Electrical Properties of Halogen-Doped CdTe Layers on Si Substrates Grown by Metalorganic Vapor-Phase Epitaxy

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Electrical properties of halogen-doped CdTe layers grown on Si substrates using iodine and chlorine dopants are presented. No change in electrical properties of the layers was observed with chlorine as a dopant. However, doping with iodine resulted in highly conductive n-type layers or highly resistive p-type layers depending upon the growth conditions, even though a similar amount of dopant was introduced into the growth chamber. Layers grown at 560°C, with a vapor-phase Te/Cd precursor ratio of 3.0, were p-type. The resistivity of the layers remained unchanged for low dopant supply rates, but increased abruptly when the dopant supply rate was increased beyond a certain value. On the other hand, layers grown at 325°C with Te/Cd ratios from 0.1 to 0.25 were n-type. A maximum free electron concentration of 1.3×10^{17} cm^{-3} was obtained at room temperature. The types and conductivities of the grown layers were strongly dependent on the growth conditions.

INTRODUCTION

CdTe and CdZnTe have emerged as the most attractive materials for development of advanced and high-sensitivity room-temperature x-ray and gamma-ray detectors. Melt-grown bulk crystals are currently used for detector fabrication. However, application of these detectors as imaging detectors is very limited due to the unavailability of high-quality large-area crystals. In recent years, there has been increased interest in vapor-phase growth of thick epitaxial CdTe single-crystal layers on large-area substrates such as GaAs or Si.[1–4] We have previously reported on metalorganic vapor-phase epitaxy (MOVPE) growth of thick single-crystal CdTe layers (100 μm to 260 μm) on Si as well as on GaAs substrates and the development of gamma-ray detectors using these epilayers.[1,4–6] The detectors were fabricated in a p-CdTe/n-CdTe/n^+-Si

heterojunction diode structure, where the p-CdTe and the n-CdTe layers were typically 100 μm and 5 μm thick, respectively.[5] The detectors were capable of detecting gamma radiation and measuring its energy distribution, when operated in pulse mode by applying a reverse bias voltage. However, the detector dark current was a major source of electronic noise, which increased with the applied reverse bias. The depletion layer width increases with the applied reverse bias; the impurity concentrations of p-CdTe and n-CdTe control the depletion layer widths on either side of the junction. The n-CdTe layer in this detector structure contains misfit dislocations resulting from the large lattice mismatch and thermal expansion coefficient difference between the CdTe and the Si substrate. Hence, it results in increased dark current through dislocation-related current leakage paths when the depletion layer width on the n-CdTe side increases. The dark current can be reduced by suppressing the spread of the depletion region towards the n-CdTe side of the junction. This can be achieved by

increasing the donor impurity concentration of the
n-CdTe layer and/or by decreasing the net acceptor
concentration (increasing the resistivity) of the
p-CdTe layer, thus extending the depletion region
mostly towards the p-CdTe side of the junction. In
order to achieve this, we studied electrical proper-
ties of halogen-doped CdTe layers. We used iodine
and chlorine as dopants and, by varying the sub-
strate temperatures and the Te/Cd precursor ratio
in the vapor phase (VI/II ratio), we were able to
obtain highly conductive n-CdTe and highly resis-
tive p-CdTe layers. Electrical properties of halogen-
doped CdTe layers grown on Si substrates using
iodine and chlorine as dopants are presented.

