KAPL-P-000085
(K98075)

CONF-9805146--

TELLURIUM DOPING OF $Ga_{0.8}In_{0.2}Sb$ LAYERS GROWN BY METALORGANIC VAPOR PHASE EPITAXY

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June 1998

NOTICE

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Tellurium Doping of $Ga_{0.8}In_{0.2}Sb$ layers grown by Metalorganic Vapor Phase Epitaxy

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ABSTRACT

N-type $Ga_{0.8}In_{0.2}Sb$ epitaxial layers have been grown on GaSb and GaAs substrates by metalorganic vapor phase epitaxy (MOVPE) using diethyltelluride (DETe) as the dopant source. The incorporation efficiency of Te in $Ga_{0.8}In_{0.2}Sb$ and the electron mobility were found to be higher with GaSb substrates compared to using GaAs substrates. The electron concentration increased from $5 \times 10^{16} cm^{-3}$ to $1.5 \times 10^{18} cm^{-3}$ as the Te concentration was increased from $1 \times 10^{17} cm^{-3}$ to $5 \times 10^{18} cm^{-3}$. As the Te concentration was increased further, the electron concentration decreased, with only about 1% of the Te electrically active at a Te concentration of $2 \times 10^{20} cm^{-3}$.

INTRODUCTION

$Ga_{1-x}In_xSb$ is a promising semiconductor alloy for the fabrication of thermophotovoltaic devices (1) and infrared detectors (2). For device fabrication, both n-type and p-type layers with precise control of doping concentration are required. Group IV elements such as Si, Ge, and Sn are amphoteric dopants in III-V compounds; and they can incorporate as n-type or p-type, depending on the growth conditions, and the relative covalent radii of the dopants and the host atoms. In $Ga_{0.8}In_{0.2}Sb$ and GaSb grown under typical growth conditions, group IV elements incorporate as p-type dopants (3,4). Thus, the choice for n-type doping is limited to group VI elements, namely Te, Se, and S.

Preliminary studies of S (5) and Se (6) for n-type doping in GaSb layers grown by molecular beam epitaxy (MBE) showed that these are not suitable as n-type dopants. The maximum carrier concentration obtained in the layers doped with these elements was below $5x0^{16}$ cm^{-3}. To date, Te is the only element successfully used as the n-type dopant in GaSb. Doping concentrations as high as 2×10^{18} cm^{-3} were obtained in GaSb grown by MBE and metalorganic vapor phase epitaxy (MOVPE). On the other hand, there are few reports on the n-type doping studies of $Ga_{0.8}In_{0.2}Sb$ layers. In this paper, we report the incorporation behavior of Te in $Ga_{0.8}In_{0.2}Sb$ layers grown on GaSb and GaAs substrates. The electrical characteristics of the layers on GaSb and GaAs substrates grown with various Te doping are also compared.

EXPERIMENTAL PROCEDURES

$Ga_{0.8}In_{0.2}Sb$ epitaxial layers were grown on high resistivity (100) GaSb and semi-insulating (100)GaAs substrates mis-oriented 2° towards (110), in a low pressure (100 Torr) horizontal MOVPE reactor. Trimethylantimony (TMSb), trimethylgallium (TMGa), trimethylindium (TMIn), and diethyltellurium (DETe) were used as the Sb, Ga, In, and Te sources, respectively. The growths were carried out at 600 °C with the V/III ratio in the 1.5 and 2 range. Both GaSb and GaAs substrates were first cleaned in organic solvents. The GaSb substrates were then dipped in HCl for 3 minutes, followed by etching in a dilute bromine-methanol solution, while the GaAs substrates were etched in a Caros-etch (H_2SO_4:H_2O_2:H_2O solution, 5:1:1 by volume) before loading into the reaction chamber. A thin GaSb (0.3 μm) buffer layer was grown on the substrates prior to the growth of $Ga_{0.8}In_{0.2}Sb$ layers. The growth conditions were optimized in order to grow device quality layers on GaSb substrates. The layers on GaAs substrates had poor morphology whereas mirror-like surface morphology was obtained on GaSb substrates.

A standard method of transporting the organometallic vapors to the reaction chamber uses a carrier gas such as H_2 from the inlet of the bubbler to the reactor. This method was initially used to transport the DETe, but the mole fraction transported to the chamber was too high to have good control on the doping concentration. To reduce the DETe mole fraction transported, the bubbler in "effuser mode" was used. Here, the bubbler inlet port remains closed, and a hydrogen carrier gas flow is used to transport the DETe vapors diffused through the outlet port to the chamber. To reduce the DETe mole fraction further, only a fraction of this flow was delivered to the reaction chamber and the rest was passed to the exhaust through a bypass line. By changing the flow of diluted DETe/H_2 gas mixture to the reaction chamber, good control of the DETe mole fraction delivered to the chamber was achieved.

Variable temperature Hall measurement was used to investigate the carrier concentration and the mobility in the layers. Secondary ion mass spectroscopy (SIMS) analysis was carried out to determine the Te concentration, and hence the percentage of electrically active Te. SIMS measurements were calibrated by implanting known quantities of Te into un-doped GaSb and $Ga_{0.8}In_{0.2}Sb$ layers. Double crystal x-ray diffraction was used to determine the crystalline quality and the composition of the layers.

RESULTS AND DISCUSSIONS

The surface morphology of 2μm thick $Ga_{0.8}In_{0.2}Sb$ layers grown on GaSb substrates was with the cross-hatched pattern as shown in figure 1. On the other hand, GaSb layers on GaSb substrates had mirror like surface morphology without a cross-hatched pattern. Figure 2 shows the double crystal x-ray diffraction spectra of a 2 μm-thick Te-doped $Ga_{0.8}In_{0.2}Sb$ layer grown on

GaSb substrate. The full width at half maximum (FWHM) of the (400) diffraction peak of the epilayer is 300 arc-sec indicating good crystal quality, considering the lattice mismatch of 1.3% between the epilayer and the substrate. The surface morphology of layers on GaAs substrates grown under the same conditions was rough, probably caused by the non-optimized initial nucleation conditions on GaAs. The FWHM of the x-ray diffraction peak of a 2 µm-thick $Ga_{0.8}In_{0.2}Sb$ layer was about 900 arc-sec. The large FWHM of the x-ray peak is probably caused by the large lattice mismatch (8%) between $Ga_{0.8}In_{0.2}Sb$ epilayer and GaAs substrate and by the non-optimized growth conditions.

