Comparison of CBr_4 and DTBSi as precursors for p−type doping of GaSb

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INTRODUCTION

Semiconductor materials based on GaSb hold the promise for improving optoelectronic and thermophotovoltaic (TPV) devices. Both p−type and n−type layers are required. TPV device structures suggested in the literature have been prepared with a thick p−type layer in both p−on−n and n−on−p layer sequences for absorbing the entire incident light in the p−doped layer [1]. Thus, a suitable precursor for p−doping is important for TPV device structures.

This paper focuses on p−type doping in GaSb(100) grown via metalorganic vapor phase epitaxy (MOVPE). Recently, silicon [4] and carbon [5] have become the most favored p−type dopants for GaSb. The activation energies of carbon and silicon acceptors differ only by 6.3meV. They were found to be 8.5meV for Si [4] and 14.8±1meV for C [5]. Up to now the hazardous, gaseous silicon precursor silane (SiH_4) and the solid carbon precursor carbon tetrachloride (CCl_4) the latter with potential negative environmental impact have been used predominantly. In the present work the liquid compound ditertiarybutyl silane (DTBSi) and solid carbon tetrabromide (CBr_4) were investigated. So far DTBSi has not been used as silicon precursor for p−type doping of GaSb [10].

EXPERIMENTAL

The samples were grown in an AIX200 horizontal MOVPE reactor at a pressure of 100mbar. The carrier gas was Palladium−diffused hydrogen at a total flow of 5.5 l/min. The precursors triethylgallium (TEGa) and triethylantimony (TESb) were used for GaSb growth on semi−insulating undoped GaAs(100)4° to (110). P−doping of the samples was achieved using the liquid source DTBSi and the solid source CBr_4. It is well known that the best morphological, optical, and electrical quality of GaSb can only be obtained within a small parameter window of V/III ratios. Reflectance anisotropy spectroscopy (RAS) is an appropriate tool for determining this parameter window [2] and was used in−situ to monitor growth behavior. The stability of the total reflectance indicated specular surfaces during growth and was observed for a V/III ratio of 1.25. Unintentionally and also C−doped GaSb were grown in addition with a V/III ratio of 1.5. For growth on GaAs substrates a low temperature buffer layer (70 nm) of undoped GaSb was grown at 450°C. After buffer layer growth the temperature was increased to 550°C, and 1−2 µm of GaSb were deposited. Hall measurements were carried out using the standard van der Pauw technique in a magnetic field of 0.32T. SIMS measurements were performed by RTG Mikroanalyse GmbH. We measured reflectance anisotropy (RAS) in−situ in the energy range from 0.8 to 5.0 eV employing LayTec spectrometers [3].

RESULTS AND DISCUSSION

CBr_4 and DTBSi doping characteristics in GaSb

Figure 1 compares hole concentrations of DTBSi and CBr_4 in GaSb derived from Hall measurements at room temperature.

The dependence of the hole concentration on the partial pressure ratio IV/TEGa is shown in Figure 1a. The Hall data show an increase of the hole concentration for both the doping sources. While the slope for Si−doped samples is near unity, it is significantly lower for C−doped samples. The dependence of the carrier mobility on the carrier concentration is shown in Figure 1b. Higher mobilities are found in Si−doped GaSb films. The mobilities of the Si−doped samples are in good agreement with [11] and [4] where silane was used as Si−source. Mobilities of C−doped GaSb are given in [5] for hole concentrations of $N_p>1\times10^{19}cm^{-3}$ only. Without introducing an annealing step this hole concentration could not be achieved with CBr_4 as carbon precursor.

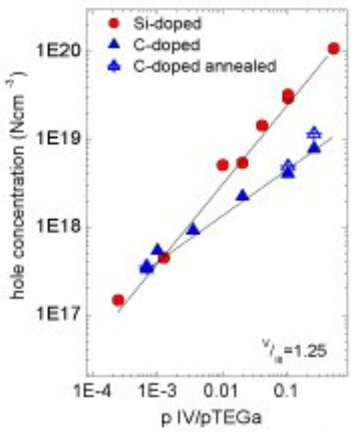

Figure1a: Hole concentrations determined from Hall measurements at 300K for as grown p-GaSb epitaxial layers. Precursors were DTBSi (circles) and CBr_4 (triangels).