EXPERIMENTAL PROCEDURES

Epitaxial growth was carried out in a vertical
MOVPE reactor working at atmospheric pressure.
Details on the growth of high-quality single-crystal
CdTe epitaxial layers on (211) Si substrates have
been reported elsewhere.[1,6] The growth was carried
out at substrate temperatures of 325°C to 560°C,
using dimethylcadmium (DMCd) and diethyl-
tellurium (DETe) as group II and group VI precur-
sors, respectively. Ethyl-iodide (EI), ethyl-chloride
(EC), and trichloromethane (TCM) were used as
dopants. The growth was carried out by varying the
dopant supply in the growth chamber at different
VI/II ratios. The DETe supply rate was fixed at
2.5×10^{-6} mol min^{-1}, while the DMCd supply was
adjusted to change the VI/II ratios. Table I sum-
marizes the typical growth condition for the n-CdTe
and p-CdTe layers. First, a 5-μm-thick undoped
CdTe buffer layer was grown on the 10 mm ×
12 mm (211) Si substrates. Afterwards, doped lay-
ers, typically 10 μm thick, were grown on these
buffered substrates. The doped layers were evalu-
ated by room-temperature Hall measurement
(van der Pauw method) and 4.2-K photolumines-
cence measurement. It should be noted that, for the
high-resistivity p-CdTe layers, the exact resistivity
of the layers could not be determined by the van der
Pauw method because the resistivity of the Si sub-
strate and the CdTe buffer layer used were many
orders lower than the p-CdTe layers. So, these are
comparative values, and represent how the resis-
tivity changes with varying dopant concentration
from that of an undoped layer. The exact resistivity
of the p-CdTe layers should be many orders larger
than reported here, as discussed elsewhere.[7,8]

RESULTS AND DISCUSSION

Growth of p-CdTe Layers

The conductivity type of the grown layer was
strongly dependent on the substrate temperature
and the VI/II precursor supply ratio, even though a
similar amount of dopant was introduced during
growth. Layers grown at a substrate temperature of
560°C, with a VI/II ratio of 3.0, exhibited p-type
conductivity. Figure 1 shows the resistivity of the
p-CdTe layers as a function of EI supply rate. The
resistivity remained almost unchanged for a dopant
supply rate up to 1.0×10^{-7} mol min^{-1}, and was on
the same order of magnitude (10^3 Ω cm) as that of
an undoped layer. As mentioned in the experimen-
tal section, this resistivity does not represent the
exact value. We made an approximate estimation of
the resistivity by fabricating a p-CdTe/n-CdTe/n^+-Si
diode, and calculated the equivalent resistivity
of about 10^6 Ω cm using forward-bias I–V
data.[8] However, the resistivity in Fig. 1 increased
rapidly by more than two orders of magnitude
when the dopant supply was increased beyond
1.0×10^{-7} mol min^{-1}. This result shows that the
resistivity of the layers does not change linearly
with the dopant supply rate, but increases abruptly
when the dopant supply is increased beyond a
certain value. This behavior could be explained
using the modified compensation model proposed
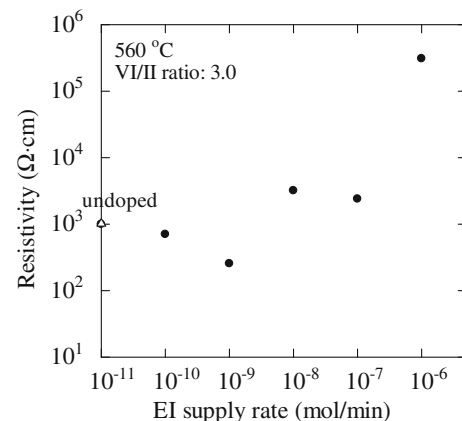by Fiederle et al., where the resistivity of CdTe is

Fig. 1. Comparative resistivity values of p-CdTe layers as a function
of EI supply rate. *Open triangle* represents resistivity of the undoped
layer.

