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Mechanism of arsenic incorporation and electrical properties in CdTe layers grown by metalorganic vapor phase epitaxy

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The As doping mechanism in (100) CdTe layers grown on (100) GaAs by atmospheric-pressure metalorganic vapor phase epitaxy was studied. Triethylarsine (TEAS) was used as a dopant source. The source materials used were dimethylcadmium (DMCd) and diethyltelluride (DETe). The As incorporation was enhanced by decreasing the DETe flow rate under a fixed DMCd flow condition, and by lowering the growth temperature. Assuming 100% activation of As, the As incorporation efficiency was estimated to be about 0.1%. The As incorporation was dominated by the sticking rate of the As species onto the Cd species. The hole concentration was controlled from 2×10^15 to 3×10^16 cm^-3 in proportion to the TEAs flow rate below 1×10^-7 mol/min. Those doped layers showed hole mobilities as high as 75 cm^2/V s. Low-temperature photoluminescence (PL) studies revealed that a neutral-acceptor bound-exciton at 1.5901 eV is due to a substitutional As acceptor on the Te site. The As ionization energy was about 90 meV from the PL and electrical measurements.

I. INTRODUCTION

The ability to p and n dope in situ with low-temperature growth methods such as metalorganic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE) has allowed for a new fabrication process for high-performance HgCdTe optoelectronic devices. For the application of these growth methods to practical devices, a better understanding of the doping mechanism is highly desired.

For p-type doping in CdTe, the group V element As has been generally used as a dopant due to its slow diffusivity. In MBE, a Cd-rich condition is reported to enhance the As incorporation. For the application of these growth methods to practical devices, a better understanding of the doping mechanism is highly desired.

In this study, we investigated the As doping mechanism in CdTe layers grown by MOVPE using triethylarsine (TEAs) as a dopant source. Since the pyrolytic temperature for TEAs (~400 °C) is much lower than for the above As sources, the use of TEAs is used to examine the effect of pyrolytic temperature on the doping mechanism. The As doping mechanism obtained in this study is compared with the MBE case, while the ionization energy for the As acceptor is determined through electrical and optical properties of the doped layers.

II. EXPERIMENTAL CONDITIONS

CdTe layers were grown in a vertical-type atmospheric-pressure MOVPE system. Dimethylcadmium (DMCd) and diethyltelluride (DETe) from Tosoh Akzo Co. were used as the source materials. The dopant source used was TEAs, which was synthesized by Trichemical Laboratory Co. Semi-insulating (100) GaAs 2.5° misoriented towards the nearest (110) was used as the substrates, which were degreased and etched in H_2SO_4:H_2O_2:H_2O (5:1:1) prior to growth.

All the CdTe layers in this study were grown to be (100) oriented as in a previous report. The doped layers were grown after the deposition of undoped CdTe buffer layers. In order to equalize the effect of lattice strain on the electrical and optical properties in the doped layers, all the buffer and doped layers were set to be about 2 and 5 µm thick, respectively. The growth temperature, which was kept constant through the growth of buffer and doped layers, was set in the range 375-425 °C. The DETe flow rate was varied from 1×10^-5 to 4×10^-5 mol/min under a fixed DMCd flow rate of 2×10^-5 mol/min. As a result, the DETe/DMCd ratio was varied from 0.5 to 2.

The TEAs flow rate was controlled from 2×10^-9 to 8×10^-7 mol/min in the following procedure. At first, the TEAs vapor, whose vapor pressure was maintained at a fixed value using a thermostat, was diffused into an evacuated container. Then the TEAs vapor in the container was diluted with H_2 pressure at 3 kg/cm^2. The TEAs dopant flow from the container was controlled by a mass-flow-controller.

The electrical properties of the grown layers were evaluated by the van der Pauw method at 300 K. Ohmic contacts to the grown layers were obtained by evaporating Cu.
FIG. 1. Dependence of hole concentrations at 300 K in undoped and doped CdTe layers on the DETe/DMCd ratio for a DMCd flow rate of $2 \times 10^{-5}$ mol/min.

