MOVPE Growth of Thick Single Crystal CdZnTe Epitaxial Layers on Si Substrates for Nuclear Radiation Detector Development

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***Abstract*—Details about the MOVPE growth of thick single crystal CdZnTe layers on (211)Si substrates are presented. The growth was carried out at a substrate temperature of 650 °C, using dimethylcadmium, dimethylzinc, and diethyltellurium precursors. Control of Zn-concentration in the range from 0 to 0.2 was performed by controlling the precursors' flow-rates and ratio. Results from the XRD showed grown layers were single crystalline with no phase separation observed. The 4.2 K PL results show high intensity bound-exciton peaks which shifted to higher energies with increasing Zn-concentrations. A p-CdZnTe/p-CdTe/n-CdTe/n^+-Si hetero-junction diode was fabricated and evaluated for its possible application in nuclear radiation detector development, which exhibited good rectification property.**

***Index Terms*— CdZnTe, epitaxial layer, heterojunction diode, nuclear radiation detector, Si substrate, vapor-phase growth.**

I. Introduction

MELT-GROWN high resistivity bulk CdTe and CdZnTe have emerged as the most promising materials for the development of advanced and high-sensitivity x-ray, gamma ray detectors operable at room temperature [1]–[4]. There are several reports on the development of spectroscopic detectors as well as imaging arrays based on these materials, which demonstrate excellent performances [1]–[4]. However, these devices have been limited to relatively smaller dimensions because of the difficulties in the growth of larger and uniform single crystals with high material qualities. Tiling several carefully screened small-area detectors in mosaic array is the only option available today for making large-area devices, which imposes manufacturing complexities as well as high system cost.

The vapor-phase growth of CdTe or CdZnTe epitaxial layers on large-area substrates such as GaAs or Si by metalorganic vapor-phase epitaxy (MOVPE) is a promising way to obtain large-area and uniform thick crystals for the detector development. Vapor-phase growth offers several advantages over the melt-growth such as; (i) growth at lower substrate temperature allows uniform layers with high crystal qualities, (ii) higher material purities and strict control of stoichiometry, and (iii) easy control of the thickness as well as electrical properties of the growth layers with controlled amounts of impurity dopings. Hence, properties of the grown layers can be tailored according to the device requirements.

We have been studying on large-area detector development using MOVPE-grown thick single crystal CdTe epilayers on Si substrates for medical imaging applications with working photon energies below 100 keV [5]–[7]. For this, we need more than 300 μm-thick CdTe epilayers to achieve a reasonable detection efficiency. For example, a 300 μm-thick CdTe epilayer absorbs about 70% of 60 keV photons. We have already reported the details about growth of thick (up to 260 μm) single crystal CdTe on Si substrates as well as spectroscopic detector fabrication and two-dimensional (2D) imaging arrays fabrication using these MOVPE-grown thick CdTe epilayers [5]–[8]. The detectors are fabricated in a p-CdTe/n-CdTe/n^+-Si heterojunction diode structure, and operated in a reverse-bias mode. We have already confirmed that these detectors are capable of detecting and spectrally resolving x-rays and gamma rays, and can be applied in spectroscopic imaging applications [5]–[8].

Alloying CdTe with Zn ($Cd_{1-x}Zn_xTe$) and controlling Zn-molar concentrations, x-values, in a wider range in the grown epilayer would offer added importance of this material. $Cd_{1-x}Zn_xTe$ with x-values from 0.04 to 0.2 is considered promising for detector development as it offers similar absorption efficiency for incident x-rays, gamma rays, but offers higher energy bandgap than that of the CdTe [9]. Hence, detectors with reduced leakage currents and improved performances can be expected. Similarly, $Cd_{1-x}Zn_xTe$ epilayers with x-value of 0.04 is used as a lattice matched substrate for the HgCdTe layers growth for the infrared detector applications, while x-value around 0.4 is considered suitable for the efficient tandem solar cells fabrication [10], [11].

