P-Type and N-Type DOPING IN GaSb and Ga_{0.8}In_{0.2}Sb LAYERS GROWN BY
METALORGANIC VAPOR PHASE EPITAXY

CONF-9805146--

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June 1998

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P-type and N-type Doping in GaSb and $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ Layers Grown by Metalorganic Vapor Phase Epitaxy

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ABSTRACT

P-type and n-type GaSb and $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers have been grown on GaSb and GaAs substrates by metalorganic vapor phase epitaxy (MOVPE) using silane and diethyltellurium (DETe) as the dopant precursors, respectively. Hall measurements show that the concentration and mobility of holes and electrons in GaSb and $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ are higher when the layers are grown on GaSb substrates than when grown on GaAs substrates. Secondary ion mass spectrometry (SIMS) results show that the incorporation of Si and Te is higher when GaSb substrates are used. The electron concentration increased from $5 \times 10^{16} \text{ cm}^{-3}$ to $1.5 \times 10^{18} \text{ cm}^{-3}$ as the Te concentration was increased from $1 \times 10^{17} \text{ cm}^{-3}$ to $5 \times 10^{18} \text{ cm}^{-3}$. 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 $2 \times 10^{20} \text{ cm}^{-3}$.

Keywords: MOVPE, GaSb, doping, IR materials, Hall measurements

INTRODUCTION

GaSb-based materials have received considerable attention recently because of their potential application in optoelectronics⁽¹⁾ and thermophotovoltaic⁽²⁾ devices. Both n-type and p-type layers are needed to fabricate these devices. Group IV elements such as Si, Sn, and Ge can be used as the dopants; but the amphoteric nature of these elements makes them incorporate as n-type or p-type depending on the growth conditions, relative tetrahedral radii, and electronegativity. In As- and P-based materials, these column IV elements incorporate as n-type under most growth conditions^(3,4). Since the typical growth conditions of GaSb-based materials are different from those of As- and P-based materials, the incorporation behavior of column IV elements in these systems can be different. For instance, the growth of As- and P-based semiconductors are generally carried out under high V/III ratio because As and P have high vapor pressure at the growth temperature. Due to this, column IV elements incorporate in column III sites and behave as n-type. On the other hand, the growth of GaSb-based materials has to be carried out with the V/III ratio close to 1. Therefore, other factors may influence the incorporation behavior of column IV dopants in GaSb-based materials. Longenbach et al.⁽⁵⁾ have shown that Ge and Sn are p-type dopants in GaSb grown by molecular beam epitaxy (MBE). Rossi et al.⁽⁶⁾ have shown that Si behaves as p-type in GaSb layers grown by MBE. Our studies show that Si is p-type in both GaSb and $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown by MOVPE⁽⁷⁾.

Since group IV elements incorporate as p-type dopants in GaSb and $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ grown under typical growth conditions, the choice for n-type doping is limited to group VI elements, namely S, Se and Te. Preliminary studies of S⁽⁸⁾ and Se⁽⁹⁾ for n-type doping in GaSb layers grown by 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 $5 \times 10^{16} \text{ cm}^{-3}$. To date, Te is the only element successfully used as the n-type dopant in GaSb⁽¹⁰⁾. Doping concentrations as high as $2 \times 10^{18} \text{ cm}^{-3}$ 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 $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers. In this paper, we report the

incorporation behavior of Si and Te in $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on GaSb and GaAs substrates. The electrical characteristics of the layers on GaSb and GaAs substrates grown with various Si and Te doping levels are also compared.

To date, all the available reports on the Hall measurements of GaSb epitaxial layers are based on the films grown on GaAs substrates. Use of GaAs substrate is necessary for these measurements since GaSb substrates were not available in semi-insulating form. For most device applications, GaSb substrates are used and the carrier concentration and mobility data of layers grown on GaSb substrates are assumed to be the same as those of layers grown on GaAs substrates. However, the large lattice mismatch (8%) and chemical incompatibility between GaSb and GaAs could influence the mobility and carrier concentration. In this paper, we report the Hall effect measurements and the SIMS results on the Si-doped and Te doped GaSb and $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on GaSb and GaAs substrates.

