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Properties of Iodine-Doped CdTe Layers on (211) Si Grown at High Substrate Temperatures by MOVPE

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The properties of iodine-doped (211) CdTe layers grown on (211) Si substrates by metalorganic vapor-phase epitaxy at high substrate temperatures from 325°C to 450°C were studied. The growth rate of the doped layer increased with increasing substrate temperature before reaching a maximum value of 2.6 μm/h at 425°C, after which it decreased slightly. On the other hand, the room-temperature electron density showed a strong dependence on the Te/Cd precursor flow-rate ratios, where the electron density increased with a decreasing Te/Cd ratio. The highest electron density of 2.5×10^{18} cm^{-3} was obtained by growing the epilayer at a substrate temperature of 400°C and Te/Cd ratio of 0.05. This was considered to be due to decreased donor compensation at a small Te/Cd ratio. Good correspondence was observed between the results obtained from Hall measurements and photoluminescence measurements.

Key words: CdTe epilayers, iodine doping, high substrate temperature, Si substrate, doping mechanism

INTRODUCTION

Epitaxial growth of single-crystal CdTe on large-area readily available substrates such as GaAs or Si is a promising way to obtain large-area crystals that are required for x-ray, gamma-ray, or infrared (IR) device technology. Actual device applications require highly doped materials with controllable electrical properties. For example, x-ray and gamma-ray detectors that are fabricated in a *p*-CdTe/*n*-CdTe/*n*$^+$-Si heterojunction diode structure require a thick and highly doped *n*-CdTe layer in order to reduce detector dark current.[1,2] The *n*-CdTe/*n*$^+$-Si heterojunction contains a large number of dislocations resulting from the large lattice mismatch and difference in thermal expansion coefficients between the two materials. Dislocations are well known as potential sources of increased diode dark currents.[3,4] The dark current can be reduced by suppressing the spread of the depletion layer towards the *n*-CdTe/*n*$^+$-Si junction, which can be achieved by making *n*-CdTe thicker and with high carrier concentrations.

There are several reports on *n*-type doping of CdTe epilayers using iodine or indium as dopant, with room-temperature electron density exceeding 10^{18} cm^{-3}.[5–7] Most of those studies, however, were performed at a low substrate temperature (< 230°C) on either CdTe or CdZnTe substrates in molecular beam epitaxy (MBE) growth. The low-temperature growth was performed to suppress the formation of native defects and hence to enhance dopant activity.[5–7] Our group also previously reported on iodine doping of CdTe epilayers on both GaAs and Si substrates using metalorganic vapor-phase epitaxy (MOVPE) growth,[3,8,9] where the growth was typically performed at 325°C. However, the maximum electron density and the growth rate of the CdTe layer on the Si substrates were limited to around 10^{17} cm^{-3} and 0.5 μm/h, respectively.[3,9] Such a low

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growth rate is not practical for the growth of thick n-CdTe layers. A further increase in electron density is also required. In this study, we grew iodine-doped n-CdTe layers at higher substrate temperatures and at various Te/Cd precursor ratios in the vapor phase (VI/II ratio). We obtained both a high level of doping and high growth rates by optimizing the substrate temperature and the VI/II flow ratios. We found that the role of the VI/II ratio is more significant than that of the substrate temperature in controlling the doping properties. The electrical properties of these iodine-doped CdTe layers, as well as the possible doping mechanism, are presented herein.

