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Photoluminescence of liquid-phase epitaxial Te-doped GaSb

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The photoluminescence (PL) spectra of Te-doped GaSb epitaxial layers grown from Ga-rich solutions by liquid-phase epitaxy have been studied in the electron concentrations from $8 \times 10^{15}$ to $4 \times 10^{18}$ cm$^{-3}$. The electron concentration can be accurately controlled by varying the growth temperature and adding the polycrystalline Te-doped GaSb to replace half or all the undoped GaSb starting material in the growth solution. The dependence of line position, line intensity, spectral shape, and broadening on the doping level, power excitation, and temperature has been investigated in detail. At concentrations as low as $1 \times 10^{16}$ cm$^{-3}$, the GaSb sample has become degenerate because of the small effective mass of electrons and the broad band consisting of five partially resolved line dominates the low-temperature PL spectra. At concentrations above $1 \times 10^{18}$ cm$^{-3}$, the 19 K PL spectra is mainly dominated by the sub-band-gap, substrate-induced line A’ at 775.8 meV which is enhanced by the scattering of light off the back surface. This line A’ is direct evidence for the band-gap shrinkage at high doping level. This is the first report to present the detailed luminescence lines in the PL spectra of the Te-doped GaSb samples.

I. INTRODUCTION

Antimony-containing III-V semiconductors, grown either lattice matched or slightly strained on gallium antimonide substrates, have received much attention both for their application to optical devices in the 1-4 μm wavelength region and for tunneling structures exploiting the heterojunction offsets by the InAs, GaSb, and AlSb material systems. Although investigations in laser diodes and photodetectors containing antimonide layers have been carried out by many workers, 1-4 problems still remain with the growth of device-quality GaSb layers. 5

Undoped GaSb usually exhibits p-type conduction, owing to native lattice defects (i.e., Sb vacancies) or antisolate defects (i.e., Ga atoms on Sb sites, $V_{GaGaSb}$). 6 The group-VI elements such as S, Se, and Te are commonly used as the n-type dopant in GaSb because of the group-VI elements such as Si and Sn are amphoteric and lead to heavily compensated p-type layers. 7 A number of workers have investigated the growth and electrical property of n-type GaSb by all the major techniques, 8-13 however, the group-VI elements have a high vapor pressure and a high segregation coefficient, making it difficult to control the electron concentration. Besides, little information has been gained on the radiative recombinations in n-type GaSb. 14-16 The lack of some features in the recombination transitions revealed in the low-temperature luminescence spectra leads us to study the luminescence of Te-doped GaSb over a wide range of electron concentration. Our previous article 17 reported that the carrier concentration of undoped GaSb layers grown from Ga-rich solutions by liquid-phase epitaxy (LPE) is dependent on the growth temperature. At higher growth temperatures, a high hole concentration associated with well-known residual acceptor defects is obtained, but it can be lowered by reducing growth temperature. Layers can exhibit n-type conduction with electron concentrations around $8 \times 10^{15}$ cm$^{-3}$ at growth temperatures less than 450 °C. To obtain the electron concentration in the range from $5 \times 10^{13}$ to $5 \times 10^{18}$ cm$^{-3}$, it seems extremely difficult to use Te as the n-type dopant in GaSb because of the high Te segregation coefficient.

In this article, we propose a new method to accurately control the electron concentration in a wide range by varying the growth temperature and adding polycrystalline Te-doped GaSb to replace some of the nominally undoped GaSb starting material in the growth solution. In addition, we present the first systematic studies of photoluminescence (PL) from the n-type GaSb layers. The results of our work can clarify some important aspects that were not reported previously.