Double-crystal x-ray rocking curves (DCRCs) of CdTe (400) peaks were measured using Cu K$_{\alpha 1}$ radiation with a beam of 2 mm diameter. PL spectra were measured at 4.2 K with a 632.8-nm He-Ne laser as an excitation source in conjunction with a 1-m Jobin-Yvon single grating monochromator.

III. EXPERIMENTAL RESULTS

A. Electrical properties

Figure 1 shows the dependence of hole concentration in both undoped and doped CdTe layers on the DETe/DMCd ratio, where the DMCd and TEAs flow rates were fixed at $2 \times 10^{-5}$ and $8 \times 10^{-8}$ mol/min, respectively, and the growth temperature was 395 °C. For undoped layers, the hole concentration increases from $4 \times 10^{14}$ to $3 \times 10^{15}$ cm$^{-3}$ with an increase in the DETe/DMCd ratio from 0.5 to 1, and a negligible change is observed in the region from 1 to 2. On the other hand, hole concentration for doped layers decreases steeply from $3 \times 10^{16}$ to $1 \times 10^{15}$ cm$^{-3}$ with an increase in the DETe/DMCd ratio from 0.5 to 1. The carrier concentrations for the DETe/DMCd ratio beyond 1 are almost the same between undoped and doped layers. These results indicate that a marked increase in hole concentration can be achieved by As doping under the DETe/DMCd ratio of 0.5.

Figure 2 shows the hole concentration of doped layers grown at DETe/DMCd = 0.5 as a function of the TEAs flow rate. In this experiment, the growth temperature was taken as a parameter. For a growth temperature of 375 °C, the hole concentration increases to $3 \times 10^{16}$ cm$^{-3}$ in proportion with the TEAs flow rate at levels below $1 \times 10^{-7}$ mol/min. Then, the carrier concentration decreases with the increase in TEAs flow rate. On the other hand, at 425 °C, the hole concentration shows an increase, which is slower than that at 375 °C, up to $1 \times 10^{16}$ cm$^{-3}$ with TEAs flow rate, and then a marked decrease at TEAs flow rates beyond $2 \times 10^{-7}$ mol/min. For both growth temperatures, good control in hole concentration was achieved for a TEAs flow rate below $1 \times 10^{-7}$ mol/min.

Except at TEAs flow rates less than $1 \times 10^{-4}$ mol/min, the hole concentration of doped layers is increased by decreasing the growth temperature. Higher hole concentrations at 425 °C than at 375 °C for TEAs flow rates less than $1 \times 10^{-8}$ mol/min could be explained in terms of the leakage current through the underlying buffer layer. This happens after increasing the growth temperature from 375 to 425 °C because the resistivity of the buffer layers changed from $10^3$ to $10^2$ Ω cm, which approached that of doped layers at the low doping range.

Figure 3 shows the corresponding hole mobilities in doped layers. For both growth temperatures, doped layers exhibit high hole mobilities around 75 cm$^2$/V s for TEAs flow rates up to $1 \times 10^{-7}$ mol/min. However, the hole mobility decreases at TEAs flow rates exceeding the above value.

The DCRC measurements on the doped layers showed that full width at half maximum (FWHM) values ranged from 130 to 180 arc s for low TEAs flow up to $1 \times 10^{-7}$ mol/min.
mol/min, whereas they increased above 230 arc s for higher TEAs flow rates.

From the above results, good control in As doping was achieved in the TEAs flow range up to $1 \times 10^{-7}$ mol/min, where hole concentrations were controlled in proportion to the TEAs flow rate, and high crystalline quality was maintained.

**B. PL properties**

Prior to assessing PL properties in As-doped layers, it is necessary to know the background in undoped layers. Figure 4 illustrates a typical PL spectrum in the near-band-edge region for an undoped CdTe layer grown at 375 °C. The spectrum is dominated by a sharp neutral-acceptor bound-exciton emission ($I_{A2}$) at 1.5890 eV with a linewidth of 0.23 meV. Several other excitonic emissions are weakly observed, where a neutral acceptor bound-exciton ($I_{A1}$) at 1.5901 eV, a neutral-donor bound-exciton (IO) at 1.5932 eV, several excited neutral-donor bound-excitons (IEX), a heavy-hole exciton (EXHH) at 1.5962 eV and a light-hole exciton (EXLH) at 1.5978 eV appear. On the other hand, a deep-level emission band, related to the extended defects, was negligibly observed. These results strongly indicate that high quality MOVPE CdTe layers are obtained, which can be used to identify the origin of impurity and defect levels in PL.

