

Electronic properties in Ga-doped CdTe layers grown by metalorganic vapor phase epitaxy

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Electronic properties in Ga-doped (100) CdTe layers on (100) GaAs grown by atmospheric pressure metalorganic vapor phase epitaxy were studied. Triethylgallium was used as a dopant source. The source materials were dimethylcadmium (DMCd) and diethyltelluride (DETe). The effects of the DETe/DMCd (VI/II) ratio on the electrical properties were evaluated by Hall measurements. Electron concentration (300 K) was controlled from $3.5 \times 10^{14} \text{ cm}^{-3}$ to $2.5 \times 10^{16} \text{ cm}^{-3}$ by the VI/II ratio in the range 0.5 to 2. Higher growth temperature lowered the electron concentration. High electron mobility of $630 \text{ cm}^2/\text{Vs}$ (300 K) was obtained for a growth temperature of 375°C and a VI/II ratio of 2. Good correspondence was observed between electrical and photoluminescence (PL) properties. Both intensity and linewidth of a neutral-donor bound-exciton (D^0, X) emission at 1.5932 eV increased with the electron concentration. The ionization energy of the Ga donor was estimated to be about 18 meV from electrical and PL properties. A Ga incorporation mechanism was deduced on the basis of the experimental results.

I. INTRODUCTION

Impurity doping in CdTe and HgCdTe layers has been extensively performed in low-temperature growth such as metalorganic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE) to control *p*- and *n*-type conductivity for developing high-performance infrared devices.^{1,2} In particular, *n*-type control is significant because these undoped materials usually exhibit *p*-type conductivity as grown, due to high vapor pressures of group II constituents.

For *n*-type doping in the above materials, group III impurity, particularly indium, has so far been a common dopant.^{3,4} For In-doped bulk CdTe grown from Te-rich melts, In_2Te_3 is known to be formed in the crystal due to its larger formation enthalpy compared to CdTe.⁵ Complex defects, such as $\text{V}_{\text{Cd}}^{2-}\text{In}_{\text{Cd}}^{+}$ and $\text{V}_{\text{Cd}}^{2-}2\text{In}_{\text{Cd}}^{+}$, which lower the electrical activity of In, have been also considered to be formed due to a high concentration of Cd vacancies.⁶

On the other hand, the doping mechanisms in the low-temperature growths of MOVPE and MBE may be different from that in bulk growth due to suppression in the formation of native defects. The doping mechanisms may also differ between MOVPE and MBE due to differences in source materials and growth ambients. A Te-rich condition is reported to be preferable for higher In activation in MOVPE of CdTe,⁷ while excess Cd is necessary to suppress the formation of complex defects in MBE.⁸ These doping mechanisms, however, have not been satisfactorily understood. The choice of other group III dopants is considered to be effective for a better understanding of the dopant behavior in CdTe and HgCdTe, since the individ-

ual formation enthalpy of complex defects could characterize the doping properties.

In this article, we report electrical and optical properties in Ga-doped (100) CdTe layers grown by MOVPE using triethylgallium (TEGa) as a dopant source. A Ga incorporation mechanism is also proposed on the basis of the experimental results.

II. EXPERIMENTAL CONDITIONS

The growth of CdTe layers was carried out in a vertical MOVPE reactor operating at atmospheric pressure. Dimethylcadmium (DMCd) and diethyltelluride (DETe) were the source materials. The Ga dopant source was TEGa. The substrates used were semi-insulating (100) GaAs 2.5° misoriented towards the nearest (110), and were degreased in acetone and etched in $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$ (5:1:1) prior to growth.

In this study, all the CdTe layers on (100) GaAs were grown to be (100) oriented.⁹ The doped layers were grown on 3- μm -thick undoped CdTe buffer layers. The buffer layers were grown at 375°C and a DETe/DMCd (VI/II) ratio of 0.5, where the DMCd flow rate was fixed at $2 \times 10^{-5} \text{ mol/min}$. For doped layers, the growth temperatures were set at 375 and 425°C . The Ga out-diffusion from the substrates at 425°C was negligible because undoped CdTe layers with thicknesses above 3 μm showed *p*-type conductivity, as reported previously.¹⁰ The VI/II ratio for doped layers varied mainly in a range 0.5–2. This was because the growth rate at the VI/II ratio below 0.5 was extremely low, and the Te precipitates were generated above the VI/II ratio of 2. The TEGa flow rate was fixed