II. EXPERIMENT

Undoped GaSb epitaxial layers were grown by LPE using a sliding boat system under a flowing hydrogen ambient. The gallium melt with adequate undoped polycrystalline GaSb was first baked at 700 °C for 10 h to reduce the background carrier concentration in the GaSb epitaxial layers. The substrates were undoped (100)-oriented GaSb with a hole concentration of $3-5 \times 10^{17}$ cm$^{-3}$ and an etch-pit density of less than $5 \times 10^{2}$ cm$^{-2}$. Prior to growth, the substrate was first etched in situ with an unsaturated GaSb solution for 3-5 s to remove the thin residual oxide layer on the GaSb surface. The epitaxial layer was immediately grown by means of the supercooling technique with a 5 °C supersaturation, at the cooling rate of 0.5 °C/min. The growth temperature was varied from 360 to 600 °C. The thickness of GaSb epitaxial layers grown during a desired growth period of 5 min was typically 3-4 μm.

In order to achieve the electron concentration of n-type GaSb in a wide range, the polycrystalline Te-doped GaSb with an electron concentration of $7.4 \times 10^{17}$ cm$^{-3}$ (from MCP Co.) was used as part of the source material to replace half of the nominally undoped GaSb (residual p-type background) starting material in the growth solu-
The room-temperature carrier concentration of Te-doped GaSb epitaxial layers grown from Ga-rich solution as a function of growth temperature. The electron concentrations can be accurately controlled by varying the growth temperature and adding the polycrystalline Te-doped GaSb to replace half or all the undoped GaSb starting material (labeled as △ or □ in this figure, respectively) in the growth solution.

Electrochemical capacitance-voltage (C-V) profiling method and the PL measurements were performed to characterize the Te-doped GaSb layers. The PL measurement was performed using argon-ion laser excitation (4880 Å line) with a spot size ~1 mm in diameter. Details of growth conditions and characterization techniques are described elsewhere. 18, 19

III. RESULTS AND DISCUSSIONS

Figure 1 shows the room-temperature carrier concentration of Te-doped GaSb epitaxial layers grown from Ga-rich solutions as a function of growth temperature. Layers prepared without compensation (labeled as ○ and ● in Fig. 1) are p type with a hole concentration of ~1×10¹⁷ cm⁻³ at the growth temperature of 600 °C. With reducing growth temperature, the hole concentration gradually decreases and the layer conduction converts from p to n with a minimum hole concentration of 2–6×10¹⁵ cm⁻³ when the growth temperature is below 450 °C. By using the polycrystalline Te-doped GaSb to replace half or all the undoped GaSb starting material (labeled as △ or □ in Fig. 1, respectively), all the layers have n-type conduction with a high electron concentration. In addition, the electron concentration increases with reduced growth temperature. Thus, the electron concentrations can be obtained in the wide range from 8×10¹⁵ to 4×10¹⁸ cm⁻³

Figure 2 shows the 19 K PL spectra excited at 30 W/cm² (i.e., ~200 mW for laser power) for Te-doped GaSb layers with various electron concentrations (8×10¹⁵–4×10¹⁸ cm⁻³). These spectra are normalized to the same main peak intensity. The undoped GaSb sample grown at 420 °C exhibits an n-type conduction with a background electron concentration of 7×10¹⁵ cm⁻³ and is used as a reference for the PL measurements. The 19 K PL spectrum of the undoped layer is dominated by the narrow emission band arising from two partially resolved lines denoted as D and BE2 and located at 808.2 meV (1.534 μm) and 802.9 meV (1.544 μm), respectively. The intensity of line D is slightly stronger than that of line BE2. A weaker line denoted as A is located at ~777.8 meV (~1.594 μm). At the long-wavelength side, there exists a broad- and weak-band G which can be resolved into five lines denoted as B, A-LO, N, B-LO, and C and located at 760 meV (1.631 μm), 749 meV (1.644 μm), 738 meV (1.680 μm), 732 meV (1.691 μm), and 726 meV (1.700 μm), respec-
tively. When the GaSb sample is doped with Te, in spite of the electron concentration as low as $8 \times 10^{15} \text{ cm}^{-3}$, the 19 K PL spectrum exhibits a different feature from that of the undoped GaSb layer with nearly the same electron concentration. As shown in curve (b) in Fig. 2, the partially resolved lines D and BE2 merge together to form a weaker and broader band denoted as F which has an asymmetric wide shape with an extended long-wavelength wing. The asymmetry is characterized in the short-wavelength side by the quasiconstancy of the steepness of the slope. Besides, the lightly doped n-type sample also exhibits a much stronger G-band intensity in the long-wavelength region. An increase in electron concentration will broaden the F-band emission and shift the F-band maximum toward short wavelengths. For carrier concentrations over $1 \times 10^{17} \text{ cm}^{-3}$, the intensity of the long-wavelength broad band G falls off rapidly while that of the line A', whose line energy located at 775.8 meV (1.598 µm) is slightly smaller than that of line A, increases dramatically. With further increasing electron concentration, the maximum of band F shifts toward short wavelengths and the shape of band F becomes broader and more symmetric. It is worth noting that heavy doping leads to a rapid increase in the intensity of line A' and above concentrations of $5 \times 10^{17} \text{ cm}^{-3}$ line A' dominates the low-temperature PL spectra. The long-wavelength broad band G nearly disappears at a concentration of $7 \times 10^{17} \text{ cm}^{-3}$.

