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Surface morphology, electrical and optical properties n-type doped MOCVD grown GaSb using dimethyltellurium

Dimethyltelluride has been used as a dopant source for GaSb epilayers grown via atmospheric pressure metal-organic chemical vapour deposition (MOCVD). It has been observed that the electron concentration \( n \) is proportional to the Te partial pressure in the vapour phase, until \( n \) saturates at high Te partial pressure. Electron concentrations as high as \( 1.36 \times 10^{18} \text{ cm}^{-3} \) have been measured with imperfect morphology, and as high as \( 1.22 \times 10^{18} \text{ cm}^{-3} \) with excellent, mirror like, morphology. These appear to be the highest electron concentrations reported to date for any MOCVD-growth epitaxial n-type GaSb doped with DMTe and grown at 540 °C with a V/III ratio of 1.4. The absorption spectra of GaSb doped with DMTe show that the heavily doped samples have a less abrupt edge. The absorption coefficient \( \alpha \) strongly depends on the free carrier concentration. PL spectra of the epilayers are also reported.

Keywords: Te-doping; Gallium antimonide; MOCVD

1. Introduction

Antimony-based III-V semiconductors grown either lattice matched or slightly strained on GaSb substrates have received much attention due to their potential applications as optical devices in the wavelength of 1–4 \( \mu \text{m} \), and for their potential use in tunnelling structures, exploiting the heterojunction offset. Although investigations in laser diodes have been carried out by many groups [1–4] problems still remain with the growth of device-quality GaSb layers [5], most significantly with doping.

Undoped GaSb usually exhibits p-type conductivity, owing to native lattice defects including Sb vacancies, antisite defects i.e., Ga atoms on Sb site, \( V_{Ga}GaaS \) [6]. The group-VI elements such as S, Se, and Te are commonly used as n-type dopants in GaSb because the group-VI elements such as Si and Sn are amphoteric and lead to heavily compensated p-type layers [7]. Researchers have investigated the n-type doping of GaSb by all major techniques [8–12]. In this work, it was identified that group-VI elements have high vapour pressure and segregation coefficient, making it difficult to control the electron concentration. Therefore, the growth of GaSb doped with Te is still a challenge and worth in-depth exploration.

In this work, dimethyltelluride (DMTe) has been used as a dopant for the MOCVD growth of GaSb. The physical properties of MOCVD grown Te-doped GaSb on semi insulating (SI) GaAs substrates are reported. The effects of dopant flow rate on surface morphology, electrical and optical properties have been determined.

2. Experimental procedure

Growth was carried out in a horizontal quartz atmospheric pressure MOCVD reactor. Six IR lamps were used to heat the graphite susceptor. TMGa (trimethylgallium) and TMSb (trimethylantimony) were used as metalorganic sources and kept at a constant bath temperature of \( –9 \) and \( 0 ^\circ \text{C} \), respectively, which correspond to a molar flow of 2.53 and 1.82 \( \mu \text{mol min}^{-1} \) respectively, for 1 sccm hydrogen flows through the metalorganics. DMTe (dimethyltellurium) was used as dopant precursor and kept at a constant temperature of 27 °C. High purity \( H_2 \) was passed through a proprietary metal hydride filter made by Ultra Pure Systems. In this work, we have used a group V mole fraction, \( X_{TMSb} = 10.1 \times 10^{-5} \), an input V/III = 1.4, a DMTe mole fraction, \( X_{DMTe} = 1.42 \times 10^{-6}–7.08 \times 10^{-6} \), a growth temperature of 540 °C and the total flow rate was 81 \( \text{ml min}^{-1} \).

Values of DMTe flow with corresponding mole fractions of DMTe in the input gas stream for various samples are given in Table 1. Substrates used were SI-GaAs(100) from Freiberger (Germany). Prior to the growth, substrates were immersed for 5 min in each of trichloroethylene at a temperature of 100 °C, acetone and methanol and then etched in \( H_2SO_4:H_2O_2:H_2O = 1:1:8 \) solution for 30 s followed by rinse with acetone and methanol.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>DMTe flow (sccm)</th>
<th>DMTe mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>2</td>
<td>( 1.42 \times 10^{-6} )</td>
</tr>
<tr>
<td>#2</td>
<td>3</td>
<td>( 2.12 \times 10^{-6} )</td>
</tr>
<tr>
<td>#3</td>
<td>5</td>
<td>( 3.54 \times 10^{-6} )</td>
</tr>
<tr>
<td>#4</td>
<td>10</td>
<td>( 7.08 \times 10^{-6} )</td>
</tr>
</tbody>
</table>
by a DI (deionised water) water rinse. The substrate were then blown dry by N2, before being loaded into the reactor.