We studied MOVPE growth of thick and uniform single crystal $Cd_{1-x}Zn_xTe$ (CZT) epilayers, with x-value from 0 to 0.2, on Si substrates and heterojunction diode-type detector fabrication for their possible applications in nuclear radiation detector development. In this paper, we present details on the growth and characterization of CZT layers, as well as heterojunction diode-type detectors fabrication and their evaluations.

II. Experimental

The CZT epitaxial layers were grown on (211) Si substrates in a vertical-type MOVPE reactor working at an atmospheric

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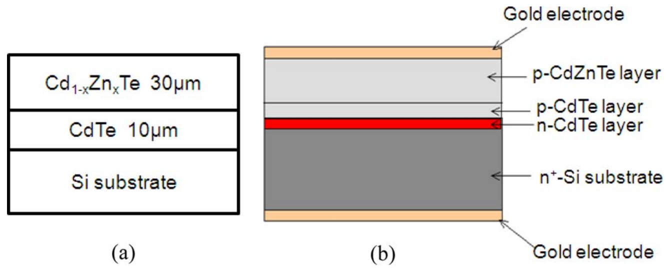

Fig. 1. (a) Sample structure used for CZT growth with different Zn-concentrations, (b) cross-sectional diagram of the CZT heterojunction diode fabricated. The CZT thickness was typically 30 μm in (a), whereas it was increased to about 80 μm in (b).

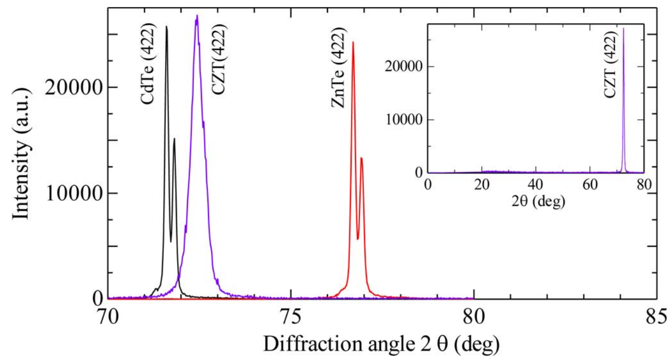

Fig. 2. Typical XRD patterns of CdTe, CZT, and ZnTe layers grown on (211) Si substrates. Zn-concentrations were varied as 0, 0.2 and 1.0 by controlling the supply ratio of DMZn, keeping the total supply rate of group II sources (DMCd+DMZn) constant. The inset shows XRD 2θ scan of CZT layer in a wide range.

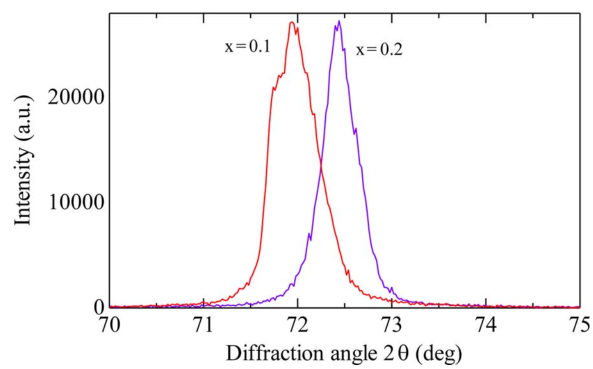

Fig. 3. The (422) diffraction peaks from the CZT layers grown with Zn-concentrations of 0.1 and 0.2 in the precursor. The Zn-concentrations were varied by controlling the supply ratio of DMZn, keeping the total supply rate of group II sources constant.

