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BY METALORGANIC VAPOR PHASE EPITAXY

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Silicon as the P-type Dopant in GaSb and $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ Grown by Metalorganic Vapor Phase Epitaxy

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ABSTRACT

P-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 as the doping precursor. Hall measurements show that the concentration and mobility of holes 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 spectroscopy (SIMS) results show that the incorporation of Si is higher when GaSb substrates are used. The compensation of Si acceptors is negligible in GaSb, but is as high as 25% in $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$.

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 dopants 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⁾.

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 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) was used as the Si source. Semi-insulating GaAs and p-type 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. An Ar-ion laser was used as the excitation source, and a liquid nitrogen cooled Ge detector or thermoelectrically cooled PbS detector was used for detecting the PL signals.

RESULTS AND DISCUSSIONS

a. Characteristics of GaSb layers

The surface morphology of 2 μ m thick GaSb layers grown on GaSb substrates was smooth and without any hillocks, whereas the morphology of the layers grown on GaAs substrates was rough with hillocks, as shown in figures 1(a) and 1(b), respectively. 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 of the GaSb layers grown on GaAs substrate was about 900-1000 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 2 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. From SIMS measurements on $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers (shown later), we conclude that this difference is caused by the higher incorporation of Si in the layers grown on GaSb substrates.

Variable temperature Hall measurements were carried out to determine the effects of temperature on the electrical characteristics. The results for two representative layers are shown as Arrhenius plots in figure 3. Since the substrate conductivity affects the Hall data at higher temperatures, data above 77K are not shown for layers grown on GaSb substrates. For lightly doped film, the carrier concentration in the layers grown on GaSb and GaAs substrates are similar. This is understandable since the Si concentration is comparable to the background hole concentration. For heavily doped layers, more than a factor of 2 increase in the carrier concentration is seen when GaSb substrate is used. Moreover, the carrier concentration increases as the temperature is decreased below 50K, indicating that a parallel conduction path through

impurity bands may be present. Similar behavior has been seen in other semiconductors where a two-band conduction model was used to explain the characteristic⁽⁸⁾. Figure 4 shows the variation of Hall mobility in GaSb layers as a function of inverse temperature. The mobility is lower when the GaAs substrate is used. This is expected since the GaAs substrate is not lattice-matched to GaSb; therefore and the film might be highly defected.

Figure 5 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-bound exciton peak that has been reported in unintentional p-type or doped n-type layers grown by melt⁽⁹⁾ or by MBE⁽¹⁰⁾ is not observed here. Rossi et al.⁽⁶⁾ have also noted the absence of donor-bound exciton in the PL spectra of Si-doped GaSb grown by MBE. 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.

b. Characteristics of $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers

The characteristics of $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers doped with Si were investigated. Figures 6(a) and 6(b) show the SIMS profiles of Si in $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on GaSb and GaAs substrates, respectively. These profiles clearly show a higher incorporation of Si when GaSb substrates are used. Note also that the incorporation of carbon is below the $3 \times 10^{16} \text{ cm}^{-3}$ detection limit. This suggests that the p-type behavior of undoped layers ($p = 4\text{--}5 \times 10^{16} \text{ cm}^{-3}$) is probably due to some native defects such as anti-sites⁽¹¹⁾, and not due to residual carbon incorporation. Results of SIMS measurements on several samples are summarized in figure 7. Consistently, we observed that higher amounts of Si get incorporated in layers grown on GaSb substrates. The reason for this difference could be related to differing surface morphology in these two film types, or residual strain in the layers.

Figure 8 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 $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$.

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 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.

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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 CAPTIONS

- Figure 1. Surface morphology of 2 μm thick GaSb layers grown on (a) GaSb substrate and (b) GaAs substrate.
- Figure 2. Variation of carrier concentrations at 77K in GaSb layers grown on GaSb and GaAs substrates as a function of silane mole fraction.
- Figure 3. Variation of carrier concentration in GaSb layers as a function of inverse temperature.
- Figure 4. Variation of Hall mobility in GaSb layers as a function of inverse temperature.
- Figure 5. PL spectra of two Si-doped GaSb layers grown on GaSb substrates.
- Figure 6. SIMS profiles of Si-doped $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on (a) GaSb substrate (b) GaAs substrate.
- Figure 7. Si concentration measured by SIMS in $\text{Ga}_{0.8}\text{In}_{0.2}\text{Sb}$ layers grown on GaSb and GaAs substrates as a function of silane mole fraction.
- Figure 8. 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.

a)

b)

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Actual photo is better.

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Figure 1

Fig 6a

Fig 6b

Silane mole fraction