EXPERIMENTAL PROCEDURES

CdTe growth was performed in a vertical-type MOVPE reactor operating at atmospheric pressure. Details regarding the direct growth of CdTe on a (211) Si substrate, including Si substrate pretreatments to facilitate single-crystal CdTe with orientation parallel to the substrate, were reported previously.[10] Dimethylcadmium (DMCd) and diethyltelluride (DETe) were used as group II and VI precursors, respectively. Ethyl-iodine (EI) was used as dopant. In this study, growth was performed on a 25 mm × 25 mm (211) n^+-Si substrate in a temperature range from 325°C to 450°C and a VI/II ratio from 0.05 to 0.3 (i.e. growth in a Cd-rich condition). The DETe flow rate was fixed, while the DMCd flow rate was adjusted to vary the VI/II ratios. First, a 10 μm-thick high-resistivity undoped CdTe buffer layer was grown on the Si substrates, after which doped layers were grown on these buffered substrates. All n-CdTe growth was performed for the same length of time. The layer thickness was measured using a stylus profiler. These layers were evaluated by room-temperature Hall measurement (van der Pauw method) and 4.2 K photoluminescence measurement, as well as double crystal x-ray rocking curve (DCRC) measurement. The surface morphology was examined using Nomarski optical microscopy. A high-resistivity CdTe buffer layer, whose resistivity is several orders of magnitude higher than that of the n^+-Si substrate, was inserted in order to minimize the effect of the substrate (i.e. to electrically insulate the doped layer from the substrate) during the Hall measurement. Indium electrodes were evaporated on the four corners of the sample to make ohmic contacts.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the iodine-doped n-CdTe epilayer growth rate as a function of substrate temperature. The growth was performed at a VI/II ratio of 0.25. The result shows that the growth rate increased with increased substrate temperature, reaching a maximum value of 2.6 μm/h at 425°C. This result shows an expected pattern where growth is dominated by thermal decomposition of DETe[8]. The maximum growth rate obtained is more than five times the growth rates reported for our previous n-CdTe layer on Si substrates[3,9]. However, the growth rate decreases slightly after reaching the maximum value. Figure 2 shows the room-temperature electron density and mobility values of the n-CdTe layers grown at different substrate temperatures. No clear variation in carrier concentration or mobility is observed with substrate temperature within this substrate temperature range. The exact reason is not known. It may be due to limited incorporation of dopant onto the growth surface due to a high surface coverage rate of Te. However, it needs further verification. Studies have reported that the doping properties in CdTe are due to the compensation effect.[3,6,11] The cadmium vacancy in the crystal forms the cadmium vacancy-donor complex, which acts as an acceptor-like defect, and neutralizes the donor in the following way.[11]

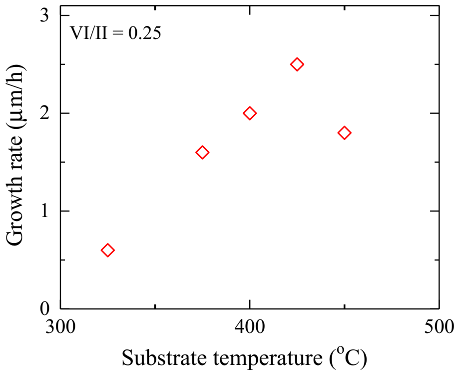

Fig. 1. Growth rate of iodine-doped n-CdTe epilayers as a function of substrate temperature.

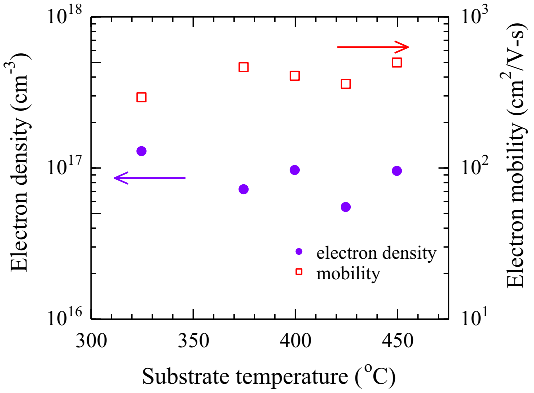

Fig. 2. Room temperature electron density and mobility values of n-CdTe layers grown at different substrate temperatures.

$$\left[V_{\mathrm{Cd}}^{-} - I_{\mathrm{Te}}^{+}\right]^{-} + I_{\mathrm{Te}}^{+} \qquad (1)$$

It has been reported that a low-temperature growth is effective for resolving this dopant compensation problem.[3,5–7] However, the results in

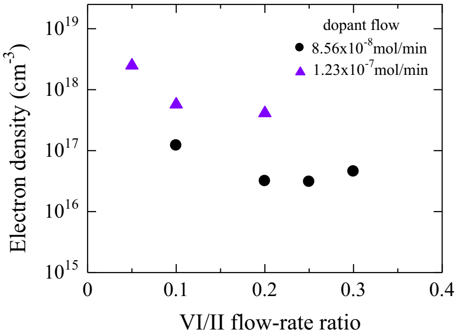

Fig. 3. The variation in room-temperature electron density with the VI/II flow-rate ratio for epilayers grown with different dopant flow rates.