pressure. The growth was performed at a substrate temperature of 650 °C, using dimethylcadmium (DMCd), dimethylzinc (DMZn) as the group II precursor, and diethyltellurium (DETe) as the group VI precursor. Challenges associated with the direct growth of high-quality, single crystal Cd(Zn)Te layers with orientation similar to that of the substrate was overcome by employing a special Si substrate pre-treatment method. In this method, the Si substrates are annealed with pieces of GaAs crystals at 800–900 °C in a hydrogen environment in a separate horizontal chamber as describe earlier [5]–[7]. The Zn-concentration in the epilayers was controlled by varying the supply ratio of DMZn, defined as DMZn/(DMCd+DMZn), while keeping the total group II precursor (DMCd+DMZn) supply rate constant at 1.3×10^{-5} mol/min. Epilayers with four different targeted Zn-concentrations of $x = 0$, 0.1, 0.2, and 1.0 were grown by controlling the supply ratio of DMZn. The ratio of group VI precursor to total group II precursor (VI/II ratio), i. e. DETe/(DMCd+DMZn) ratio was kept constant at 6 for all growths. These growth conditions were adopted based on our earlier investigation of CZT growth on GaAs substrates, where we found that higher growth temperatures and higher VI/II precursor ratios are necessary to strictly control the Zn-concentration of CZT epilayers in a wider range [12], [13]. Typically 30 μm-thick CZT layers were grown, with the sample structure as shown in Fig. 1(a) for studying the Zn-concentrations in the grown epilayers. The actual Zn-concentration of the grown epilayers was evaluated from the lattice parameter of the (422) plane using x-ray diffraction. The crystal quality was also evaluated by a low temperature (4.2 K) photoluminescence measurement using an Ar^+-ion laser excitation at power density less than 1 W/cm^2.

A heterojunction diode was fabricated in a p-CdZnTe/p-CdTe/n-CdTe/n^+-Si structure as shown in Fig. 1(b), for its possible application in nuclear radiation detection. The typical thicknesses of n-CdTe (iodine doped) and p-CdTe (undoped) layers were 5 and 10 μm, respectively, whereas the CZT was about 80 μm thick, and undoped. Gold electrodes were deposited on both sides of the diode as ohmic contact. The heterojunction diodes were evaluated by the current-voltage $(I-V)$ measurements.

III. Results and Discussion

A. Epitaxial Growth

Fig. 2 shows the typical XRD pattern of the CZT layer together with that of CdTe and ZnTe grown on the (211) Si substrates. The layers were grown by controlling the Zn-concentrations as 0 (CdTe), 0.2 (CZT), and 1.0 (ZnTe) by varying the supply ratio of DMZn, keeping the total supply of group II precursor (DMCd+DMZn) constant. The peak position of the CZT has shifted to higher angular position than that of CdTe due to the Zn-incorporation. Shown in the inset is the XRD 2θ scan of the CZT layer in a wide range, which shows no peaks other than the CZT (422) peak. The plot indicates that the layer is monocrystalline with the growth orientation similar to that of the Si substrate. For all grown epilayers, there were no other notable peaks, but only a single peak associated with the CZT (422) diffraction was observed. This indicates there is no phase separation in the grown CZT epilayers. Fig. 3 shows the (422) diffraction peaks from the CZT layers grown with Zn-concentrations of 0.1 and 0.2, as determined by the supply ratio of DMZn. Using this diffraction data, we calculated the actual Zn-composition of the layer as presented in Table I. The result suggests a linear trend exists between the Zn-concentration in the source precursor (i.e. supply ratio of DMZn) and that in the grown CZT layers. Similar results were obtained in case of CZT grown on GaAs substrates in the same growth system using similar precursors, where Zn-concentrations could be controlled in the entire range from 0 to 1.0 [13].

The results from the 4.2 K PL measurement of the CZT layers with different Zn-concentrations ($x = 0.07$ and 0.14, as deter-

TABLE I
Zn-CONCENTRATION OF THE CZT EPILAYERS AS A FUNCTION OF DMZn SUPPLY RATIO

Zn-concentration	
Supply ratio of DMZn (targeted)	Calculated from the shift of the XRD peak (actual)
0.1	0.07
0.2	0.14