EXPERIMENTAL PROCEDURE

Epitaxial layers of GaSb and $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ were grown in a low-pressure (100 Torr) horizontal reactor with a rf-heated, SiC-coated graphite susceptor. Trimethylgallium (TMGa), trimethylindium (TMIn), and trimethylantimony (TMSb) were used as Ga, In and Sb precursors respectively. These were held in a temperature-controlled bath at -10°C , 20°C , and 5°C , respectively. Silane diluted in H_2 (100 ppm) and diethyltellurium (DETe) were used as the Si and Te sources, respectively. Semi-insulating (100) GaAs, mis-oriented 2° towards (110) and p-type, (100) GaSb wafers were used as the substrates. The GaSb substrates were of high resistivity with low carrier concentration ($18\text{--}23\ \Omega\text{-cm}$ and $4\text{--}8 \times 10^{14}\ \text{cm}^{-3}$ at 77 K), so that reliable Hall measurements on the epitaxial films could be made at low temperature.

After cleaning in organic solvents, the GaAs substrates were etched in Caros etch ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O}$, 5 : 1 : 1 by volume) before loading into the reaction chamber. GaSb substrates were given a short etch in diluted Br_2 -methanol solution before loading into the

reactor. A thin GaSb buffer layer ($0.3\mu\text{m}$) was first grown on both substrates, prior to the growth of $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ films. The growth conditions were optimized to obtain the best surface morphology on GaSb substrates. The typical growth temperature was 600°C and the V/III ratio was 1.5.

The structural properties and the composition of the layers were measured using double crystal x-ray diffraction. Variable temperature Hall measurements and secondary ion mass spectrometry (SIMS) measurements were used to determine the hole concentration, mobility, and the extent of compensation. Photoluminescence (PL) measurements at low temperature were used to determine the optical properties.

RESULTS AND DISCUSSIONS

a. Characteristics of the layers doped with Si

The surface morphology of GaSb layers grown on GaSb substrates was mirror-like, whereas that of GaInSb layers was smooth with the cross-hatched patterns, caused by the lattice mis-match. The morphology of layers grown on GaAs was rough with many hillocks. Double crystal x-ray diffraction measurements showed that the full width at half maximum (FWHM) of the (400) peaks of GaSb layers grown on GaSb substrates is about 13-16 arc-sec (comparable to those of the best GaSb substrates). The FWHM values of $2\mu\text{m}$ $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on GaSb substrates were in the range 270-300 arc-sec. Un-doped GaSb epitaxial layers were p-type with the carrier concentration of about $3.5 \times 10^{16} \text{ cm}^{-3}$ at 300K.

Figure 1 shows the variation of carrier concentration measured at 77K as a function of silane mole fraction in GaSb layers grown on GaAs and GaSb substrates. These substrates were loaded side-by-side in the reaction chamber in order to eliminate the effects of any run-to-run variation. As shown, the hole concentration in the layers grown on GaSb substrates is higher by at least a factor of 2 than in the layers grown on GaAs

substrates. SIMS measurements on $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers showed that higher amounts of Si get incorporated in layers grown on GaSb substrates as shown in Fig. 2. The reason for this difference in incorporation could be related to different substrate mis-orientation or different surface morphology in these two types of films. We can also conclude that the higher hole concentration observed in GaSb layers grown on GaSb substrates is caused by the higher incorporation of Si.

Figure 3 shows the photoluminescence spectra of Si-doped GaSb layers grown on GaAs substrates. At low doping concentrations, two clearly resolved peaks at 0.80 eV and 0.809 eV are observed. The higher energy peak is believed to be caused by free exciton, and the one at 0.801 eV is probably due to acceptor-bound exciton. The donor-bond exciton peak that has been reported in unintentional p-type or doped n-type layers grown by melt ⁽¹¹⁾ or by MBE ⁽¹²⁾ is not observed here. The results suggest negligible compensation of Si in GaSb. As the doping concentration increases, the acceptor-bound exciton peak dominates the PL spectra. The FWHM of the exciton peak of the lightly doped film is only 5 meV, indicating high crystalline quality.