In order to assign the main recombination lines of low-temperature PL spectra for the Te-doped GaSb samples, it is necessary to identify the luminescence lines for the undoped layers first. Figure 3 shows the PL spectra of the undoped sample with an electron concentration of $7 \times 10^{15} \text{ cm}^{-3}$ measured with the identical excitation density of 30 W/cm$^2$ at various temperatures. All the PL curves are normalized to the same PL line intensity. As previously described in curve (a) in Fig. 2, the intensity of line D is stronger than that of line BE2 in the 19 K PL spectrum. An increase in the temperature above 19 K gives rise to a decrease of PL intensity of line BE2 but to an increase of line D. With increasing temperature, no displacement of the emission line energy is observed; however, the BE2-line intensity decreases rapidly compared with the emission of line D. As the temperature is increased beyond 35 K, the line BE2 quenches off thermally and the PL spectra are dominated by a single peak. The relative intensity of the line A and the broad band G decreases with increasing temperature and they disappear completely at 115 K.

Figure 4 presents the temperature dependence
FIG. 5. Photoluminescence spectra of Te-doped GaSb samples with \( n = 1 \times 10^{17} \text{cm}^{-3} \) at various temperatures between 19 and 150 K to show the gradual evolution of the lines.

\( T = 19 - 150 \text{ K} \) of emission spectra from the Te-doped sample with an electron concentration of \( 1 \times 10^{16} \text{cm}^{-3} \). The main feature for this sample is that the long-wavelength broad band \( G \) dominates the low-temperature PL spectrum. The five lines in the broad band \( G \) can be clearly resolved even though the temperature is raised as high as 150 K. The relative intensity of band \( F \) with respect to band \( G \) is first decreased when the temperature is raised from 19 to 77 K and then is increased with further increasing temperature. It is noted that the positions of the five lines in the broad band remain constant, whereas band \( F \) shifts slightly toward long wavelengths with increasing temperature. Beyond 150 K, the broad band \( G \) quenches off thermally and the PL spectra are completely dominated by the symmetric and broad band \( F \). For the heavy doping, as shown in Fig. 6, the low-temperature PL spectrum is dominated by the line \( A' \) and the broader band \( F \). The lines of the long-wavelength broad band \( G \) cannot be resolved in this PL spectrum. As the temperature is increased, the intensity of line \( A' \) decreases while that of the band \( G \) slightly increases to broaden the line \( A' \). Meanwhile, a new line, denoted as \( H \), starts to emerge at the position of 791.7 meV (1.566 \( \mu \text{m} \)) in the temperature range of \( T = 19 - 50 \text{ K} \). Beyond 50 K, the line \( H \) quenches off thermally, while another new band denoted as \( E \) and located at 800.9 meV (1.548 \( \mu \text{m} \)) emerges as a weak peak on the long-wavelength side of band \( F \) and disappears above 90 K. It is noted that the position of line \( H \) almost remains constant;
however, that of band E shifts toward long wavelengths with increasing temperature. A further increase in temperature causes the symmetric and broad band F to dominate the PL spectra.

