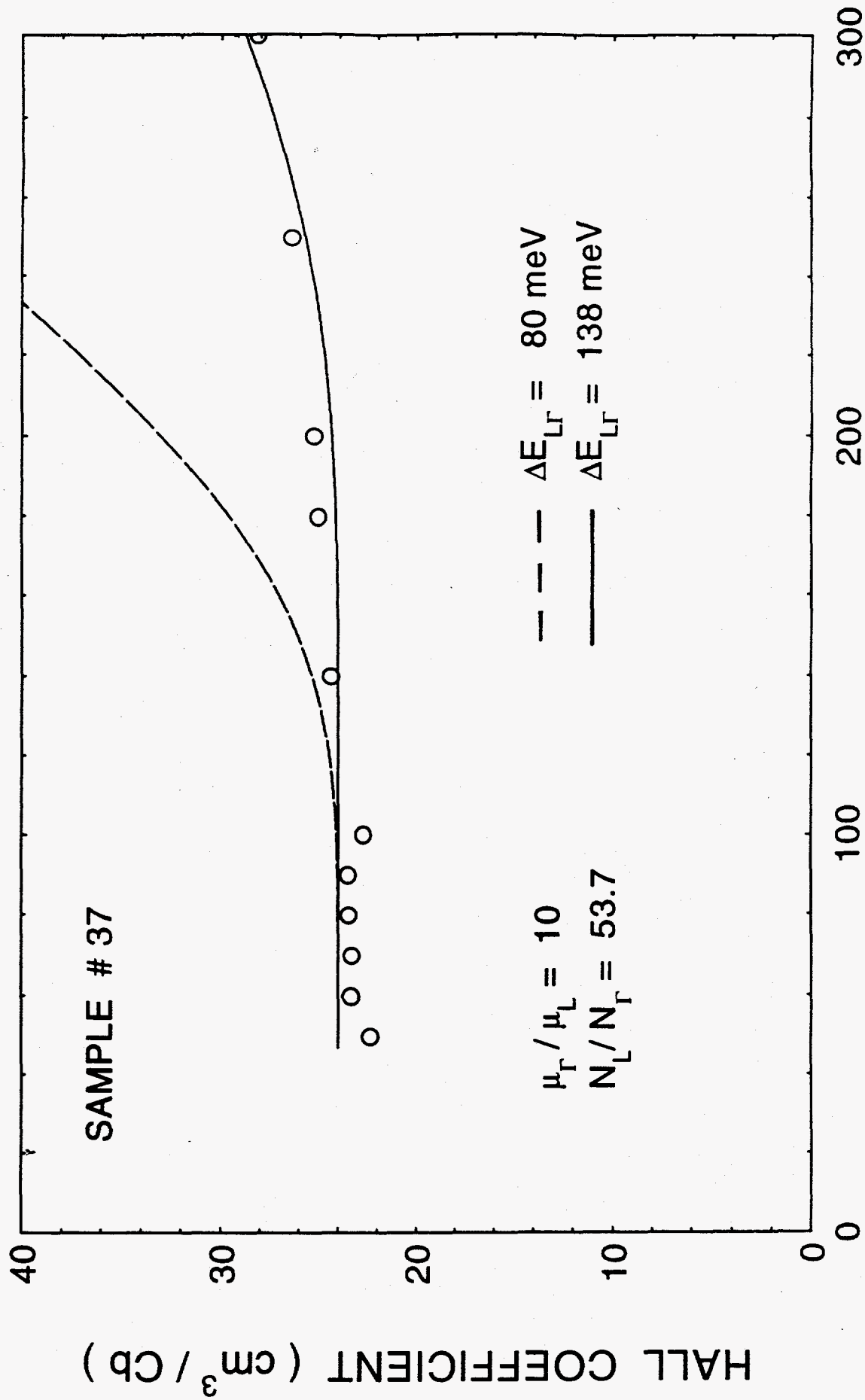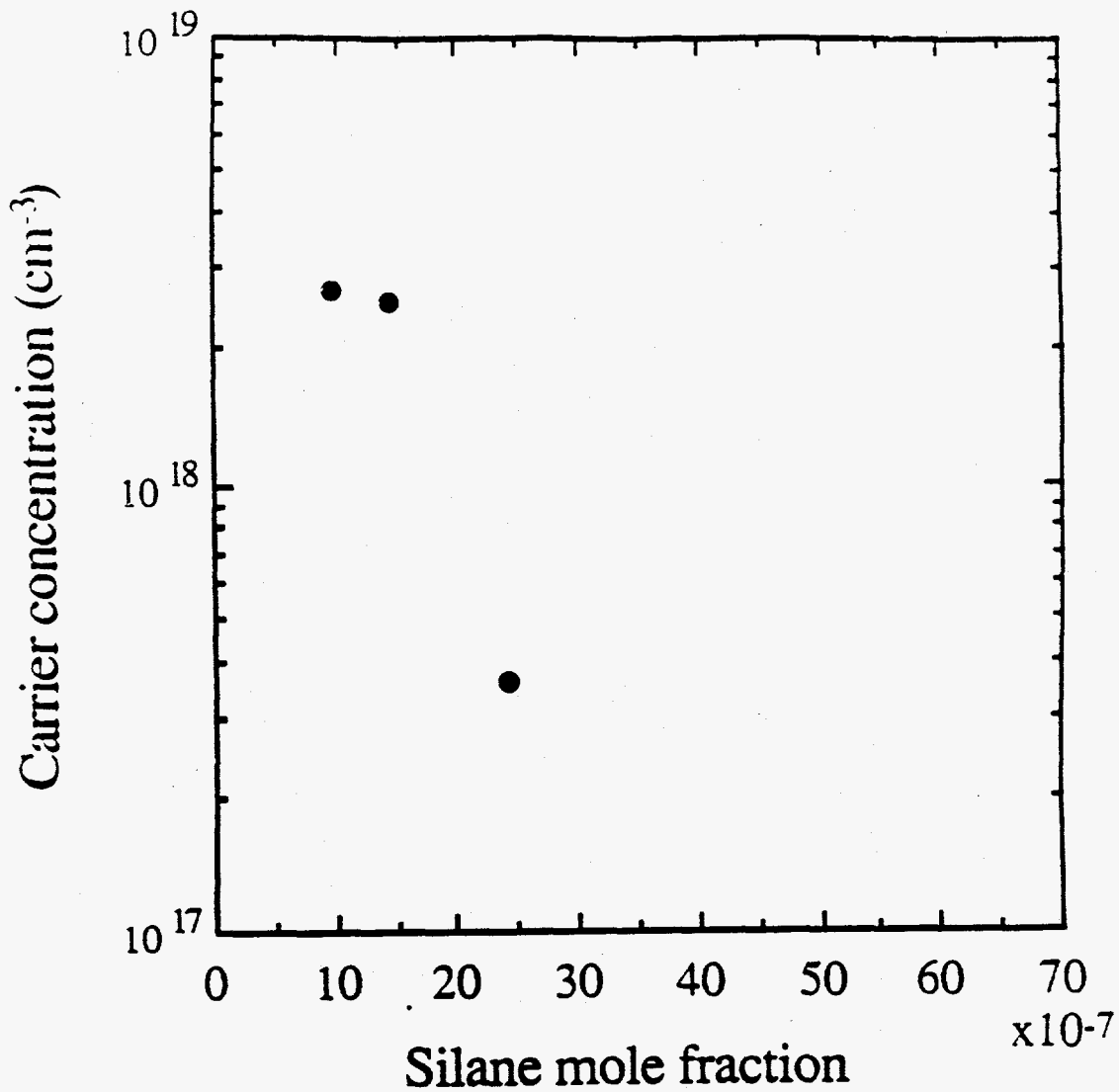HALL COEFFICIENT OF GaInSb SAMPLE