For obtaining Hall measurements on $Ga_{0.8}In_{0.2}Sb$ layers, high resistivity (23-28 Ω-cm) p-type GaSb substrates with low carrier concentration ($6\text{-}8\times10^{14}$ cm^{-3}) at 77K were used. Semi-insulating GaAs substrates were also loaded side-by-side with the GaSb substrates. The results are summarized in figure 3, which shows that the electron concentration varies from 5×10^{16} cm^{-3} to 1.5×10^{18} cm^{-3}, as the DETe mole fraction is increased from 7×10^{-9} to 2.5×10^{-7}. When the DETe mole fraction was increased further, the electron concentration actually decreased. This behavior could be due to the high reactivity of Te with Ga, In, and Sb. The heat of formations of Ga_2Te_3, GaTe, In_2Te_3, In_2Te, InTe, and Sb_2Te_3 are about -65 Kcal/mole, -29 Kcal/mole, -46 Kcal/mole, -19 Kcal/mole, -17 Kcal/mole, and -13.5 Kcal/mole, respectively. On the other hand, the heat of formation of GaSb and InSb are -10 Kcal/mole and -7.4 Kcal/mole, respectively; thus indicating that Te atoms are significantly more reactive with Ga and In than Sb. Therefore, when the DETe mole fraction in the gas phase is very high, a large portion of incorporated Te may be in the form of undesirable phases in the layers. Precipitation of Te could also be a factor for the low electrical efficiency of incorporated Te.

In order to determine whether Te will react when introduced in high concentrations, a GaSb sample was exposed to DETe vapors in H_2 for 1 hour at 600 °C in the reaction chamber. The mole fraction of the DETe and other reactor parameters were kept similar to the conditions used when high Te doping was required. The GaSb surface was severely degraded after this step indicating some surface reaction between DETe and GaSb surface. Figure 4 shows the single crystal x-ray diffraction spectra of the GaSb substrate, which was exposed to DETe at 600°C for

1 hour. In addition to the (002) and (004) diffraction peaks of GaSb, several peaks of Ga_2Te_3 are also observed. Ga_2Te_3 is a semiconductor with the lattice constant of 5.899 A (close to that of GaSb which has a lattice constant of 6.0959 A). The x-ray data shows that this Ga_2Te_3 layer is highly textured toward (100) orientation of the substrate.

The measured electron concentration in $Ga_{0.8}In_{0.2}Sb$ layers grown on GaSb substrates is always higher (by a factor of 2) than in the layers grown on GaAs substrates (see figure 3). There can be several reasons for this difference. The incorporation of Te may be the same in both layers, but the electrical activity of Te can be higher when GaSb is used. Another possibility is that since GaSb is not as highly insulating as GaAs, systematic error in the Hall measurements may be introduced. Alternatively, the incorporation of Te may be different in layers grown on these two substrates. From SIMS analysis, we conclude that the latter one is applicable here. Figure 5 shows the Te concentration measured by SIMS on several samples, indicating higher incorporation efficiency when GaSb substrate was used. The reason for this difference in the incorporation rate is not clear, but probably related to the differences in the surface morphology that result when these two substrates are used. Also, relative strain in the material may also be different during growth, which may affect the incorporation efficiency. Figure 6 shows the electron concentration measured by Hall at 77K and the Te concentration measured by SIMS versus DETe mole fraction. As the Te concentration in the layer increases from $7x10^{16}$ cm^{-3} to $5x10^{18}$ cm^{-3}, the percentage of Te that are electrical active decreases from 75% to 35%. For DETe mole fraction of $1.4x10^{-6}$ (not shown here), only about 1% of the incorporated Te is electrically active.

Figure 7 shows electron concentration versus temperature in the layers grown on GaSb and GaAs substrates. The data for temperatures above 77 K are not plotted for the layers grown on GaSb substrates since the substrate conductivity influences the measurements. As seen, the carrier concentration actually increases as the temperature is lowered. This phenomenon is observed in GaSb (7) because Γ and L valleys are close together (only 80 meV separation). As the temperature is lowered, more electrons move to the lower energy band and result in an anomalous increase in the carrier concentration. Similar behavior is observed in $Ga_{0.8}In_{0.2}Sb$ as well. Hence, to obtain true donor concentrations in GaSb and $Ga_{0.8}In_{0.2}Sb$, Hall measurements at low temperature are necessary.

Figure 8 shows the electron mobility at 77K as a function of DETe mole fraction. The electron mobility in $Ga_{0.8}In_{0.2}Sb$ layers is 2-3 times larger when grown on GaSb substrates than when grown on GaAs substrates. This large difference in mobility can be attributed to the high density of defects in the layers grown on GaAs. The electron mobility rapidly decreases for higher DETe mole fractions. The correlation between the decrease in the electron concentration and the mobility for high DETe mole fraction is an indication that the incorporation of excess Te results in poorer quality layers.

Figure 9 shows the variation of electron mobility versus carrier concentration in 2μm thick $Ga_{0.8}In_{0.2}Sb$ layers grown on GaSb substrates. The electron mobility increases as the carrier concentration is increased, reaches a maximum value, and then decreases. Similar phenomena has also been reported by Turner et al.(8) and Pascal et al.(7) on GaSb layers, and by Zitter et al.(9) on InSb layers. The decrease of electron mobility at higher Te concentration can be explained by the scattering of carriers from defects that are generated in the layers due to undesirable phases or Te precipitation. Turner et al. suggest that this phenomena is due to the reduction in the electrostatic screening of the charge scattering centers, especially native acceptors, because of the decrease in electron concentration. Pascal et al.(7) believe that this anomalous behavior is due to an inhomogeneous distribution of Te in the layer, and the limiting case of this inhomogeniety being the presence of p- and n-type regions in the same layer. However, the nature of this behavior is not well understood at present.