From the above descriptions of Figs. 2–6 we can identify the luminescence lines for the undoped and Te-doped GaSb sample. As observed in Fig. 3 for the undoped sample, the position of line BE2 does not change as the temperature is increased, while its intensity decreases rapidly because of the thermal release of bound exciton from a complex. The behavior is typical for the thermal decay of a bound exciton and the emission is assigned as excitons bound to neutral acceptors, as reported previously.

The energy position is slightly smaller than the value of 810 meV (1.530 μm) which is the free-exciton energy in GaSb at 4 K, but it is slightly larger than the reported value of 805.4 meV (1.539 μm) of line BE1 which is also due to excitons bound to neutral acceptors. Thus, line D can be attributed to the recombination from excitons bound to donors with a donor binding energy of ~2 meV. As the temperature is increased above 35 K, the PL spectra are dominant by a single peak associated with free-electron–to–free-hole recombination. On the other hand, the A-line maximum shifts slightly to higher energies and the FWHM of line A decreases as the excitation intensity increases (not shown in Fig. 3). In addition, the intensity of line A decreases with increasing temperature. Line A has the features of donor-acceptor (D-A) pair emission and is related to native lattice defects or antisite defects (i.e., \( V_{Ga,Ga} \)). This acceptor has been identified to be doubly ionizable with ionization energies of ~33 and ~102 meV for the first and second holes, respectively.

The luminescence observed at energies lower than 775 meV includes the five partially resolved lines and can be further identified from Figs. 2 and 4 for the lightly doped samples with an electron concentration around \( 1 \times 10^{16} \) cm\(^{-3} \). From the excitation-power dependence of low-temperature PL spectra, the lines B at 760 meV and line C at 726 meV shift to higher energies and their intensity will saturate with increasing power density. As previously stated for line A, the lines B and C are due to the other unknown deep acceptors with an acceptor ionization energy of 50 and 84 meV, respectively. Klein and Chang reported the longitudinal optical (LO) phonon mode at ~29.4 meV in the bulk GaSb by Raman scattering experiments. Thus, the transitions A-LO and B-LO at 749 and 732 meV are attributed to the LO phonon replica of lines A and B, respectively. However, the PL signal at 710 meV of the ionized state for the native acceptor A is too weak to be resolved in this long-wavelength broad band G. Because of the larger acceptor ionization energy of line B \( E_A = 50 \text{ meV} \) than that of line A \( E_A = 33 \text{ meV} \), line B will appear in the PL spectra above 60 K, as shown in Fig. 5. As shown in curves (a)–(c) in Fig. 2, the N-line intensity increases with increasing the Te concentration. It may be confirmed that line N is associated with the effective radiative transition due to Te doping. Lebedev and Strelnikova reported that the double ionizable acceptor \( V_{Ga,Ga} \) in the presence of Te atoms will form an effective radiative recombination center \( \left( V_{Ga,Ga,Te} \right) \) in which a Te atom is a donor alongside a stoichiometric defect. Thus the line N at 738 meV can be attributed to the effective radiative recombination from the \( V_{Ga,Ga,Te} \) structure with the activation energy of ~72 meV; however, line N is also observed in the 19 K PL spectrum for the undoped sample. This evidence can be due to (a) the out-diffusion of Te atoms in the used Te-doped GaSb substrate during LPE growth and/or (b) the incomplete melt wipe-off after the in situ etching by the undersaturated GaSb solution from the Te-doped GaSb substrate.

At the electron concentration of \( 8 \times 10^{15} \text{ cm}^{-3} \), the narrow partially resolved lines D and BE2 are merged together to form a broader band F. With increasing electron concentration, the F-band maximum shifts toward short wavelengths and is larger than the free-exciton energy (810 meV) above the concentrations of \( 1 \times 10^{17} \text{ cm}^{-3} \). An assumption of momentum-conserving recombination transition would yield PL spectral widths much too narrow since the thermalized holes occupy only a small region in \( k \) space and the recombination of band F would be forbidden for the higher-energy and higher-momentum electrons. It often fails to explain the features of band F as shown in Fig. 2.