Table I. Typical growth condition

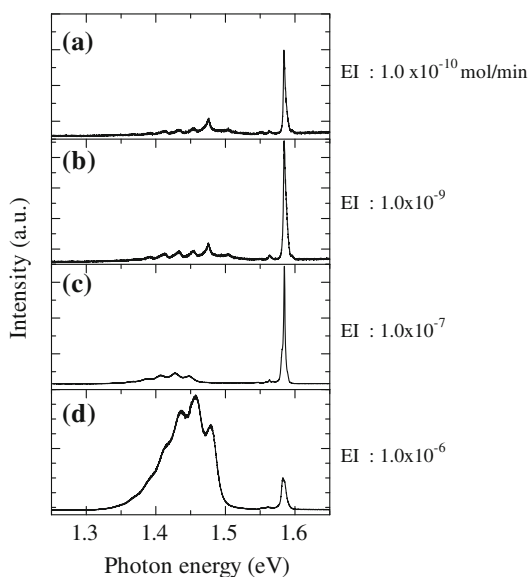| Layer Type	Substrate Temp. (°C)	VI/II Ratio	Dopant	Dopant Flow Rate (mol min^{-1})
p-CdTe	560	3.0	Iodine (EI)	1.0×10^{-10}–1.0×10^{-6}
			Chlorine (EC, TCM)	1.0×10^{-10}–1.0×10^{-5}
n-CdTe	325	0.1–0.25	Iodine (EI)	1.0×10^{-10}–1.0×10^{-6}

Fig. 2. PL spectra (4.2 K) of *p*-CdTe layers grown at 560°C and VI/II ratio of 3.0. The supply rate of dopant (EI) was varied from 1.0×10^{-10} mol min^{-1} to 1.0×10^{-6} mol min^{-1}, as indicated in the figure. Ar$^+$-ion laser at 514.5 nm with power density less than 1 W/cm^2 was used as the excitation source. Note that the *y*-axis of figure (d) has a larger scale than the other figures.
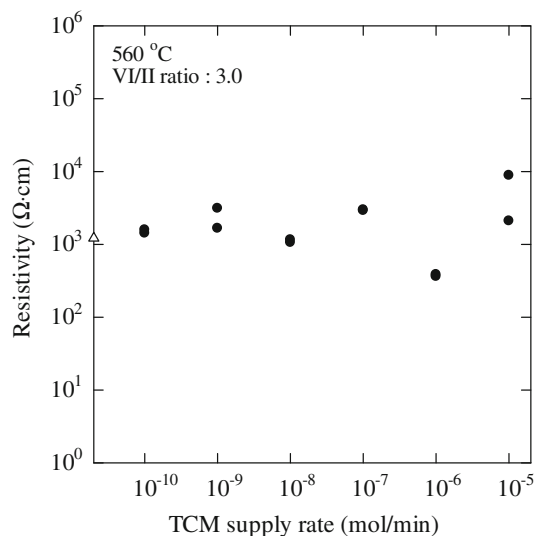

Fig. 3. Comparative resistivity values of *p*-CdTe layers as a function of TCM supply rate. *Open triangle* represents resistivity of the undoped layer. The resistivity of the doped layers remains almost similar to that of the undoped layer.

determined due to compensation of excess shallow acceptor impurities (N_a–N_d) by deep intrinsic donors (N_{dd}).[9–11] We considered cadmium vacancy as the dominant acceptor, iodine as the donor, and tellurium antisite defects as the deep intrinsic donors.[11] The resistivity of CdTe remains low until the concentration of excess shallow acceptors is higher than that of deep intrinsic donors, but increases abruptly when the concentration of deep intrinsic donors becomes higher.[9–11]

PL spectra of the high-resistivity *p*-CdTe layers are shown in Fig. 2. For an EI supply rate up to 1.0×10^{-7} mol min^{-1}, the PL spectra do not exhibit any differences and are similar to that of an undoped CdTe layer (Fig. 2a–c). Typically, the PL spectrum exhibits a sharp peak at 1.5844 eV, which is associated with acceptor-bound exciton (A°,X) recombination. Also, there is a weak and broad deep-level luminescence band extending from 1.3 eV to 1.5 eV. However, a dramatic change in the PL spectrum was observed when the EI supply was increased to 1.0×10^{-6} mol min^{-1} (Fig. 2d). The emission intensity of the (A°,X) peak remains similar to that of the layers grown with a low amount of dopant supply, but it broadens, probably due to the contribution from the (D°,X) transition. However, the emission intensity of the deep-level luminescence band (1.3 eV to 1.5 eV) increases strongly. This deep-level band exhibits a zero-phonon line at 1.4786 eV, with several LO-phonon replicas separated by an average energy of 21 meV. Based on the intensity distribution of the phonon replicas, this band was identified as a donor–acceptor pair (DAP) recombination involving an iodine donor and the

iodine A-center (V_{Cd}–I_{Te}) acceptor.[12,13] The DAP band becomes dominant due to the increased dopant incorporation in the crystal. However, they are in compensated states, which increase the crystal resistivity.[14–16] This result is consistent with those obtained from the resistivity measurements.