CONCLUSIONS

The electrical characteristics of $Ga_{0.8}In_{0.2}Sb$ layers grown on both high resistivity GaSb and semi-insulating GaAs substrates were investigated. The incorporation of Te in $Ga_{0.8}In_{0.2}Sb$ layers grown on GaSb substrate is higher than in the layers grown on GaAs substrates. Also, as the Te concentration in the layer increases, the percentage of Te that are electrically active decreases. The electron mobility is 2-3 times larger in layers grown on GaSb substrates than in the layers grown on GaAs substrates.

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FIGURE CAPTIONS

Figure 1. Surface morphology of 2μm thick $Ga_{0.8}In_{0.2}Sb$ layer grown on GaSb substrate.

Figure 2. Double crystal x-ray diffraction spectra of 2μm thick $Ga_{0.8}In_{0.2}Sb$ layer grown on GaSb substrate.

Figure 3. Variation of electron concentration as a function of DETe mole fraction for 2μm thick $Ga_{0.8}In_{0.2}Sb$ layer grown on GaSb and GaAs substrates.

Figure 4. Single crystal x-ray diffraction spectra of GaSb substrate that was exposed to DETe at 600 °C for 1 hour.

Figure 5. Variation of electron and Te concentration as a function of DETe mole fraction for 2μm thick $Ga_{0.8}In_{0.2}Sb$ layer grown on GaSb and GaAs substrates.

Figure 6 SIMS and Hall data for $Ga_{0.8}In_{0.2}Sb$ layers grown on GaSb substrates.

Figure 7. Variation of electron concentration as a function of inverse temperature for 2μm thick $Ga_{0.8}In_{0.2}Sb$ layer grown on GaSb and GaAs substrates.

Figure 8. Variation of electron mobility as a function of DETe mole fraction for 2μm thick $Ga_{0.8}In_{0.2}Sb$ layer grown on GaSb and GaAs substrates.

Figure 9. Variation of electron mobility as a function of electron concentration for 2μm thick $Ga_{0.8}In_{0.2}Sb$ layer grown on GaSb substrates.