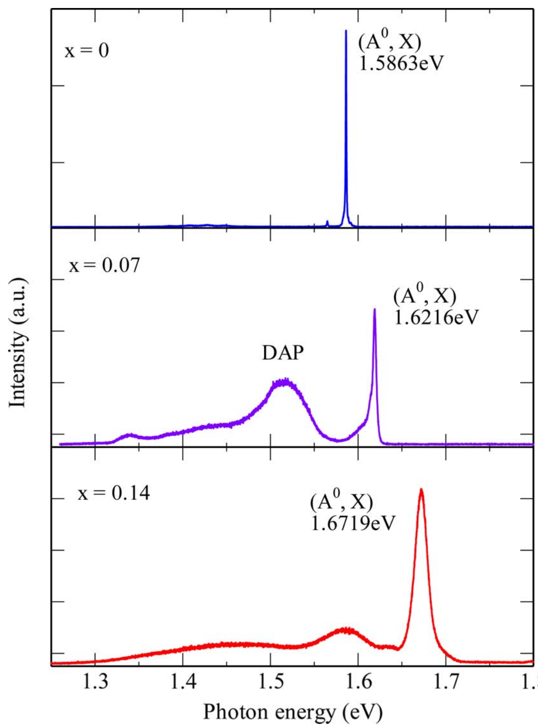

Fig. 4. The 4.2 K PL spectra of CZT layers with different Zn-concentrations of 0.07 and 0.14, and that of a CdTe ($x = 0$) layer. Zn-concentration of the epilayers was determined from the XRD data.

mined from the XRD data, see Table I) along with that of a CdTe epilayer are shown in Fig. 4. The results show distinct bound-exciton emission (BE) and donor-acceptor (DAP) emission. The BE peak shifts to higher energies with the Zn-concentrations, indicating bandgap increment with the Zn-incorporation. Also, due to the alloy broadening, width of the BE peak increases with the Zn-concentration [14]. Deep level emission, which is related to crystal defects, is weak. The distinct bound-exciton emission and weak deep-level emission on the PL spectrum indicate the grown epilayers are of high crystalline quality. The dominant BE peak could be identified as the acceptor bond exciton (A°, X) depending on the position and the shape of the peak [15]. Making an approximate comparison, we can say the (A°, X) peaks in our epilayers are located at lower energies than their corresponding values in melt-grown CZT bulk crystals, reported as 1.6514 eV and 1.690 eV for Zn-concentrations of 0.1 and 0.2, respectively [16]–[18]. This energy shift shows CZT epilayers on Si are strained and a residual tensile stress is present, which is induced by the difference of the thermal expansion coefficients of CZT $(\sim 5.0 \times 10^{-6}\ K^{-1})$ and that of the Si $(2.6 \times 10^{-6}\ K^{-1})$ substrate [19], [20].

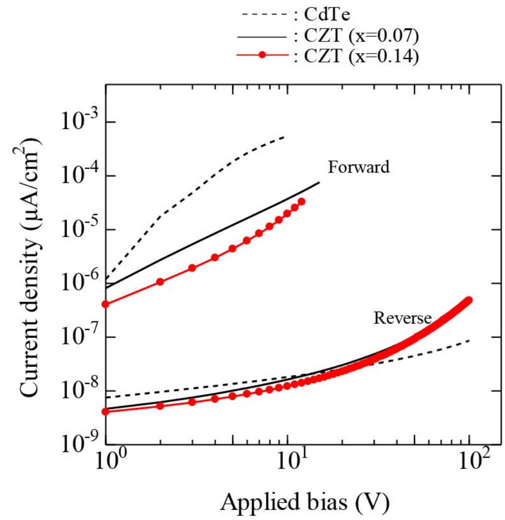

Fig. 5. Typical room-temperature $I-V$ characteristics of the CZT diodes fabricated with different Zn-concentrations ($x = 0.07$ and 0.14). For comparison I-V characteristics of a CdTe diode is also presented.