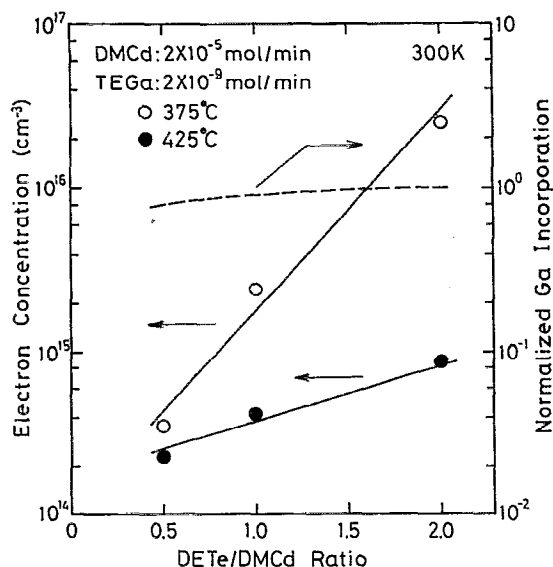


FIG. 1. The dependence of electron concentrations at 300 K in Ga-doped CdTe layers grown at 375 and 425 °C on the DETe/DMCd ratio. A dashed curve shows a variation of normalized Ga incorporation that was estimated from the growth rate.

at 2×10^{-9} mol/min in order to prevent a memory effect that causes scattered experimental results. The thicknesses of doped layers were in the range 3–6 μm .

The electrical properties of doped layers were evaluated by the van der Pauw method. Ohmic contacts were formed by evaporating indium onto the grown layers etched briefly with 0.1% bromine in methanol. Photoluminescence (PL) measurement was performed at 4.2 K using a He-Ne laser (632.8 nm) as an excitation source in conjunction with a 1 m Jobin-Yvon single grating monochromator with an energy resolution of 0.1 meV.

III. EXPERIMENTAL RESULTS

Figure 1 shows the dependencies of electron concentration (300 K) in doped layers grown at 375 and 425 °C on the VI/II ratio in the range 0.5–2. As will be discussed later, the variation of Ga incorporation (375 °C calculation) with the VI/II ratio is also shown as a dashed curve. For the growth temperature of 375 °C, the electron concentration increases dramatically from $3.5 \times 10^{14} \text{ cm}^{-3}$ to $2.5 \times 10^{16} \text{ cm}^{-3}$ with increasing the VI/II ratio from 0.5 to 2. For 425 °C, a similar variation of carrier concentration is observed as the VI/II ratio is varied; however, the concentrations are lower. These results indicate that the electron concentration in Ga-doped layers is enhanced by increasing the VI/II ratio or by lowering the growth temperature.

Figure 2 shows the variations of electron mobility (300 K) in the above doped layers. For 375 °C, the electron mobility increases from 300 to 630 cm^2/Vs as the VI/II ratio is increased from 0.5 to 2. For 425 °C, the mobility shows a similar tendency with respect to the VI/II ratio. However, the electron mobilities for 425 °C are lower. These electrical properties show that good Ga doping char-

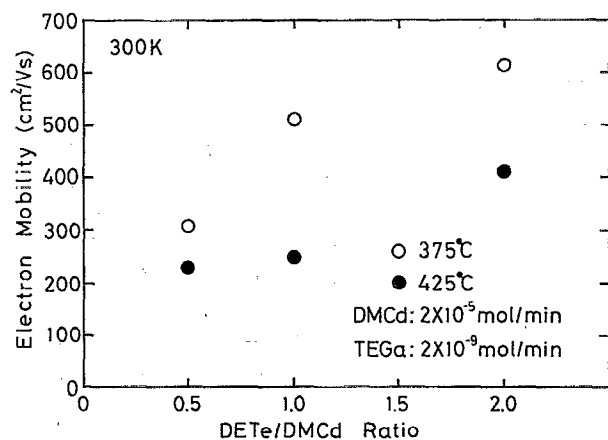


FIG. 2. The variations of electron mobility at 300 K in Ga-doped CdTe layers grown at 375 and 425 °C with the DETe/DMCd ratio.

acteristics with high electron concentration and mobility are achieved under 375 °C and a VI/II ratio of 2.

Figure 3 shows PL spectra in the bound-exciton region for doped layers grown at 375 °C that were shown in Fig. 1, where the electron concentrations are (a) $3.5 \times 10^{14} \text{ cm}^{-3}$ (VI/II=0.5), (b) $2.5 \times 10^{15} \text{ cm}^{-3}$ (VI/II=1), and (c) $2.5 \times 10^{16} \text{ cm}^{-3}$ (VI/II=2). There appears a neutral-donor bound-exciton (D^0, X) emission at 1.5932 eV, and two neutral-acceptor bound-exciton (A^0, X) emissions at 1.5890 and 1.5901 eV. The (D^0, X)/(A^0, X) intensity ratio increases with the electron concentration. Also, the line-width of the (D^0, X) emission broadens from 0.3 to 0.8 meV with increasing electron concentration. The (D^0, X) emission at 1.5932 eV is, therefore, attributed to an exciton bound to neutral donor of Ga that occupies Cd sites.