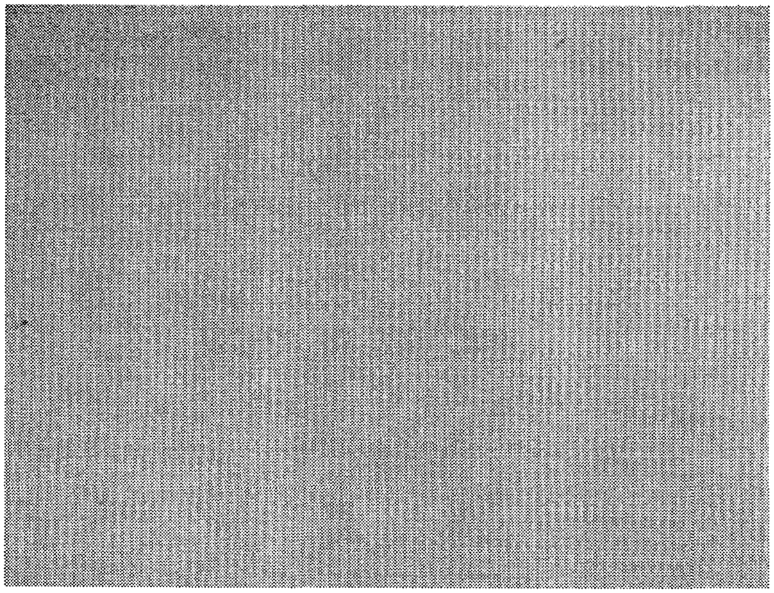


Figure 1

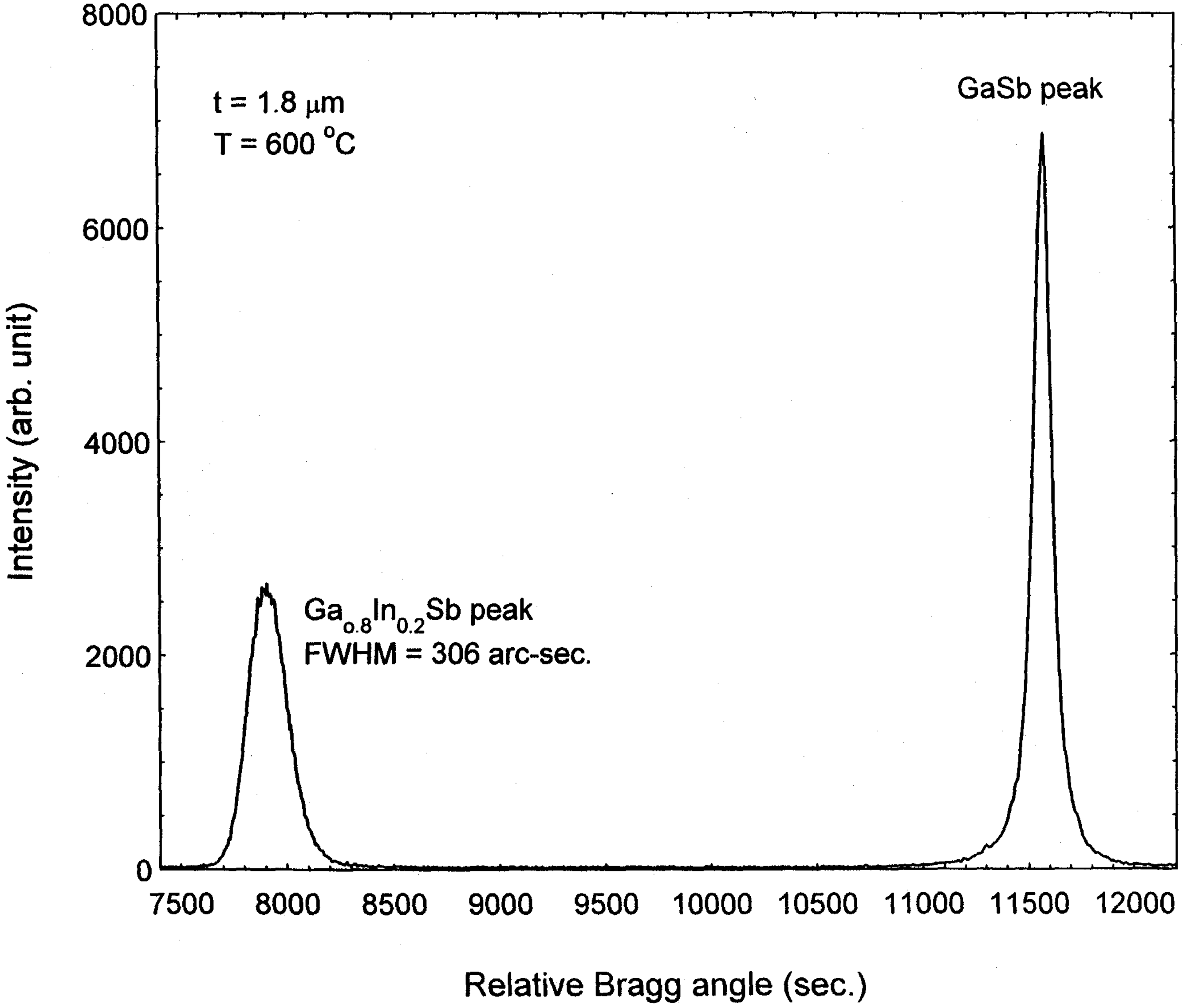

8000
6000
4000
2000
0
Intensity (arb. unit)
7500
8000
8500
9000
9500
10000
10500
11000
11500
12000