Doping studies performed with EC and TCM as the chlorine source, on the other hand, resulted in no change in the electrical properties of the grown layers compared with that of an undoped layer. The resistivities and the PL spectra of the layers grown with different amounts of dopants are shown in Figs. 3 and 4, respectively. All layers were grown under similar conditions as that of the iodine-doping studies (i.e., 560°C, VI/II ratio of 3); the dopant (TCM) supply rates were varied from 1.0×10^{-10} mol min^{-1} to 1.0×10^{-5} mol min^{-1}. Figure 3 shows that the resistivity of the layer remains around 10^3 Ω cm over the entire range of dopant supply rates. This value is similar to that of undoped layers. Similarly, there is no change in the PL spectra. The spectrum exhibits a sharp (A°,X) peak, but the deep-level luminescence band is very weak and almost invisible. This result indicates that chlorine atoms do not incorporate into the CdTe lattice, neither activated nor in a compensated state. It is most likely that both EC and TCM do not decompose at the growth conditions we have used. The C–Cl bond strength in EC and TCM is about 323 kJ/mol, which is higher than the C–I bond strength of 212 kJ/mol in EI.* Further investigations into growth conditions, or different organometallic sources, are needed.

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*Data provided by organometallic source supplier (Tri-Chemical Laboratories Inc.).
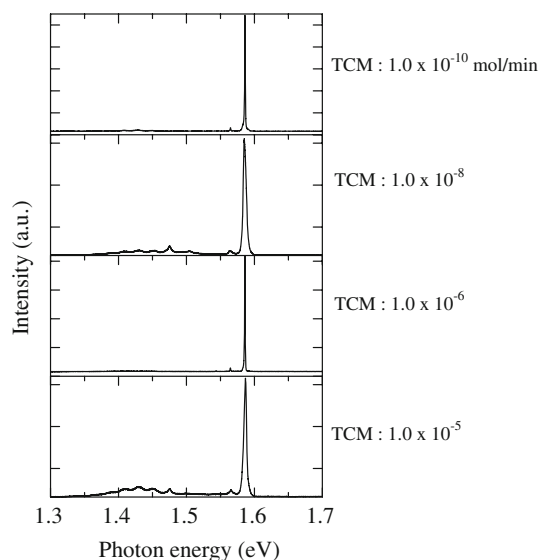
Fig. 4. PL spectra (4.2 K) of the *p*-CdTe layers doped with chlorine. The supply rate of the dopant (TCM) was varied from 1.0×10^{-10} mol min^{-1} to 1.0×10^{-5} mol min^{-1}. Other growth and the PL measurement conditions were the same as in Fig. 2. No remarkable change in the spectra is visible with changing dopant supply rate during the growth.
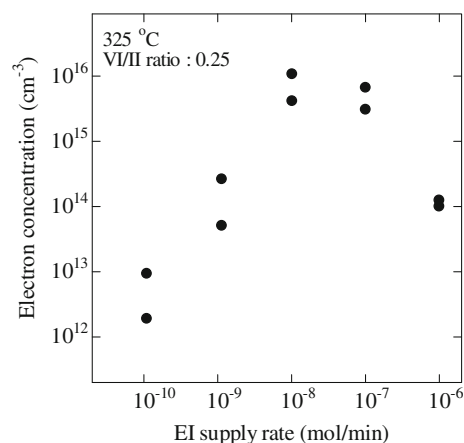