SAMPLE # 37
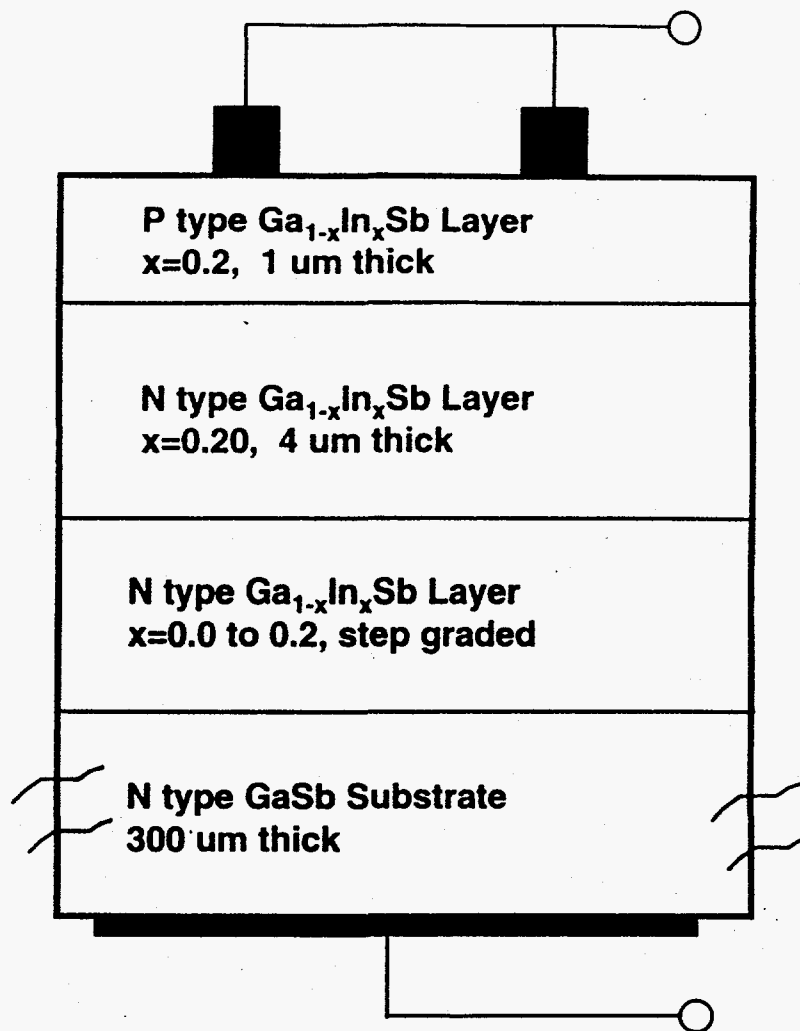
$\mu_\Gamma / \mu_L = 10$
$N_L / N_\Gamma = 53.7$

$--- \quad \Delta E_{L\Gamma} = 80$ meV
$--- \quad \Delta E_{L\Gamma} = 138$ meV

HALL COEFFICIENT (cm^3 / Cb)

TEMPERATURE ($^\circ$K)

Fig. 9

Carrier concentration vs silane mole fraction of GaInSb grown on GaAs substrate.

Fig 10

P type $Ga_{1-x}In_xSb$ Layer
x=0.2, 1 um thick

N type $Ga_{1-x}In_xSb$ Layer
x=0.20, 4 um thick

N type $Ga_{1-x}In_xSb$ Layer
x=0.0 to 0.2, step graded

N type GaSb Substrate
300 um thick

$Ga_{1-x}In_xSb$ TPV Cell Structure