Relative Bragg angle (sec.)
t = 1.8 μm
T = 600 °C
GaSb peak
$Ga_{o.8}In_{0.2}Sb$ peak
FWHM = 306 arc-sec.

Fig 2

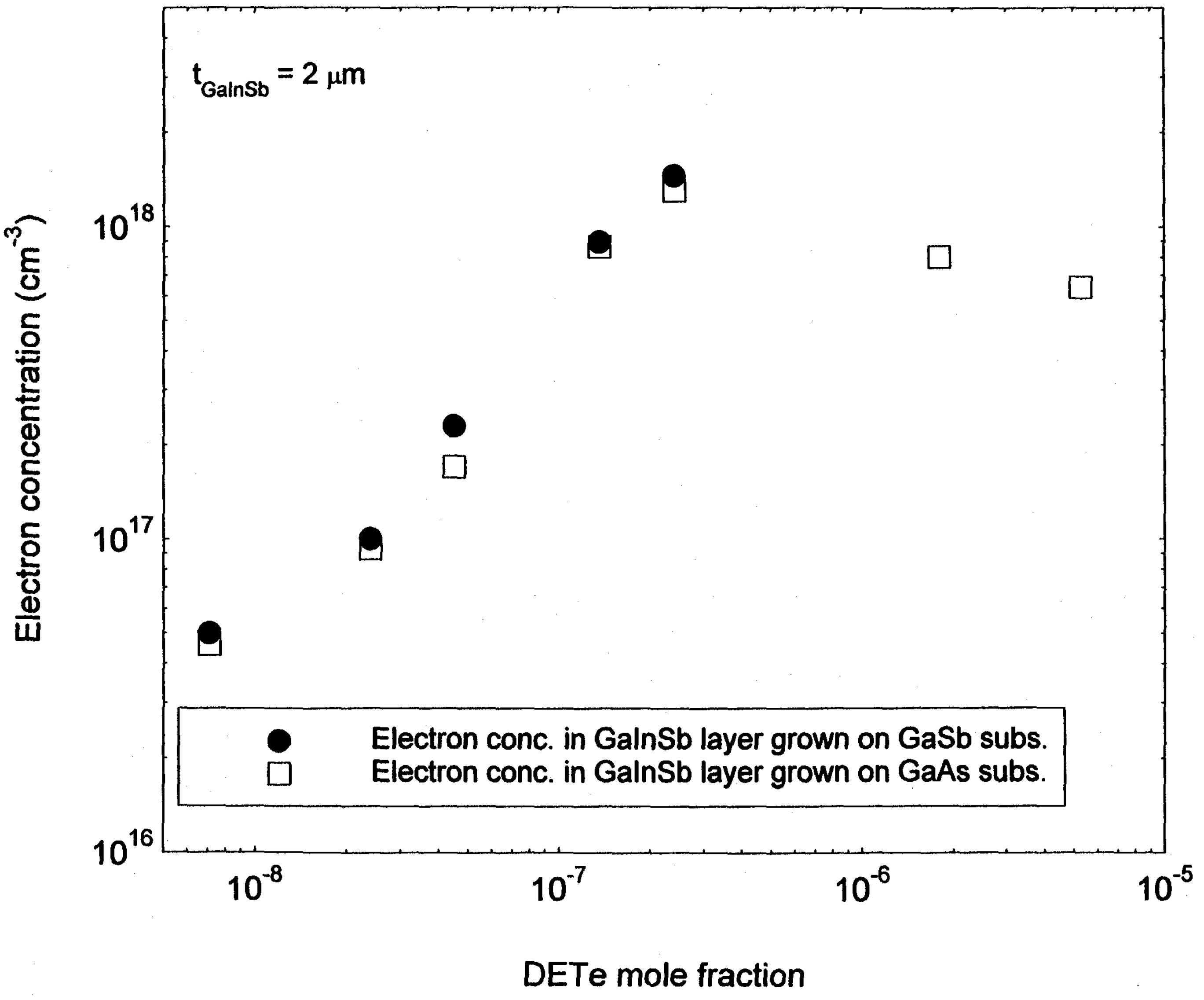
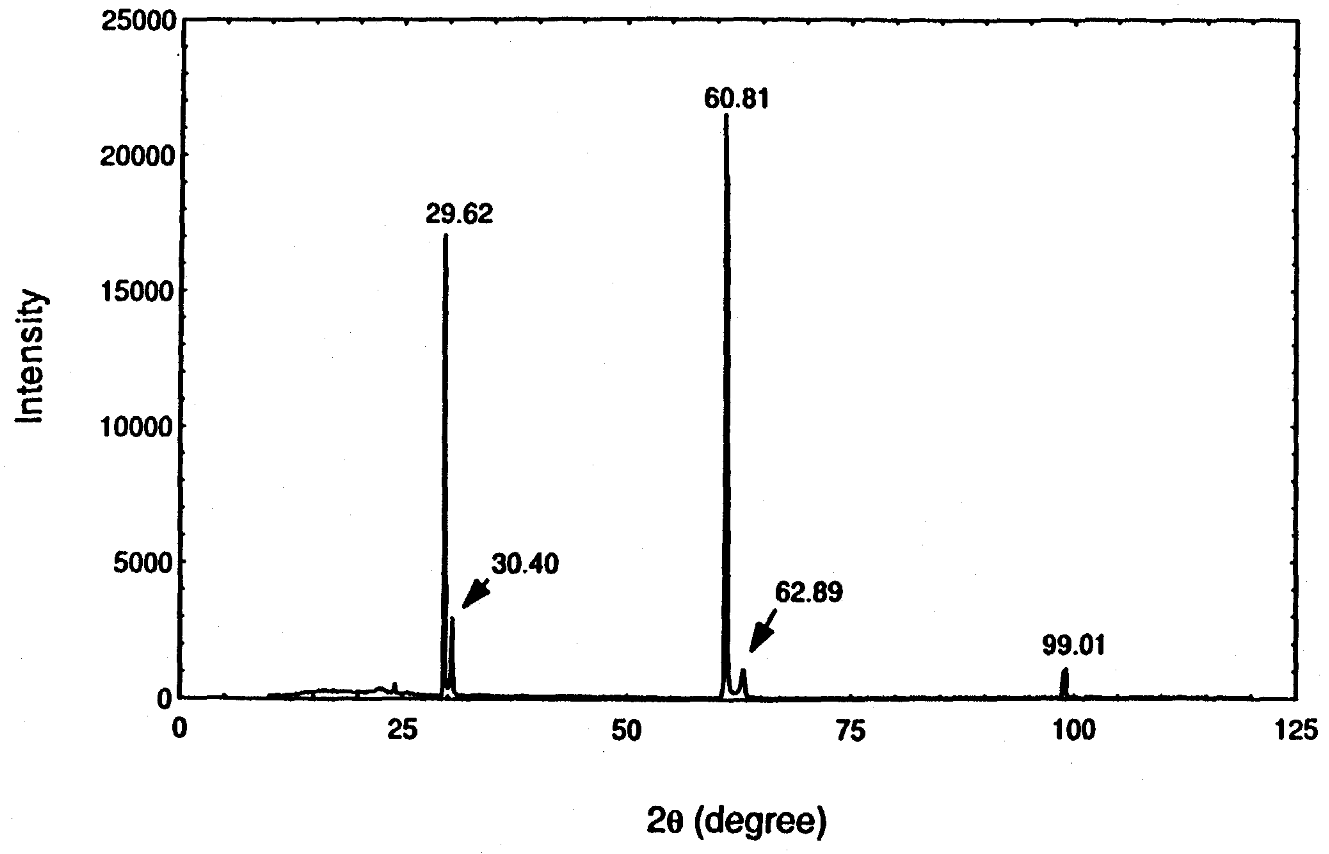