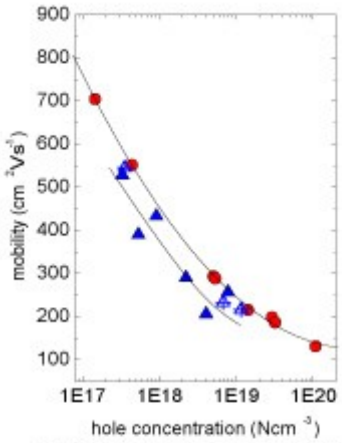

Figure1b: Hall mobilities corresponding to Figure 1a

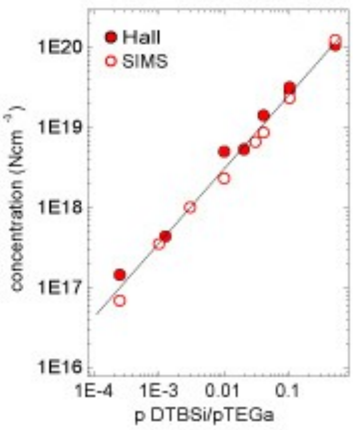

Figure2a: Comparison of Hall- and SIMS-measurements for Si-doped GaSb

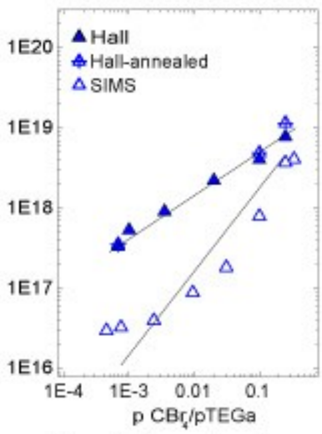

Figure2b: Comparison of Hall- and SIMS-measurements for C-doped GaSb

In Figure 2a Hall and SIMS measurements are shown for Si−doped samples and in Figure 2b for C−doped samples. The silicon concentration of the Si−doped samples is in good agreement with the hole concentration. Hence the dopant activity is close to 100% over the whole doping range. In contrast, the carbon concentration of the C−doped samples determined with SIMS is well below the hole concentration shown by Hall measurements. Samples in the lower doping levels show hole concentrations that are clearly higher than the concentration of carbon atoms, even taking into account a potential systematic error in the SIMS measurements by a factor of 2. A similar discrepancy between Hall and SIMS measurements has been reported for AlGaSb containing oxygen. The authors suggested that an increase of the native acceptor concentration in the vicinity of oxygen impurities could explain the increased hole concentrations. The oxygen concentration of our samples measured by SIMS was $X_O=1\times10^{17}cm^{-3}$ near the epilayer−substrate interface and decreased to $X_O=1\times10^{16}cm^{-3}$ during growth for both the doping sources. Photoluminescence spectra at 2K did not show an increase of the native acceptor concentration compared to undoped samples. So far the background doping level of the carbon doped samples remains unclear.

Annealing effects

A deactivation of the acceptor occurs in C−doped GaAs(100) due to the formation of C−H complexes. Thus, adequate annealing is necessary for cracking the C−H bonds and removing the hydrogen from the carbon doped layer [12]. To answer the question whether this effect occurs also in C−doped GaSb Hall measurements were carried out on as−grown samples and additionally after in−situ annealing for 2 minutes at 400°C under N_2−flow. In Figure 1 samples measured after annealing are represented by crossed triangels. Annealing the heavily doped samples increases the hole concentration significantly. This indicates that the formation of C−H complexes occurs during growth. Annealing of the Si−doped samples did not change the hole concentration. In contrast to C−doped GaAs [12] an enhancement of the carrier mobility was not observed when annealing the C−doped samples (Figure

1b). After the annealing procedure the carrier concentration was enhanced to the $1\times10^{19}cm^{-3}$ range and the corresponding mobility was $\mu=216cm^2/Vs$. This value is slightly smaller than has been reported for GaSb samples doped with CCl_4 ($\mu=247cm^2/Vs$)[5].

Variation of the V/III ratio

Table 1: Hole concentrations and mobilities of samples grown with V/III ratios of 1.25 and 1.5 for unintentionally doped GaSb, and with CBr_4 /TEGa ratios of 3.5×10^{-3} and 0.25 for C−doped GaSb. The hole concentration of unintentionally doped GaSb is not affected by the variation in the V/III ratio. In contrast, the hole concentration of C−doped GaSb decreases by a factor of 2−3 with increasing V/III ratio, i.e. from 1.25 to 1.5. Variation of the V/III ratio does not affect the carrier mobility of either unintentionally doped or C−doped samples.

Sample	V/III	CBr_4/TEGa	Doping (cm^{-3})	Mobility (cm^2/Vs)
32	1.25	-	2.8×10^{16}	710
26	1.5	-	2.2×10^{16}	730
49	1.25	3.5×10^{-3}	9.2×10^{17}	433
75	1.5	3.5×10^{-3}	3.2×10^{17}	540
101	1.25	0.25	1.2×10^{19}	216
103	1.5	0.25	7.5×10^{18}	238

Reduction in the growth rate due to CBr_4

Figure 3 shows the reduction in the growth rate as a function of the CBr_4 /TEGa ratio. The data are derived from SIMS measurements of a sample where the CBr_4 /TEGa ratio was increased stepwise. Assuming a constant sputter velocity during the SIMS measurement the width of each step gives the growth rate for the respective CBr_4 /TEGa ratio. For ratios below 1×10^{-3} CBr_4 reduces the growth rate by less than 5%. Further increase in the CBr_4 /TEGa ratio by one order of magnitude reduces the growth rate by about 20%.