Fig. 5. Room-temperature free electron concentration of the *n*-CdTe layer as a function of EI supply rate. The growth was carried out in a Cd-rich condition (VI/II ratio of 0.25) and at low substrate temperature of 325°C.
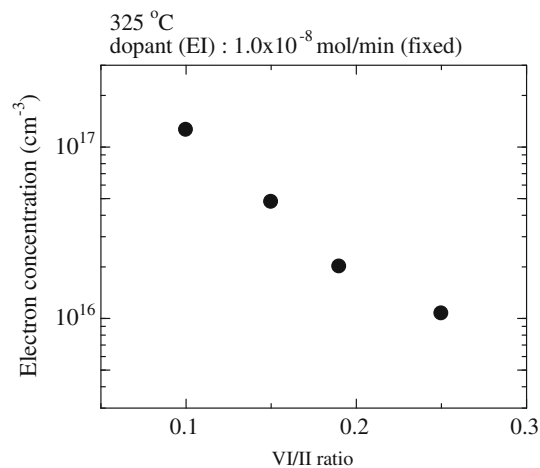

Fig. 6. Dependence of room-temperature free electron concentration of *n*-CdTe layer as a function of Te/Cd ratio (VI/II ratio) in the vapor phase. The dopant (EI) supply was kept fixed at 1.0×10^{-8} mol min^{-1} during growth.

Growth of *n*-CdTe Layers

For the *n*-type CdTe growth, we lowered the substrate temperature to 325°C, and growth was carried out in a Cd-rich condition (i.e., VI/II ratio of 0.1 to 0.25). This growth condition is favorable to prevent self-compensation and to achieve high dopant incorporation into the CdTe crystal. EI was used as a dopant source, and its supply rate was varied from 1.0×10^{-10} mol min^{-1} to 1.0×10^{-6} mol min^{-1}. Figure 5 shows the dependence of the room-temperature free electron concentration of the CdTe layers, determined by Hall measurement, as a function of EI supply rate. The VI/II ratio was fixed at 0.25. The free electron concentration increased with the EI supply, attaining a maximum value of 2.0×10^{16} cm^{-3} at an EI supply rate of 1.02×10^{-8} mol min^{-1}. Further increment in the dopant supply rate results in saturation and subsequently a decrease of the electron concentration. This indicates that compensation of the donors increases with increasing dopant atoms in the crystal. It has been reported that compensation of the donors occurs through generation of ionized Cd vacancies as well as due to the donor transition to an interstitial site resulting in acceptor-like states.[17,18]

Generation of Cd vacancies can be suppressed by using an even higher Cd-rich growth condition, and we can expect delayed onset of donor compensation and hence increased free electron concentration. In order to examine this, we varied the VI/II ratio from 0.1 to 0.25, keeping the EI supply fixed at 1.0×10^{-8} mol min^{-1}. All other growth conditions remained unchanged. Figure 6 shows the room-temperature free electron concentration as a function of VI/II ratio. The highest electron concentration of 1.3×10^{17} cm^{-3} was obtained for a VI/II ratio of 0.1, and as expected, the electron concentration decreased with increasing VI/II ratio.