t_{GaInSb} = 2 μm
Electron concentration (cm^{-3})
10^{16}
10^{17}
10^{18}
DETe mole fraction
10^{-8}
10^{-7}
10^{-6}
10^{-5}
● Electron conc. in GaInSb layer grown on GaSb subs.
□ Electron conc. in GaInSb layer grown on GaAs subs.

Fig 3



Intensity
25000
20000
15000
10000
5000
0
0
25
50
75
100
125
2θ (degree)
29.62
30.40
60.81
62.89
99.01

Fig 4

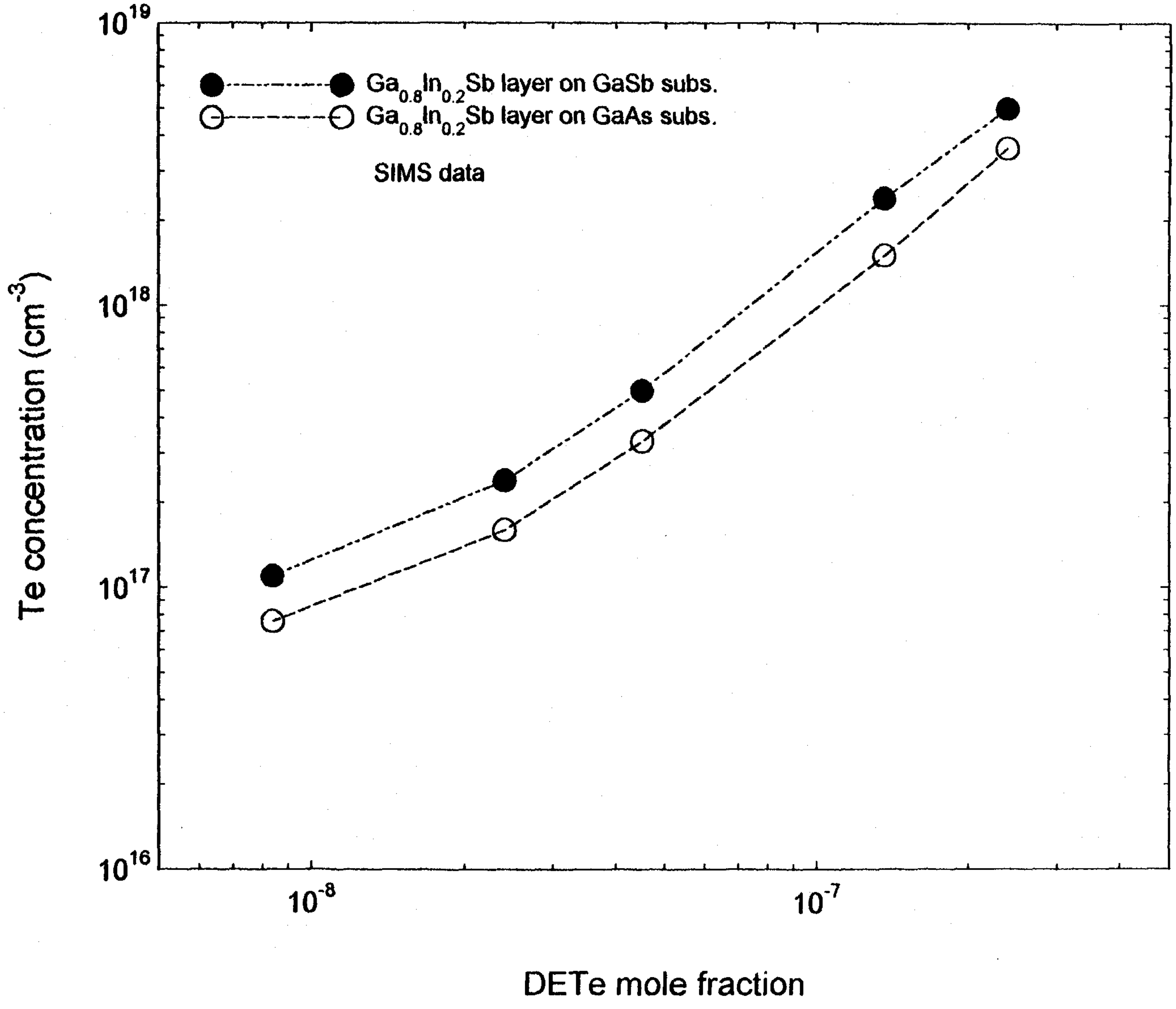

10^{19}
10^{18}
10^{17}
10^{16}
Te concentration (cm^{-3})
$Ga_{0.8}In_{0.2}Sb$ layer on GaSb subs.
$Ga_{0.8}In_{0.2}Sb$ layer on GaAs subs.
SIMS data
10^{-8}
10^{-7}
DETe mole fraction

Fig 5

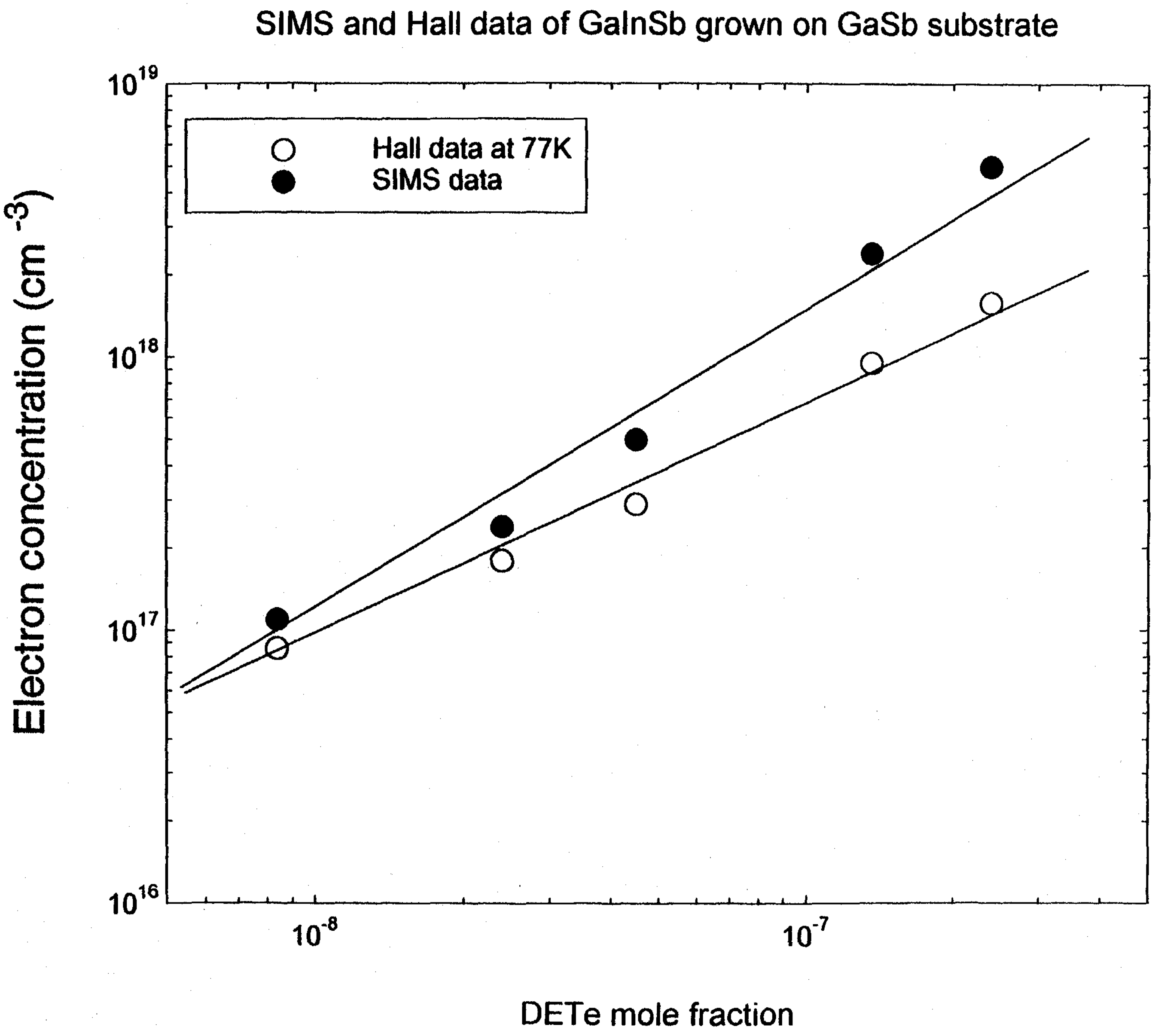

SIMS and Hall data of GaInSb grown on GaSb substrate
Electron concentration (cm $^{-3}$)
10^{19}
10^{18}
10^{17}
10^{16}
10^{-8}
10^{-7}
DETe mole fraction
Hall data at 77K
SIMS data