Because of the small effective mass of electrons in GaSb \( (m_e^* \approx 0.041 m_0) \), the lower density of states at the bottom of the conduction band in GaSb would be beneficial to obtain a degenerate n-type material even though the electron concentration is as low as \( 8 \times 10^{15} \text{ cm}^{-3} \) in this study. For the degenerate semiconductor, the enhanced carrier scattering by the ionized donor impurities relaxes the \( k \) selection rule and thus enables all electrons distributed up to the Fermi level which is inside the conduction band to participate in optical transitions. With increasing electron concentration, the development of a density-of-states tail in the energy gap due to electron–electron interaction, electron–impurity interaction, and potential fluctuations in heavily doped semiconductors becomes more important for the radiative recombination process. The localized states in such a band tail can be treated as acceptorlike centers distributed above the top of the valence band. As a result, any or all of the radiative recombination mechanisms can occur. With this assumption, various models including not only the band filling effect but also band-gap shrinkage due to the exchange interaction among free carriers as well as the band-tailing effect due to the Coulomb interaction of free carriers with ionized impurities in heavily doped semiconductors such as GaAs, InP, GaSb, and InGaAsP have been developed in good agreement with the observed PL spectral shift and broadening of band F. Alternatively, such a band F should be expected in a degenerate semiconductor and hints that the band F is due to the transition from the indirect free electron to the valence-band tails, created by the inhomogeneous impurity distribution.

At low electron concentrations and low temperatures, band F has an asymmetric wide shape with an extended long-wavelength wing. As shown in Figs. 4 and 5, the low-
energy slope closely follows the \( I(hv) \sim (E_0 - hv)^{1/2} \) dependence which is a consequence of the electron density distribution \( \sim (E - E_0)^{1/2} \) in the parabolic conduction band, while the high-energy slope is exponential decay caused by a decrease in the electron population above the Fermi energy level. As the temperature increases, the shape of the low-energy slope changes little (e.g., 19 and 35 K of Fig. 5), but the high-energy slope broadens strongly (e.g., 55 and 77 K in Fig. 4, 55 and 90 K in Fig. 5). Therefore, the shape of the high-energy side is determined by thermal broadening of the electron distribution near the Fermi level. The spectra will become more symmetric with increasing temperature. Finally, a Gaussian shape occurs above 150 K due to the thermal excitation of electrons near the Fermi level and additional thermal broadening effects.

With increasing electron concentrations in the range of \( 1 \times 10^{16} - 1 \times 10^{18} \text{ cm}^{-3} \), as shown in Fig. 2, band F shifts to higher energies because states near the increased Fermi levels participate in the radiative recombinations. When the electron concentration is above \( 1 \times 10^{18} \text{ cm}^{-3} \), the F-band maximum seems to remain constant. The absence of any such shift in the heavily doped GaSb is due to the stabilization of the Fermi level, the smaller \( \Gamma - L \) energy separation (61 meV at 300 K, 63 meV at 30 K, and 89 meV at 0 K), and the majority of electrons being at the (111) minimum of the conduction band \( L \) with its high density of states \((\mu_L = 0.226 \mu_0 \) and \( \mu_F = 0.0412 \mu_0 \))\(^\text{28}\). The increase in the electron concentration will cause the spectral broadening due to the rise in the height of the Fermi level inside the conduction bands.

As shown in Fig. 6 for the highly doped sample with an electron concentration of \( 2 \times 10^{18} \text{ cm}^{-3} \), line H at 791.7 meV appears at \( T = 19 - 35 \text{ K} \). The relative intensity of line H with respect to line A' increases with increasing temperature and above 55 K line H is merged into the short-wavelength wing of line A'. Because line H cannot be completely resolved in these spectra and its intensity is weaker than those of line A' and band F, it is difficult to identify this line further. At \( T = 55 \text{ K} \), another new line E begins to emerge in the long-wavelength hump of band F and shifts toward long wavelengths with increasing temperature. The position of line E is the same as that of the single peak which dominates the PL spectra for the undoped sample, as shown in Fig. 3, at the same measured temperatures. Thus, this line E can be attributed to the free-electron-to-free-hole transition.