IV. DISCUSSION

For Ga doping at 375 °C, as shown in Fig. 1, the increase of the DETe flow rate by factors of 4 enhanced the electron concentration by nearly two orders of magnitude. Here, we will discuss what mechanism governs this electrical behavior. The probable cause is either (1) the in-

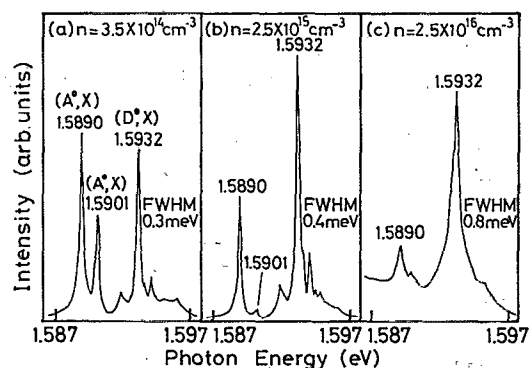


FIG. 3. 4.2 K PL spectra in the bound-exciton region for Ga-doped layers with the electron concentration; (a) 3.5×10^{14} , (b) 2.5×10^{15} , and (c) $2.5 \times 10^{16} \text{ cm}^{-3}$. The samples were grown at 375 °C and a VI/II ratio of (a) 0.5, (b) 1, and (c) 2.

crease of Ga incorporation or (2) the increase of Ga electrical activity at the larger VI/II ratio.

First, we will note the variation of Ga incorporation with the VI/II ratio, assuming the surface reaction will occur for Ga species. In a Cd-Ga-Te growth system, Ga atoms are considered to be incorporated into the layer in combination with Te atoms because the formation enthalpy of Ga_2Te_3 is larger than that of CdTe .¹¹ Previous studies revealed that the CdTe growth rate at 375 °C showed a sublinear increase with the VI/II ratio below 2, and the saturation above 2.¹² This indicates that the CdTe growth under the VI/II ratio below 2 is limited by the Te surface coverage rate. Thus, the Ga incorporation at the VI/II ratio below 2 can be estimated in terms of the growth rate that is limited by the amount of Te. The variation of Ga incorporation with the VI/II ratio is shown in Fig. 1 (dashed curve), where the data are normalized by that at the VI/II ratio of 2. The calculated amount of Ga incorporation is almost the same in the VI/II ratio range 0.5–2. This result strongly indicates that all the incorporated Ga do not act as donors, and that Ga activity becomes lower at the lower VI/II ratio.

We consider that almost all the Ga atoms are incorporated into the layer in the stable form of Ga_2Te_3 . The Ga atoms in Ga_2Te_3 are electrically inactive because Ga_2Te_3 is identical to an electrically neutral $\text{V}_{\text{Cd}}^{2-}\text{-Ga}_{\text{Cd}}^+$ complex. Consequently, the small amount of Ga species remaining that do not contribute to the formation of Ga_2Te_3 could possibly become donors substituting on Cd sites. For the VI/II ratio of 0.5, the rest of the Ga would be hard to substitute on Cd sites due to a Cd-rich growth interface. On the other hand, for the VI/II ratio of 2, the incorporation of the rest of the Ga into Cd sites would be enhanced due to a Te-rich growth interface. A further increase in electron concentration did not, however, occur above the VI/II ratio of 2, where the growth rate saturates. This may be due to the variation of growth mechanism above the VI/II ratio of 2.

As shown in Fig. 1, higher growth temperature yielded lower carrier concentration. This may be attributed to an enhancement in an electrically neutral Ga_2Te_3 formation due to the increased pyrolysis efficiency of DETe and TEGa.

From the above discussions, the electrical activity of Ga in MOVPE becomes higher at the larger VI/II ratio. Similar VI/II ratio dependence is also reported for In-doped CdTe by MOVPE.⁷

Next we will discuss PL properties in Ga-doped layers. As shown in Fig. 3(a), a Ga-doped layer grown at 375 °C and the VI/II ratio of 0.5 exhibits a (D^0, X) emission at 1.5932 eV that is comparable to the (A^0, X) emission at 1.5890 eV in intensity. Previous PL studies revealed that undoped CdTe layers grown under the same condition exhibited a predominant (A^0, X) emission at 1.5890 eV.¹² These results indicate that for Ga doping at the VI/II ratio of 0.5, the incorporation of the Ga donor is small and the grown layer still retains the *p*-type characteristics in undoped layers. The incorporation of the Ga donor, however, becomes predominant at a higher VI/II ratio, as shown in