Fig 6

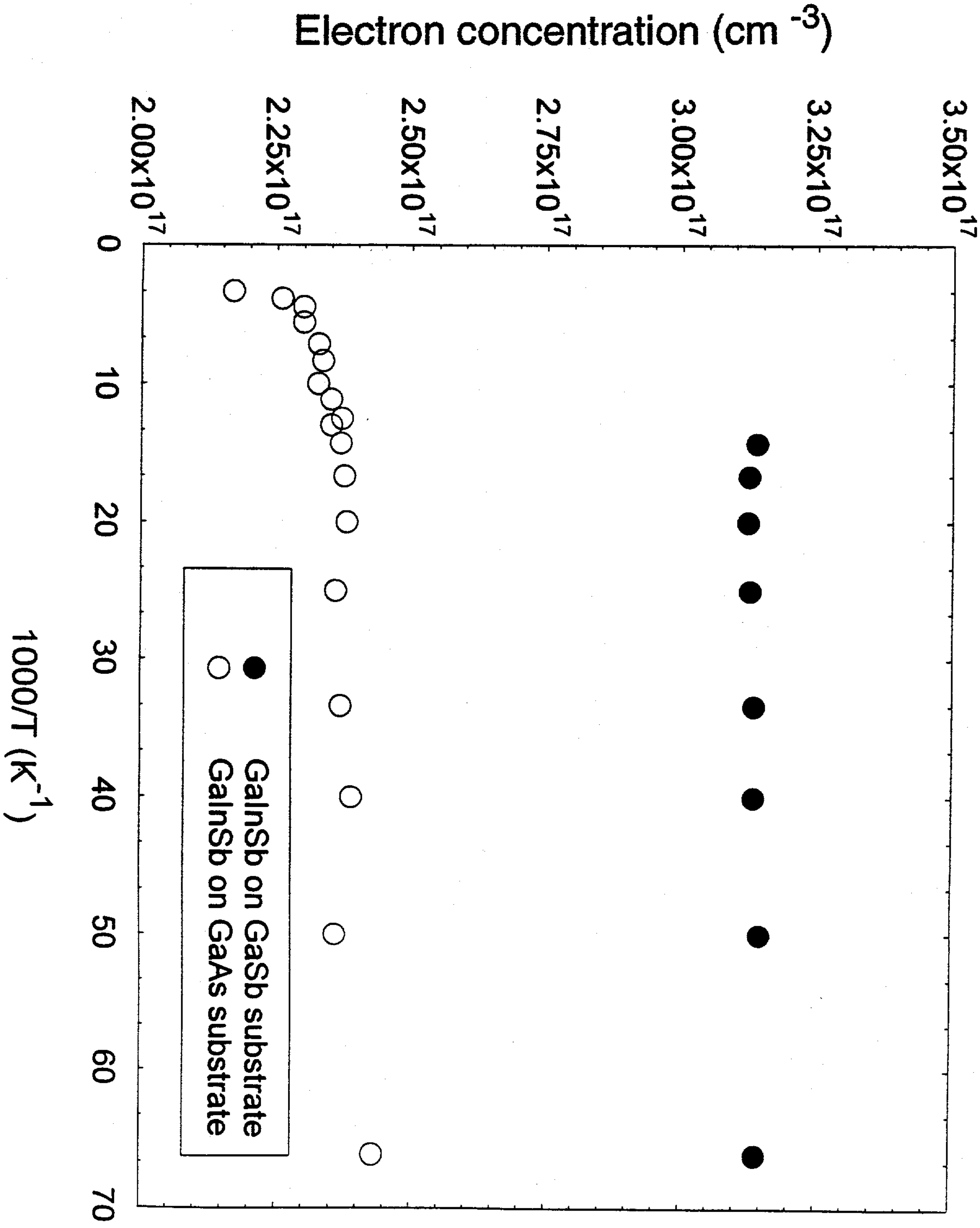

Electron concentration (cm -3)
2.00x10^17
2.25x10^17
2.50x10^17
2.75x10^17
3.00x10^17
3.25x10^17
3.50x10^17
0
10
20
30
40
50
60
70
1000/T (K^-1)
● GaInSb on GaSb substrate
○ GaInSb on GaAs substrate