2.2. Characterisation

Van der Pauw Hall measurements were performed in the temperature range of 300–10 K on the 3 μm thick epilayers grown on the SI-GaAs substrates. The absorption of Te-doped GaSb samples was measured using a UV-Vis-NIR Spectrophotometer. Photographs of sample morphology were taken using a Nomarski phase contrast microscope. Photoluminescence (PL) was measured at a temperature of 100 K using a cryogenic system. The PL spectra were detected using an InGaAs photodetector. A diode laser, emitting photons at 950 nm, used for excitation.

3. Results and discussion

3.1. Surface morphology

The morphology obtained from samples grown using dimethyltellurium (DMTe) as a dopant is illustrated in Fig. 1. The epilayers shown in Fig. 1a–d were grown with the DMTe flow rate in the range of 2–10 sccm for a growth temperature of 540 °C. Some degradation of morphology can be seen for the samples grown with a 5 and 10 sccm DMTe flow, where hillocks and ripples are typically observed. The sample grown with 10 sccm DMTe shows pyramid-like hillocks about 10 μm across. This may be due to Te precipitation. Similar results reported for Te-doped GaAs using diethyltelluride (DETe) in low pressure organometallic vapour phase epitaxy (LPOMVPE) [13, 14] show that the degradation of morphology occurs at the highest electron concentrations. Figure 1a shows the surface morphology for the GaSb sample doped with 2 sccm DMTe. The surface is mirror like and fewer hillocks occur. The sample shown in Fig. 1b was grown at 3 sccm and the surface morphology is mirror-like.

3.2. Electrical properties

Table 2 shows the electrical properties obtained from Hall measurements of 3 μm-thick GaSb layers doped with Te. Hall concentrations from $3.54 \times 10^{17} \text{ cm}^{-3}$ to $1.36 \times 10^{18} \text{ cm}^{-3}$ were obtained by varying the DMTe source vapour pressure. It should be noted here that the measured Hall concentration, particularly at room-temperature, is not considered to be the total free-carrier concentration. It was observed that electron concentration $n$ is proportional to Te partial pressure in the vapour phase until it saturates at high Te partial pressure. Measured electron concentrations were as high as $1.36 \times 10^{18} \text{ cm}^{-3}$ with imperfect morphology and as high as $1.22 \times 10^{18} \text{ cm}^{-3}$ with excellent, mirror like, morphology. These appear to be the highest electron concentrations reported to date for any epitaxial n-type GaSb. The electron concentration shows a linear dependence on $X_{\text{DMTe}}$ and saturates near $n = 1.36 \times 10^{15} \text{ cm}^{-3}$ when $X_{\text{DMTe}} > 3.5 \times 10^{-6}$ as shown by the circles in Fig. 2. A possible explanation for this behaviour is that Te incorporation results from a competition between Sb and Te atoms for Sb free-site occupation [15]. The squares in Fig. 2 show the results obtained by Wang et al. [16] using a DETe dopant MOCVD growth at a growth temperature of 550 °C, and with V/III = 1.8. The higher mole fraction of DMTe in the saturation region is presumably caused by the higher vapour pressure of DMTe compared with DETe. Similar results were reported by Ehsani et al. [17] for the growth of InGaSb with DETe doping, the electron concentration was found to increase linearly as the DETe increased, reaching a saturated concentration of $1.5 \times 10^{18} \text{ cm}^{-3}$. When the DETe mole fraction was increased further, the electron concentration decreased.

Temperature-dependent Hall mobilities for four GaSb layers are shown in Fig. 3. Meanwhile the electron concentration is displayed in Fig. 4. The mobility for a low-doped GaSb layer with $n_{H} = 3.54 \times 10^{17} \text{ cm}^{-3}$ (2 sccm DMTe flow) at 300 K is 2 543 cm$^2$·V$^{-1}·$s$^{-1}$ and peaks at about 100 K with a value of 4 478 cm$^2$·V$^{-1}·$s$^{-1}$. Below this temperature, the mobility drops due to ionised impurity scattering, the dominating scattering mechanism at low temperatures. A similar behaviour was observed for the sample grown with 3 sccm DMTe flow where the donor concentration was equal to $n_{H} = 1.22 \times 10^{18} \text{ cm}^{-3}$. For a more highly-doped GaSb layer $n_{H} = 1.36 \times 10^{18} \text{ cm}^{-3}$, the mobility does not show a peak and remains relatively constant with decreasing temperature. A considerably lower mobility was observed for GaSb layers when the sample was doped with Te higher than the saturation level.