When the doping level is beyond \( 1 \times 10^{17} \text{ cm}^{-3} \), the A'-line intensity dramatically increases to dominate the low-temperature PL spectra. This line A' is due to PL signal which emitted through the bulk GaSb substrate (\( \sim 350 \mu\text{m} \) thick) internally reflecting off the back surface to be collected along with the light emitted directly from the epitaxial layer surface. Because of the roughness of the back surface (one-side polished substrate) and the small critical angle in GaSb (\(-17^\circ\)), the intensity of line A' will be enhanced by light scattering at the back surface. This demonstrates that the low-energy transition occurs in the reduced band gap of the heavily doped epitaxial layer. Line A' becomes stronger with increasing doping level due to the increase in the band shrinkage. Thus, this line A' is direct evidence for the band-gap shrinkage at high density.\(^\text{41}\) This was recently observed and described by Szmyd and Majerfeld\(^\text{42}\) on the 300 K PL spectra of heavily doped GaAs. The 19 K PL energy line position, interpretation of transition lines, and the notation used in the literature to identify them are summarized in Table I.

<table>
<thead>
<tr>
<th>Energy (meV)</th>
<th>Transition</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>808.2</td>
<td>Excitons bound to donors</td>
<td>D</td>
</tr>
<tr>
<td>802.9</td>
<td>Excitons bound to neutral acceptor</td>
<td>BE2</td>
</tr>
<tr>
<td>777.8</td>
<td>Residual acceptor</td>
<td>A</td>
</tr>
<tr>
<td>757.8</td>
<td>Induced by substrate</td>
<td>A'</td>
</tr>
<tr>
<td>760</td>
<td>Acceptor</td>
<td>R</td>
</tr>
<tr>
<td>749</td>
<td>LO phonon replica of A</td>
<td>A-LO</td>
</tr>
<tr>
<td>738</td>
<td>( V_0 \GaAsTe_a ) complex</td>
<td>N</td>
</tr>
<tr>
<td>732</td>
<td>LO phonon replica of D</td>
<td>D-LO</td>
</tr>
<tr>
<td>726</td>
<td>Acceptor</td>
<td>C</td>
</tr>
</tbody>
</table>

**IV. CONCLUSIONS**

We have presented a detailed photoluminescence study of LPE-grown Te-doped GaSb layers with electron concentrations of \( 8 \times 10^{15} - 4 \times 10^{18} \text{ cm}^{-3} \). The electron concentration can be controlled by using the different growth temperatures and polycrystalline Te-doped GaSb to replace half or all the undoped GaSb starting material in the growth solutions. By the PL measurements at various temperatures and excitation levels, the luminescence lines observed in the PL spectra can be further identified and explained in this study. For the undoped layer with \( n = 7 \times 10^{16} \text{ cm}^{-3} \), the band consisting of two partially resolved lines D and BE2 is dominant in the low-temperature PL spectra. As the electron concentration is around \( 1 \times 10^{17} \text{ cm}^{-3} \), the broad band containing five partially resolved lines in the long-wavelength region (750–720 meV) dominates for the degenerate samples. Meanwhile, both the band filling as well as band tailing due to the carrier scattering with the ionized donor impurities and band shrinkage due to the exchange interaction between free carriers are considered to account for the observed luminescence behavior. At concentrations beyond \( 1 \times 10^{18} \text{ cm}^{-3} \), the low-temperature PL spectra are mainly dominated by line A' at 775.8 meV which arises from the band-gap reduction caused by the heavy doping, travels through the GaSb substrate, reflects off the back surface, and is emitted from the epitaxial layer.

**ACKNOWLEDGMENT**

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