Fig 7

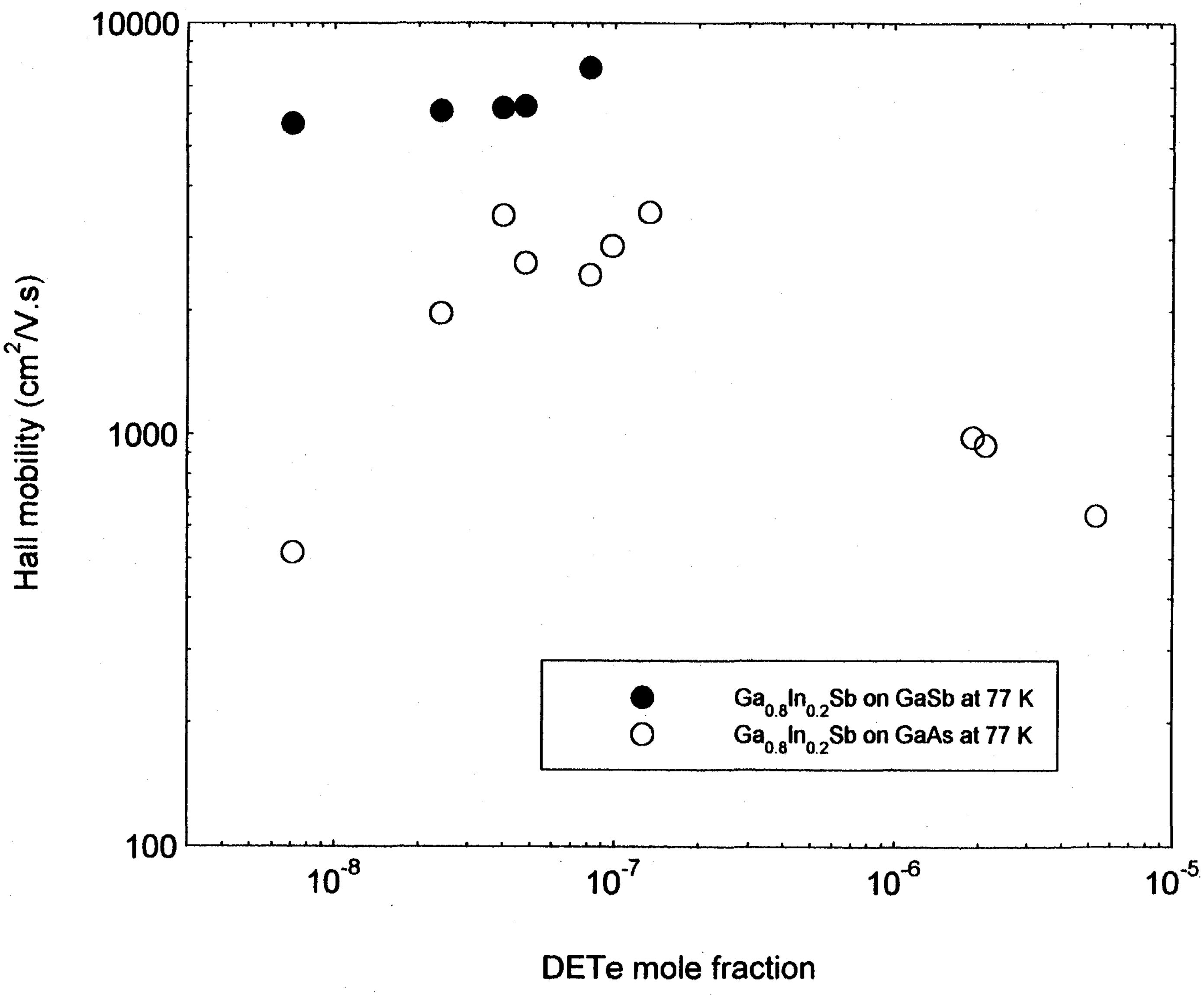

Hall mobility (cm^2/V.s)
10000
1000
100
10^{-8}
10^{-7}
10^{-6}
10^{-5}
DETe mole fraction
● $Ga_{0.8}In_{0.2}Sb$ on GaSb at 77 K
○ $Ga_{0.8}In_{0.2}Sb$ on GaAs at 77 K

Fig 8

Fig 8

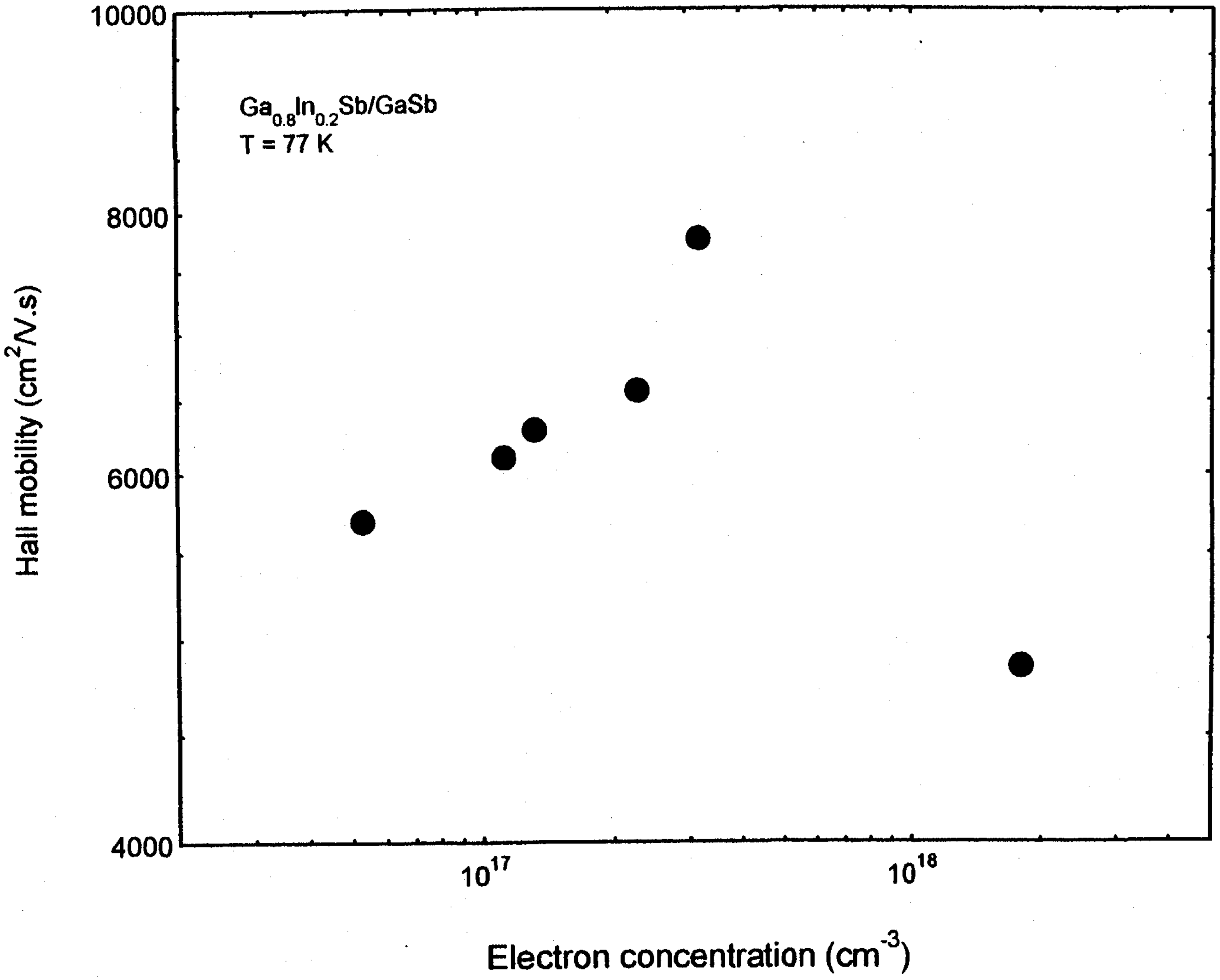

Ga$_{0.8}$In$_{0.2}$Sb/GaSb
T = 77 K
Hall mobility (cm^2/V.s)
10000
8000
6000
4000
10^{17}
10^{18}
Electron concentration (cm^{-3})

Fig Fig 9