3.3. Optical properties

3.3.1. Absorption spectra

The absorption spectra at 300 K for the four samples with different DMTe concentration of

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**Fig. 1.** Nomarski photograph of Te doped n-GaSb grown on SI-GaAs: (a) 2 sccm; (b) 3 sccm; (c) 5 sccm; (d) 10 sccm.
...are shown in Fig. 5. The most heavily doped sample showed a less abrupt absorption edge. The absorption coefficient \( \alpha \) strongly depends on the free carrier concentration. The absorption spectra (1) of the GaSb sample is shifted towards lower energies due to the effective band gap shrinkage resulting from the merger of the acceptor band and valence band [18, 19]. However, the energy shift for band edge absorption for the GaSb with low concentration of DMTe is very small due to low hole concentration. In constrast, the spectra (2), (3) and (4) for the Te-doped n-type GaSb samples are shifted towards higher energies with increasing electron concentration. This shift, known as the Burstein–Moss shift [20], is due to the filling of the conduction band and has been reported in many heavily doped n-type materials such as InP [21], GaAs [22], and GaSb [23]. With the small effective electron mass for GaSb \( m_e^* = 0.14 \) \( m_0 \) [2], the lower density of states at the bottom of the conduction band may result in a degenerate n-type material, even at electron concentrations as low as \( 8 \times 10^{15} \) cm\(^{-3} \) [24].

### 3.3.2. Photoluminescence (PL) spectra

The PL spectra of Te-doped n-GaSb samples grown at 540 °C and V/III = 1.4 with various concentrations of DMTe are shown in Fig. 6. All PL spectra of the highly doped samples \( n \geq 10^{17} \) cm\(^{-3} \) consist of a single peak, i.e. emission band which is attributed to a free-to-bound (or donor-to-acceptor pair) recombination involving an acceptor level at about 82 meV, as reported by Bignazzi et al. [25]. Only conjectures can be proposed concerning its origin; a complex defect consisting of a Te donor and a stoichiometric defect seems the most reasonable choice [24, 26]. As the doping level increases typical emission doping effects appear. The acceptor related band becomes less well resolved and the band broadens.

The PL spectra of heavily doped samples are characterised by a broadening and blue shift of the PL bands when...
the free carrier concentration increases as depicted in Fig. 6. These features can be explained by considering the interplay of different effects connected with heavy doping:

(i) conduction-band filling,
(ii) bandgap narrowing due to carrier–carrier and carrier–impurity interactions and
(iii) formation of band tails due to doping inhomogeneities [27, 28].

4. Conclusions

n-type GaSb has been grown using MOCVD with DMTe as a dopant in the range of 2 and 10 sccm. It has been observed that the electron concentration \( n \) is proportional to the Te partial pressure in the vapour phase, until \( n \) saturates at high Te partial pressure. Electron concentrations as high as \( 1.36 \times 10^{18} \text{cm}^{-3} \) have been measured with imperfect morphology, and as high as \( 1.22 \times 10^{18} \text{cm}^{-3} \) with excellent, mirror like, morphology. These appear to be the highest electron concentrations reported to date for any MOCVD-growth epitaxial n-type GaSb doped with DMTe and grown at 540°C with a V/III ratio of 1.4.

The absorption spectra of GaSb doped with DMTe show that the heavily doped samples have a less abrupt edge. The absorption coefficient \( \alpha \) strongly depends on the free carrier concentration. The absorption spectra of the GaSb sample shift towards lower energies due to the effective band gap shrinkage resulting from the merger of the acceptor band and valence band. The absorption edge shifts towards higher energies with increasing electron concentration. This is due to the Burstein–Moss effect.

All PL spectra of the highly doped samples \( (n \geq 10^{17} \text{cm}^{-3}) \) consist of single peak, i.e. emission band which is attributed to a free-to-bound (or donor-to-acceptor pair) recombination involving an acceptor level at about 82 meV. The PL spectra of heavily doped samples are characterised by a broadening and blue shift of the PL bands with increasing free carrier concentration.

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Fig. 6. PL spectra of GaSb doped with different concentrations of DMTe.

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