PL spectra of the *n*-CdTe layers doped with different amounts of iodine are shown in Fig. 7. At a low doping level (supply rate of EI = 1.0×10^{-10} mol min^{-1}), the spectrum is dominated by a sharp bound-exciton emission peak. There is no distinct deep-level emission band, and this PL spectrum is similar to that of an undoped CdTe layer. However, the intensity and width of the bound-exciton emission peak gradually change with increasing donor incorporation, as shown in Fig. 7b and c. Moreover, a broad band with strong emission intensity, which is followed by several LO-phonon
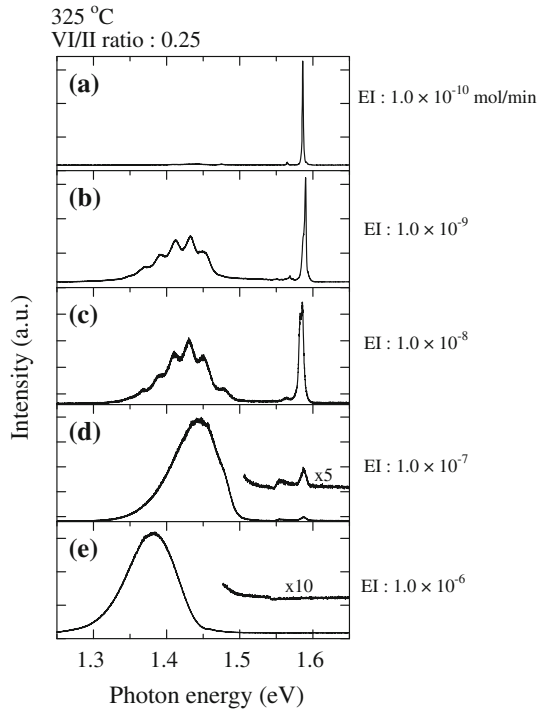
Fig. 7. PL spectra (4.2 K) of the *n*-CdTe layers doped with iodine. The supply rate of the dopant (EI) was varied from 1.0×10^{-10} mol min^{-1} to 1.0×10^{-6} mol min^{-1}. The growth was carried out at 325°C and VI/II ratio of 0.25. PL measurement conditions were the same as in Fig. 2.

replicas, appears in the range from 1.3 eV to 1.5 eV. This was identified as donor–acceptor pair (DAP) recombination involving an iodine donor, as explained above. The PL spectrum changes dramatically with a further increase of the dopant supply, as shown in Fig. 7d and e. The exciton emission decreases significantly and then disappears, while the DAP band increases with increasing donor concentration. The LO-phonon replicas of the DAP band could not be resolved because of poor crystal quality, possibly a result of increased donor incorporation. It was observed that layers grown with high EI supply rates had higher x-ray rocking-curve full-width at half-maximum (FWHM) values [CdTe (422) plane] than undoped layers. Furthermore, DAP band in Fig. 7e has shifted to lower energy region; the reason is not clear at this moment. This may be due to the composition change of CdTe due to excessive iodine atoms introduced into the crystal. This PL result is consistent with the Hall measurements, in which the free electron concentration increases up to an EI supply rate of 1.0×10^{-8} mol min^{-1} and then decreases (Fig. 5). As a result, we obtained a bound-exciton emission in the PL spectrum until the EI supply rate was 1.0×10^{-8} mol min^{-1} (Fig. 7a–c). A further increase of the EI supply results in a decrease of the free electron concentration owing to donor compensation. Hence, the bound-exciton emission reduces and then disappears, while the DAP emission increases.

CONCLUSIONS

We have presented electrical properties of halogen-doped CdTe layers grown on Si substrates in an MOVPE reactor using iodine and chlorine dopants. No change in electrical properties of the layers was observed with chlorine as a dopant. We suggest that ethyl-chloride and trichloromethane, which were used as chlorine sources, do not properly decompose under the growth conditions used. However, we were able to control the types and conductivities of the CdTe layers doped with iodine (ethyl-iodide). A highly conductive *n*-type or a highly resistive *p*-type layer was obtained, depending upon the growth conditions, even though a similar amount of dopant was introduced into the growth chamber. Layers grown at 560°C, with a vapor-phase Te/Cd precursor ratio of 3.0, were *p*-type. The resistivity of the layers remained unchanged for low dopant supply rates, but increased abruptly when the dopant supply was increased beyond 1.0×10^{-7} mol min^{-1}. On the other hand, layers grown at a low substrate temperature of 325°C with Te/Cd ratios from 0.1 to 0.25 were *n*-type, where a maximum room-temperature free electron concentration of 1.3×10^{17} cm^{-3} was obtained. The growth conditions strongly affect whether the dopant atoms remain in a compensated state or are activated as a free donor, and hence controls the types and conductivities of the layers.

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