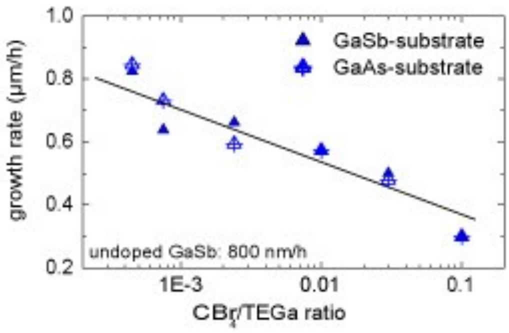

Figure 3: Reduction of the growth rate by CBr_4

RA spectra of Si and C doped GaSb

Figure 4 shows in−situ RA spectra of GaSb epilayers at 200°C under hydrogen for different concentrations of the Si−dopant. The spectra correspond to hole concentrations ranging from $N_p=3.0\times10^{16}cm^{-3}$ of an unintentionally doped layer to $N_p=1.3\times10^{20}cm^{-3}$ of a highly Si−doped layer. The main features in the RA spectra agree with spectra of oxide free GaSb substrates and C−doped epilayers of other authors [6]. Increasing the hole concentration leads to an increase in the peak hights at the energetic positions of the E_1 and $E_1+\Delta_1$ bulk transitions. A dependence of RAS peak intensities on the carrier concentration in the vicinity of these transitions is typical for the so−called linear electro-optic (LEO) effect. This effect has been reported earlier for GaAs [7], [8], ZnSe [9] and very recently for GaSb [6].

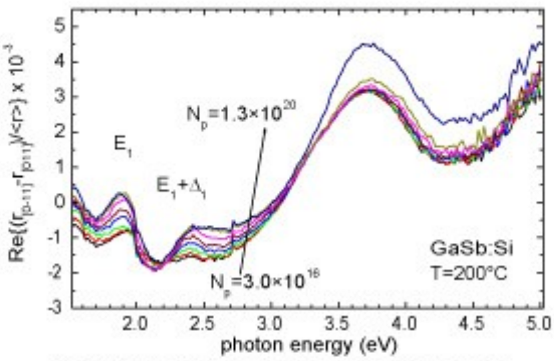

Figure 4: In-situ RA spectra of Si-doped GaSb epitaxial layers with different hole concentrations at 200°C. Increasing the doping level increases the LEO intensity between the E_1 and $E_1+\Delta_1$ transitions.

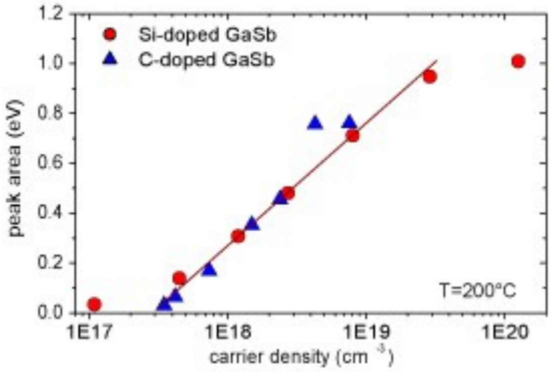

Figure 5: Dependence of the integrated LEO-Peaks and carrier concentration.

To check on the LEO effect we compared the peak intensities of Si− and C−doped GaSb epilayers by integrating the intensities around the E_1 and $E_1+\Delta_1$ transitions. Figure 5 shows the correlation between the integrated peak areas in the RA spectra at 200°C and the hole concentration. For hole concentrations between $N_p=3\times10^{17}cm^{-3}$ and $N_p=2\times10^{19}cm^{-3}$ both p−doping sources show the same linear dependence of the peak area on the hole concentration. The LEO peak area is proportional to the average surface electric field in the [001] direction [9]. Figure 5 suggests that the enhancement of the surface electric field strength with the hole concentration is independent of the doping source. At high doping levels the width of the depletion region becomes shorter than the penetration depth of the incident light. The peak intensity saturates at hole concentrations higher than $N_p=2\times10^{19}cm^{-3}$, and an enhancement of the peak area cannot be observed any more.

SUMMARY

CBr_4 and DTBSi were successfully employed as p−type precursors for GaSb over a wide doping range. DTBSi emerged as the preferred precursor, since a wider range of doping levels can be covered (from $N_p=1.5\times10^{17}cm^{-3}$ up to $N_p=1.1\times10^{20}cm^{-3}$). The agreement between Hall measurements and SIMS for Si−doped samples indicates that all of the incorporated silicon atoms are active. In contrast, a strong background level of acceptors was found for CBr_4 doped GaSb films. A surface electric field generated peaks in the in−situ RA spectra of p−doped GaSb (linear electro−optic effect). The field strength increased with the hole density, and it was independent of the type of precursor employed.

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