Figures 5(a)–5(c) show PL spectra in As-doped CdTe layers for TEAs flow rates of $2 \times 10^{-6}$, $8 \times 10^{-6}$, and $8 \times 10^{-7}$ mol/min, respectively. These samples also correspond to ones in the linearly doped region, shown in Fig. 2. The variation of excitonic emissions in the low TEAs flow region is as follows: With increasing hole concentration, the $I_{A1}$ line at 1.5901 eV is enhanced at the expense of the $I_{A2}$ line at 1.5890 eV. A broadening of the $I_{A1}$ line (0.58 meV) also occurs for $p = 3 \times 10^{16}$ cm$^{-3}$, although the linewidth is narrow ($0.3$ meV) for $p = 2-8 \times 10^{15}$ cm$^{-3}$. The $I_2$ line and the $I_D$ line become stronger in intensity with increasing hole concentration.

The above PL results demonstrate that high quality doped layers can be obtained under the low TEAs flow ($< 10^{-7}$ mol/min) condition.

**IV. DISCUSSION**

**A. Doping mechanism**

Prior to discussing the doping mechanism, the understanding of CdTe growth kinetics seems to be essential.
Among several growth parameters, the growth temperature and the flow rates of source materials are considered to have the greatest influence on the growth kinetics. Figure 7 shows the variation of undoped CdTe growth rates as a function of the DETe flow rate, where the DMCd flow rate was fixed at $2 \times 10^{-5}$ mol/min. In this experiment, the growth temperature was taken as a parameter. For any growth temperature, the CdTe growth rate increases sublinearly with the DETe flow rate, and saturates beyond $4 \times 10^{-5}$ mol/min. These sublinear dependences of the growth rate on the source flow rate demonstrate that the growth is dominated by the surface kinetically controlled reaction, the so-called Langmuir–Hinshelwood-type growth.\textsuperscript{16,19} In contrast with the above experiments, no change in the growth rate was observed when the DMCd flow rate was increased under a fixed DETe flow rate in the range $1 \times 10^{-5}$ to $4 \times 10^{-5}$ mol/min. This does not mean, however, that Cd is deficient with respect to Te at the growing interface below the DETe flow rate of $4 \times 10^{-5}$ mol/min, namely $\text{DETe}/\text{DMCd} = 2$.

On the other hand, for any DETe flow rate, the growth rate becomes larger with increasing growth temperature. This is attributed to an enhancement in the Te/Cd atomic ratio at the growing interface, because the pyrolysis of DETe is significantly increased above 400 °C whereas that of DMCd is less affected.\textsuperscript{20}

The above results indicate that MOVPE CdTe growth under 400 °C and up to $\text{DETe}/\text{DMCd} = 2$ is dominated by the surface coverage rate of Te, and not by that of Cd.

On the basis of the above CdTe growth mechanism, higher As doping under the lower DETe flow rate, as shown in Fig. 1, could be explained as follows: Lowering the DETe flow rate has an effect on the decrease of the surface coverage rate of Te species over Cd species at the growing surface. This offers more opportunities for As species to stick on Cd species, which leads to an effective incorporation of As into the Te sites. No significant difference in carrier concentrations between undoped and doped layers for a $\text{DETe}/\text{DMCd}$ ratio from 1 to 2 is possibly attributed to insignificant incorporation of As into the grown layers due to a high surface coverage rate of Te.