Fig. 2 suggest that growth parameters other than substrate temperature play a more important role.

Figure 3 shows room-temperature electron density as a function of the VI/II flow-rate ratio at two different dopant flow rates. The substrate temperature during the growth was 400°C, and the DMCd flow rate was adjusted to vary the VI/II ratios. The n-CdTe layer thickness was typically 5μm. The results in Fig. 3 show that the electron density gradually increased with decreasing VI/II ratio, and the highest electron density of 2.5×10^{18} cm^{-3} was obtained with a VI/II ratio of 0.05. This could be explained by the decrease in donor compensation with the decreasing VI/II ratio, as this growth condition suppresses the formation of Cd vacancies. On the other hand, increasing the VI/II ratio leads to less Cd-rich growth, and hence the compensation increases. Also, as shown in Fig. 3, for a fixed VI/II ratio and with these small dopant flow rates, the electron density increases with the increase in dopant flow rates as dopant incorporation in the crystal increases. However, with a further increase in dopant flow rate (above 1.3×10^{-7} mol/min), the electron density starts to decrease (not shown here) due to the onset of donor compensation.[3] These results suggest that there exists an optimum supply of dopants governed by growth conditions that produce epilayers with high electron density.

In order to examine how the amount of iodine in the epilayer differs with different growth conditions, we performed secondary-ion mass spectrometry (SIMS) measurements on two randomly selected samples (data not presented here). We found that, irrespective of the VI/II ratio, the amount of iodine in the epilayer increased if the dopant flow rate was increased. Moreover, an increase in the VI/II ratio resulted in a net decrease in electron density even if the total iodine amount in the epilayer was high. This result indicates that donor compensation increases when the dopant flow rate as well as when the VI/II ratio is increased during growth. Further investigation is under way and will be presented in the future.

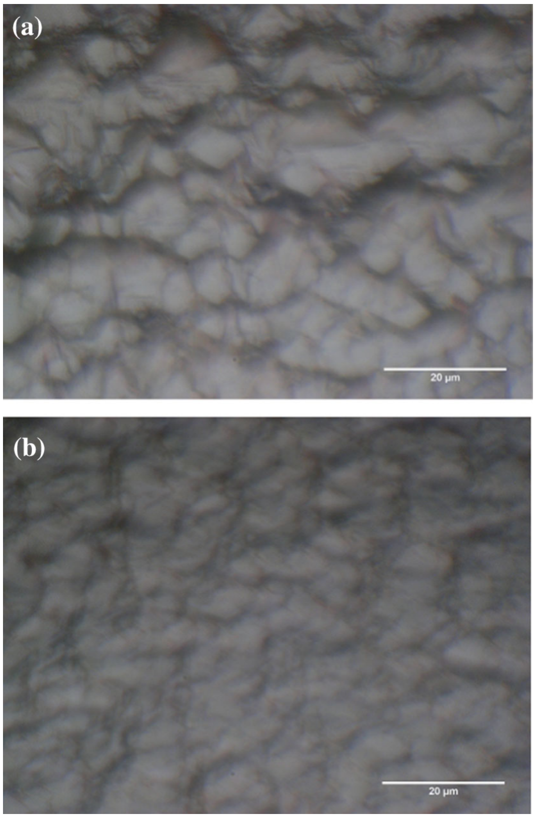

Fig. 4. Surface morphology of n-CdTe layers grown at 400°C at VI/II ratios of (a) 0.1 and (b) 0.3.

X-ray diffraction measurements were performed on these CdTe layers grown at different VI/II ratios. A θ-2θ scan showed a single diffraction peak corresponding to CdTe (422) reflection. The rocking curve measurement revealed that the full width at half maximum (FWHM) values were 540, 405, and 447 arcsec for layers grown with VI/II ratios of 0.1, 0.25 and 0.3, respectively. These results suggest that the structural quality of crystal degrades slightly when the VI/II ratio is lowered to 0.1. The surface morphology of the layers grown at the two different VI/II ratios is shown in Fig. 4. Both images show dense characteristic hillock structures, which may be the result of Cd-rich growth. The morphology is somewhat smoother for the layer grown at a VI/II ratio of 0.3 compared with a ratio of 0.1.