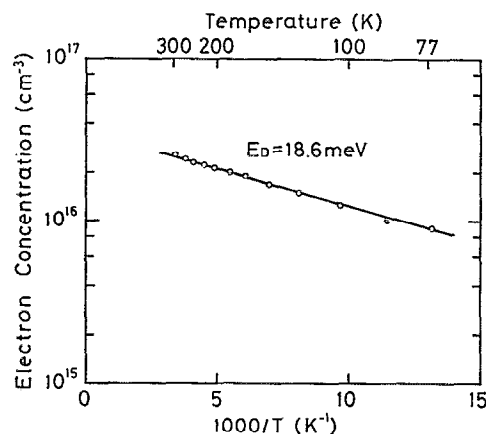


FIG. 4. The temperature dependence of electron concentration in Ga-doped layers grown at 375 °C and a VI/II ratio of 2.

Fig. 3(c). Another (A^0, X) emission at 1.5901 eV becomes negligible above the VI/II ratio of 1. This emission was also observed predominantly in As-doped CdTe layers in which the As incorporation decreased with increasing the VI/II ratio.¹² Thus, the (A^0, X) emission at 1.5901 eV could be attributed to As acceptors substituting on Te sites, which possibly originate from the GaAs substrate.

The ionization energy of the Ga donor (E_D) can be estimated in terms of Haynes' rule expressed by $(D^0, X) = E_g - E_{ex} - 0.1E_D$. Here, E_g and E_{ex} represent the bandgap energy and the free-exciton binding energy, respectively. Assuming $E_g = 1.606$ eV (4.2 K) and $E_{ex} = 11$ meV, the Ga ionization energy is estimated to be 18.0 meV. The ionization energy was also evaluated from a temperature dependence of electron concentration in the doped layer grown at 375 °C and the VI/II ratio of 2, shown in Fig. 4. The activation energy in the electron concentration is estimated to be 18.6 meV, which is very close to the above value obtained from PL properties. This sample exhibits a very weak (A^0, X) emission at 1.5890 eV compared to the (D^0, X) emission, as shown in Fig. 3(c). In addition, while using the Haynes' rule, an ionization energy of the acceptor related to the (A^0, X) emission at 1.5890 eV is estimated to be about 60 meV, which gives an acceptor level much deeper than the above Ga donor level. The activation energy of 18.6 meV can be, therefore, considered to be largely due to the Ga donor level. Thus, both PL and electrical properties deduce a Ga ionization energy of about 18 meV, indicating that Ga is a shallow donor.

In high-resistivity Ga-doped bulk CdTe, a sharp emission is reported to be observed at 1.5841 eV.¹³ The 1.5841 eV recombination center has been attributed to an acceptor-like $\text{V}_{\text{Cd}}^{2-}\text{-Ga}_{\text{Cd}}^+$ complex because the samples were converted to *n*-type low resistivity and the 1.5841 eV line disappeared by Cd-saturated annealing. However, our high-resistivity Ga-doped layers grown by MOVPE did not exhibit such an emission around 1.584 eV. A broad emission around 1.586 eV was observed only for the doped layer in Fig. 3(c), which is not shown in the figure. These results indicate that the defect structure probably differs

between MOVPE and bulk growth, due to considerable difference in the growth temperature.

V. CONCLUSIONS

The electrical and optical properties in Ga-doped (100) CdTe layers grown on (100) GaAs by atmospheric pressure MOVPE were investigated by Hall effect and PL measurements. The Ga dopant source was TEGa. For a growth temperature of 375 °C, the electron concentration increased from $3.5 \times 10^{14} \text{ cm}^{-3}$ to $2.5 \times 10^{16} \text{ cm}^{-3}$ when the VI/II ratio was raised from 0.5 to 2. High electron mobility of $630 \text{ cm}^2/\text{V s}$ was obtained at the VI/II ratio of 2. Higher growth temperature lowered the electron concentration and mobility. Thus, good Ga doping was achieved at a lower growth temperature, and a larger VI/II ratio. The PL properties were well correlated with electrical properties. Both intensity and linewidth of the neutral-donor bound-exciton (D^0, X) emission at 1.5932 eV were enhanced by the electron concentration. The (D^0, X) was attributed to an exciton bound to a neutral Ga donor. Applying Haynes' rule, the ionization energy of the Ga donor was estimated to be about 18 meV, which was in close agreement with a value obtained from the temperature-dependent Hall effect. We proposed a Ga incorporation mechanism in which the Ga atoms are largely incorporated in the form of electrically neutral Ga_2Te_3 , and the rest of the Ga occupies Cd sites as donors, depending on the VI/II ratio.

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