As shown in Fig. 2, higher As doping was also achieved by decreasing the growth temperature. Lowering the growth temperature is considered effective in increasing the adsorption of As species onto the Cd species. In the linearly doped region for 375 °C in Fig. 2, the As incorporation efficiency was estimated to be about 0.1%, assuming 100% electrical activation of As. This efficiency was similar to that for AsH$_3$ using GaAs substrates.\textsuperscript{5} These results strongly propose a doping mechanism that the As incorporation is not dominated by the pyrolytic efficiency of the dopant species, but by the sticking efficiency of the dopant species. The above result is consistent with the enhanced As incorporation by lowering the growth temperature using disopropyltelluride.\textsuperscript{6} When a (100) CdTe substrate was used, the hole concentration increased to $3 \times 10^{17}$ cm$^{-3}$ in contrast to $3 \times 10^{16}$ cm$^{-3}$ for a GaAs substrate at the TEAs flow rate of $8 \times 10^{-8}$ mol/min and 375 °C as shown in Fig. 2. This tendency was consistent with a previous report.\textsuperscript{21} This result indicates that the electrical activity of As for GaAs substrates becomes approximately 10% of that for CdTe substrates. This may be caused by As segregation around higher density of dislocations.

In addition, lowering the growth temperature has also another effect to decrease the Te/Cd atomic ratio at the growing interface, due to the reduction in the DETe pyrolysis. This decrease in the Te/Cd atomic ratio enhances the As incorporation into the Te sites, as discussed above.

The above study on the As doping in MOVPE clearly deduces that the Te deficient condition is preferable for...
higher As incorporation. This condition is similar to the case in MBE. In PAMBE, laser illumination enhances the Te desorption from the CdTe surface, thus changing the surface during growth to a Cd-rich one, which can also be obtained in conventional MBE under additional Cd flux.\textsuperscript{22} This Cd-rich surface condition leads to the effective substitutional doping of group V elements on the Te sites.

The increase in hole concentration for undoped layers in the DETe/DMCd ratio from 0.5 to 1, as shown in Fig. 1, is not due to an increase in Cd vacancy concentration. This is because in this DETe/DMCd range, Cd is not deficient at the growing interface, as mentioned above. In addition, the pyrolytic efficiency of DMCd is larger than that of DETe at the growth temperature. In order to examine the origin in this electrical behavior, PL spectra for undoped layers were compared for the DETe/DMCd ratios of 0.5 and 2. The sample grown at the DETe/DMCd = 0.5 exhibited stronger donor-related emissions. Thus, it is likely that the generation of donor-like defects such as Te vacancy or Cd interstitial, which can reduce the net hole concentration, could occur under the lower DETe flow condition. The exact mechanism that dominates the relation between the hole concentration and the DETe/DMCd flow ratio is under investigation.

B. PL and electrical properties

At first, we discuss the correlation between electrical and PL properties in doped layers. As shown in Fig. 7, the I\textsubscript{AI} line at 1.5901 eV is enhanced and becomes broad, as the TEAs flow rate is increased up to 1 \times 10^{-7} mol/min. In this TEAs flow region, the hole concentration is a linear function of TEAs flow rate. The I\textsubscript{AI} line can be, therefore, attributed to an exciton bound to a neutral As acceptor which is substituted onto the Te site. The I\textsubscript{AI} broadening is originated from an exciton delocalization due to a decrease in the average distance between acceptor sites. Although the I\textsubscript{AI} line is very weakly observed even in an undoped layer, as shown in Fig. 4, this is probably due to the residual As species in the growth reactor.

As shown in Fig. 6, the I\textsubscript{D} and I\textsubscript{Z} lines are also enhanced with the increase in TEAs flow rate. This I\textsubscript{Z} emission also appears in As-doped CdTe layers grown by PAMBE.\textsuperscript{23} On the other hand, it is reported that unidentified emissions appear around 1.586 eV in the high resistive CdTe doped with donor impurities such as In, Ga, and Cl.\textsuperscript{13,24} Thus, we tentatively propose that these I\textsubscript{Z} and I\textsubscript{D} emissions involve the formation of compensating centers induced by doping.