The photoluminescence spectra of iodine-doped n-CdTe layers grown at a substrate temperature of 400°C with different VI/II ratios are shown in Fig. 5. The PL spectrum of the layer grown with a VI/II ratio of 0.1 (Fig. 5a) shows a distinct edge-emission peak and a broad donor–acceptor pair (DAP) emission peak, accompanied by LO-phonon replicas. Also, there is a distinct peak near 1.5 eV. The edge-emission peak is attributed to an exciton bound to a neutral I donor, whereas the emission peak near 1.5 eV could be due to the iodine donor recombining with residual acceptor impurities.[12] The broad band DAP emission is related to the A-

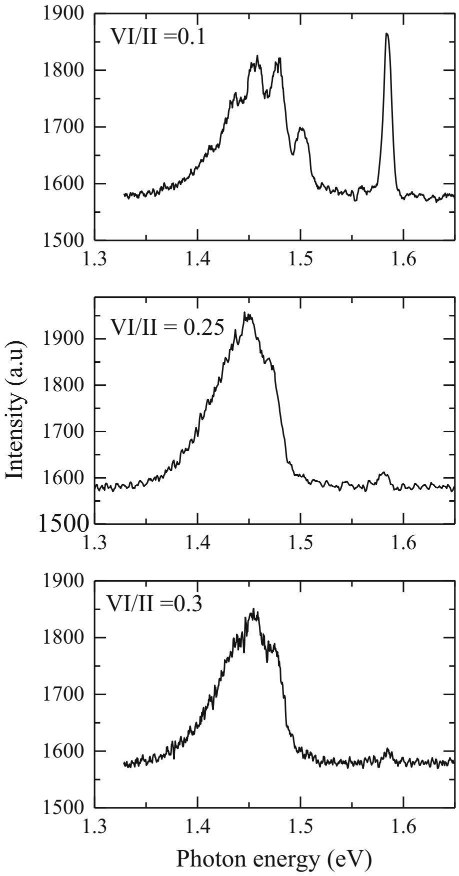

Fig. 5. The 4.2 K PL spectra of iodine-doped *n*-CdTe layers grown at a substrate temperature of 400°C, with different VI/II flow-rate ratios.

center (V_{Cd}-I_{Te}) acceptor and isolated I donors (I_{Te})[3,12–14], though dislocation-related peaks also appear in this region. This is the characteristic PL spectrum of an iodine-doped CdTe, where electrical compensation of the dopant is low.[13] However, the bound-exciton emission peak decreases drastically and the 1.5 eV peak mostly disappears, while the DAP emission becomes broad and the phonon replicas become less prominent, for the layers grown with higher VI/II ratios, as shown in Fig. 5b and c, which is indicative of the onset and increase of electrical compensation.[13]

As discussed above, growth at a low VI/II ratio (i.e. Cd-rich condition) helps to suppress the formation of V_{cd}, leading to small donor compensation as the probability of iodine A-center formation decreases. Hence, the free electron carrier density increases, as shown in Fig. 3, and distinct bound-exciton emission appears in the PL spectrum (Fig. 5a). However, V_{Cd} increases when the growth is performed at higher VI/II ratios, resulting in increased donor compensation, and hence the free electron carrier density decreases.

CONCLUSIONS

This work has investigated iodine doping of CdTe layers grown on (211) Si substrates by metalorganic vapor-phase epitaxy at high substrate temperatures. The growth rate increased with an increase in substrate temperature, reaching a maximum growth rate of 2.6 μm/h at a substrate temperature of 425°C. The room-temperature free electron density, on the other hand, showed strong dependence on the VI/II flow ratio during growth. The electron density increased, while the VI/II ratio decreased. Maximum electron density of 2.5x10^{18} cm^{-3} was obtained for epilayers grown at a substrate temperature of 400°C and VI/II ratio of 0.05. As discussed, the improvement in electron density is due to the suppression of cadmium vacancy formation, which in turn decreases the donor compensation effect. It was found that the VI/II flow-rate ratio has a more pronounced effect in controlling cadmium vacancy formation than the substrate temperature in the temperature range investigated in this work.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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