B. Heterojunction Diode Fabrication

The heterojunction diodes of cross-section shown in Fig. 1(b) were fabricated by growing about 80 μm-thick CZT epilayers, with Zn-concentrations of 0.07 and 0.14 (see Table I). Fig. 5 shows the typical $I - V$ characteristics of the CZT diodes at room temperature. For comparison, typical $I - V$ characteristic of our CdTe heterojunction diode (p-CdTe/n-CdTe/$n^+$$-$Si) with p-CdTe thickness similar to that of CZT is also presented. The results clearly show rectifying behavior of the CZT heterojunction diodes, where a large current flows when a positive bias is applied on the electrode on CZT side (forward bias), but the current is suppressed to a low value in the opposite case (reverse bias). Our detectors are operated in a reverse bias mode, and low reverse bias leakage current is a required criterion for obtaining good detector performances. There are no remarkable differences between the CZT layers with different Zn-concentrations, especially in the reverse bias case. The typical reverse bias current (leakage current) of the CZT diode was about 0.4 μA/cm^2 at 100 V, which is higher than that of the CdTe diode as seen from Fig. 5. The leakage current shows a square root dependence with applied reverse bias up to 10 V. This turns linear and then superlinear at higher biases. This suggests that generation current from the depletion layer is prominent at lower voltages, while the surface leakage and other transport mechanisms become dominant at higher biases. Based on previous reports on reverse current mechanism of a p-n diode, we consider that dislocation and other structural defects, as well as low surface resistivity due to presence of electrically active surface states are the major sources of the high currents in our CZT diodes. [21]–[23].

In order to investigate the origin of the leakage currents in our CZT diodes and to compare them with the CdTe diode, we measured the temperature dependence of reverse leakage currents in -20 to 60 °C range. The results are plotted in Fig. 6 for CZT (Zn concentration: 0.14) and CdTe heterojunction diodes at 100 V reverse bias (Arrhenius plot). The characteristics follow

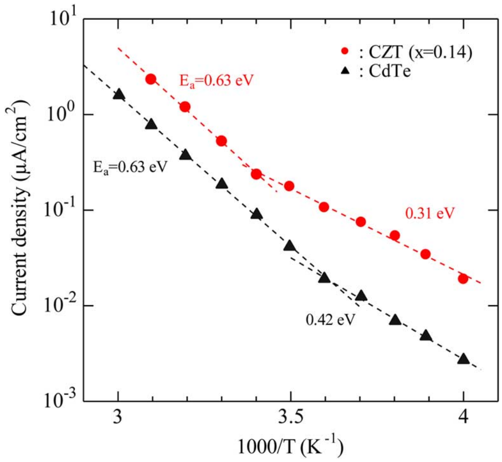

Fig. 6. Arrhenius plot of reverse leakage current density of CZT ($x = 0.14$) and CdTe heterojunction diodes at 100 V applied bias.

the thermally activated recombination process and give two different activation energies as mentioned in the Fig. 6. In higher temperature regions, both CdTe and CZT exhibit similar activation energies, which is 0.63 eV. This value represents to the ionization of states located closer to the mid-gap above the valence band, and attributed to a deep acceptor complex involving Cd-vacancy [24], [25]. However, CZT diode showing higher leakage current suggests that concentration of this level is higher in CZT when compared to that of CdTe. On the other hand, in lower temperature range, the activation energy of CZT is 0.31 eV, while that of CdTe is 0.42 eV. The 0.31 eV shallow states in CZT may be Zn-related defect, but needs further investigations [24], [26]. The activation energy for CZT changes at around 21 °C, while that of CdTe at 5 °C. This suggests that shallow levels contribute for higher leakage currents in CZT, and should be minimized.

IV. Conclusion

We presented details about the metalorganic vapor-phase epitaxial growth of thick single crystal CdZnTe layers on (211) Si substrates. The growth was performed at a high substrate temperature of 650 °C, using dimethylcadmium, dimethylzinc, and diethyltellurium precursors. Control of Zn-concentration in the range from 0 to 0.2 was obtained in the grown epilayers by controlling the precursors' flow rates and ratio. The XRD measurement showed grown layers were single crystalline with no phase separation observed. Likewise, results from the 4.2 K PL measurements show high-intensity bound-exciton emission peaks, which shift to higher energies with increasing Zn-concentration in the grown epilayers indicating bandgap increase. We further fabricated a p-CdZnTe/p-CdTe/n-CdTe/n+-Si heterojunction diode, which exhibited good rectification properties. However, the reverse bias leakage current of the diode was higher than that of CdTe heterojunction diode. We suggested that Zn-defect related shallow levels as well as Cd-vacancy related deep levels are responsible for the high leakage currents in these diodes which should be minimized for their application as a radiation detector.

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