For the high TEAs flow above 1 \times 10^{-7} mol/min, on the other hand, PL spectra exhibit no excitonic emissions, but only a deep-level defect band around 1.47 eV. In this TEAs flow region, hole concentration and mobility decrease with the increase in the TEAs flow. In addition, FWHM values of DCRC become larger, which means the deteriorated crystallinity of doped layers. These results could be attributed to the strong compensation effect. Although its mechanism is not clear yet, this compensation may be caused by As segregation to the high density of defect sites stemming from the large lattice mismatch between CdTe and GaAs, as suggested by Taskar et al.\textsuperscript{25} According to their results using AsH\textsubscript{3} as a dopant source, however, a decrease in hole concentration was not observed, but rather a saturation in hole concentration occurred. Therefore, the compensation in the present work may also be attributed to the incorporation of hydrocarbon from an organoarsine source of TEAs. We are now investigating the exact mechanism.

Finally we estimate an electronic level of As acceptor in CdTe. The As ionization energy \( E_A (\text{As}) \) can be calculated in conjunction with the photon energy formula for the DAP transition given by

\[
\text{hv} = E_g - E_D - E_A + \frac{\phi^2}{4\pi e \epsilon_0 R},
\]

where \( E_g \) represents the band gap, and \( E_D \) and \( E_A \) are the donor and acceptor ionization energy, respectively. Here we adopt 1.6072 eV as the band gap energy at 4.2 K, which is the sum of the heavy-hole exciton \( E_{XHH} \) energy (1.5962 eV) and the free-exciton binding energy (11 meV). The mean DAP distance \( R \) for \( p = 3 \times 10^{16} \text{cm}^{-3} \) is estimated to be about 200 Å in terms of 4\( \pi R^3/3 = N_A^{-1} \), where \( N_A \) represents the acceptor concentration. Using \( \text{hv} = 1.510 \text{eV}, E_g = 1.6072 \text{eV}, E_D = 14 \text{meV}, e = 10.2, \) and \( R = 200 \text{Å}, \) the \( E_A (\text{As}) \) is estimated to be 90.2 meV. This value is very close to 92.0 meV by Molva et al.\textsuperscript{26} and Arias et al.\textsuperscript{4} However, an additional value of 60 meV for As ionization energy has also been reported by several workers, which was based on either PL or Hall analysis.\textsuperscript{5,5}

The As ionization energy was also estimated from the temperature dependent Hall effect. Figure 8 shows a temperature dependence of hole concentration in a doped layer with \( p = 3 \times 10^{16} \text{cm}^{-3} \) at 300 K, plotted as \( \log p / T^{0.75} \) vs \( 10^3 / T \). Ohmic contact was obtained only down to 240 K due to a low carrier concentration. From the slope of data, we estimated an ionization energy of As to be about 106 meV, which involved some experimental error. We therefore propose a value of about 90 meV for As ionization energy from both Hall and PL analyses.
V. CONCLUSIONS

The mechanism of As incorporation in the atmospheric-pressure MOVPE-grown (100) CdTe layers on (100) GaAs was studied by Hall effect and PL measurements. A dopant source was TEAs. Higher As doping was achieved by lowering the growth temperature and the DETe flow rate. The former enhances the adsorption of As species on the Cd species, and also reduces the Te/Cd atomic ratio at the growing interface. The latter is equivalent to the reduction in the surface coverage rate of Te, which is effective to incorporate As into the Te sites. The As incorporation efficiency was estimated to be about 0.1%, which was similar to that for AsH3. These results indicate that the dominant factor for As incorporation in MOVPE is the sticking efficiency of As species over the growing surface. The electrical activity of As for GaAs substrates was about one order of magnitude lower than that for CdTe substrates. Good control of As doping was achieved up to a TEAS flow rate of 1 X 10^{-15} mol/min. In this region, the hole concentration was controlled from 2 X 10^{15} to 3 X 10^{16} cm^{-3} in proportion to the TEAs flow rate, and the hole mobility was as high as 75 cm²/V s. Good correspondence was also obtained between electrical and PL properties. The 1.5901-eV line was enhanced, and the linewidth was broadened with the increase in As doping level, which attributes the 1.5901-eV line to an exciton bound to a neutral As acceptor which substituted onto the Te site. In addition, a DAP emission at 1.510 eV appeared with the doping level. The DAP transition and temperature-dependent Hall analyses proposed a value of about 90 meV for an As acceptor ionization energy.

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