Figure 4 illustrates the net hole and Si concentrations as a function of silane mole fraction in $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on GaAs substrates. At low doping levels (below $3 \times 10^{17} \text{ cm}^{-3}$), the compensation ratio is less than 10%. As the Si concentration increases, the compensation ratio gradually increases and reaches 25% at the doping level of $2 \times 10^{18} \text{ cm}^{-3}$. Table 1 shows the Hall data on GaSb and $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ films grown with the same flow of silane. A lower carrier concentration in $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers indicates that Si acceptors are compensated in $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$.

b. Characteristics of the layers doped with Te

Figure 5 shows the electron concentration as a function of DETe mole fraction measured at 77 K in $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on GaSb and GaAs substrates. As the DETe mole fraction is increased from 7×10^{-9} to 2.5×10^{-7} , the electron concentration

increases from $5 \times 10^{16} \text{ cm}^{-3}$ to $1.5 \times 10^{18} \text{ cm}^{-3}$. 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. 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.

Figure 6 shows the Te concentration measured by SIMS on several samples, indicating higher incorporation efficiency when GaSb substrate was used. Similar behavior was also seen in the layers doped with Si. Figure 7 shows the electron concentration measured by Hall at 77K and the Te concentration measured by SIMS versus DETe mole fraction for layers grown on GaSb substrates. As the Te concentration in the layer increases from $7 \times 10^{16} \text{ cm}^{-3}$ to $5 \times 10^{18} \text{ cm}^{-3}$, the percentage of Te that are electrically active decreases from 75% to 35%. For DETe mole fraction of 1.4×10^{-6} (not shown here), only about 1% of the incorporated Te is electrically active.

Figure 9 shows the variation of electron mobility versus carrier concentration in $2 \mu\text{m}$ thick $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ 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.⁽¹²⁾ and Pascal et al.⁽¹³⁾ on GaSb layers, and by Zitter et al.⁽¹⁴⁾ 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.⁽¹³⁾ believe that this anomalous behavior is due to an inhomogeneous distribution of Te in the layer, and the limiting case of this inhomogeneity 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

In conclusion, it was shown that uncompensated p-type GaSb can be grown using Si as the p-type dopant. However, in $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$, compensation of the Si acceptors is observed, especially at high doping levels. The incorporation of Si and Te in both GaSb and $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ depends on whether the films are grown on GaAs or GaSb substrates. This result is significant because one has to take this into consideration in growing device structures. 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. Variation of carrier concentrations at 77K in GaSb layers grown on GaSb and GaAs substrates as a function of silane mole fraction.
- Figure 2. Si concentration measured by SIMS in $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on GaSb and GaAs substrates for various silane mole fractions.
- Figure 3. PL spectra of two Si-doped GaSb layers grown on GaSb substrates.
- Figure 4. Si concentration measured by SIMS and hole concentration measured by Hall effect in $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on GaAs substrates for various silane mole fractions.
- Figure 5. Variation of electron concentration as a function of DETe mole fraction for 2 μm thick $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layer grown on GaSb and GaAs substrates.
- Figure 6. Variation of electron and Te concentration as a function of DETe mole fraction for 2 μm thick $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layer grown on GaSb and GaAs substrates.
- Figure 7. SIMS and Hall data for $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on GaSb substrates.
- Figure 8. Variation of electron mobility as a function of DETe mole fraction for 2 μm thick $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layer grown on GaSb and GaAs substrates.

Table 1 Concentration and mobility of holes in GaSb and $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on GaAs substrates.

Silane M.F.	Epilayer	$p \text{ (cm}^{-3}\text{)}$ at 300K	$p \text{ (cm}^{-3}\text{)}$ at 77K	$\mu \text{ (cm}^2\text{/V.s)}$ at 300K	$\mu \text{ (cm}^2\text{/V.s)}$ at 77K
1.84×10^{-6}	GaSb	7.81×10^{17}	7.86×10^{17}	473	511
1.84×10^{-6}	$\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$	5.55×10^{17}	5.00×10^{17}	384	478
7.34×10^{-6}	GaSb	3.80×10^{18}	3.86×10^{18}	275	340
7.34×10^{-6}	$\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$	1.69×10^{18}	1.96×10^{18}	328	349

Figure 3
Ehsani

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Fig. 5

1.36

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