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 high substrate temperature of 650 °C. Strict control of Zn-concentration in the grown epilayers was achieved by controlling the source materials flow-rates and ratio. 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 applications, which exhibited good rectification property.

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 x-ray, gamma ray detector development using MOVPE-grown thick single crystals of CdTe on Si substrates for low to medium photon energies up to 100 keV [5]-[7]. We have already reported the details about the spectroscopic detector fabrication as well as two-dimensional (2D) imaging array fabrication using these MOVPE-grown thick CdTe crystals. The detectors are fabricated in a p-CdTe/n-CdTe/n$^+$-Si heterojunction diode structure, which 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. 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 [9], [10].

In order to improve performances of the thick epitaxial CdTe layers based detectors further, we studied MOVPE growth of $Cd_{1-x}Zn_xTe$ (CZT) as a detector material on Si substrates, and heterojunction diode-type detector fabrication. 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 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 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. Epilayers with four different Zn-concentrations ($x = 0, 0.1, 0.2$, and 1.0) were grown by controlling the supply ratio of DMZn. The ratio of group VI precursor to total group II precursor, i. e. DETe/(DMCd+DMZn) ratio was kept constant at 6 during the entire growths. Typically 30 µm-thick CZT were grown, with the sample structure as shown in Fig. 1(a). The 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.
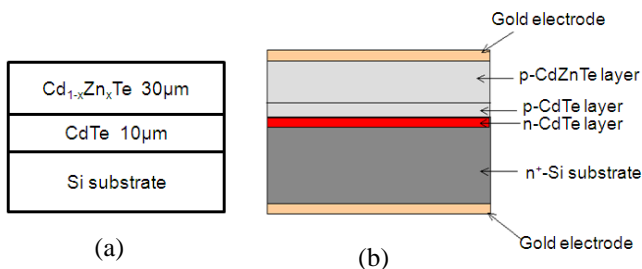

(a)   (b)

Fig. 1. (a) Sample structure used during CZT growth, (b) cross-sectional diagram of the CZT heterojunction diode fabricated.

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 and p-CdTe layers were 5 and 10 µm, respectively, whereas the CZT was about 80 µm thick. Gold electrodes were deposited on both sides of the diode as ohmic contact. The heterojunction diodes were evaluated by the current-voltage (I-V), and capacitance-voltage (C-V) measurements at room temperature.

III. RESULTS AND DISCUSSION

A. Epitaxial growth

Fig. 2 shows the typical XRD pattern of the CZT layers grown on the (211) Si substrate, where the Zn-concentrations were varied as 0 (CdTe), 0.2 (CZT), and 1.0 (ZnTe) by controlling the supply ratio of DMZn. This indicates that peak position shifts to higher angular location with increasing the Zn-concentrations. 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. 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. 1. The result indicates that, though with very limited data, the actual Zn-concentration in the CZT layer varies linearly with the Zn-concentration in the

precursor, i.e. supply ratio of DMZn. 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 [11].
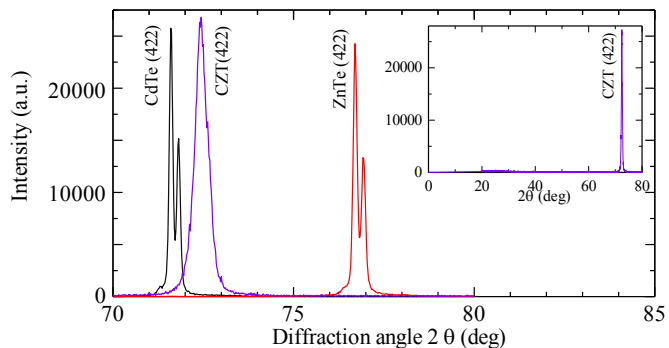

Fig. 2. Typical XRD patterns of CZT layers grown on (211) Si substrates. Zn-concentrations were varied as 0, 0.2 and 1.0 by controlling the supply ratio of DMZn, keeping the total supply rate of group II sources (DMCd+DMZn) constant. The inset shows XRD 2θ scan of CZT layer in a wide range.
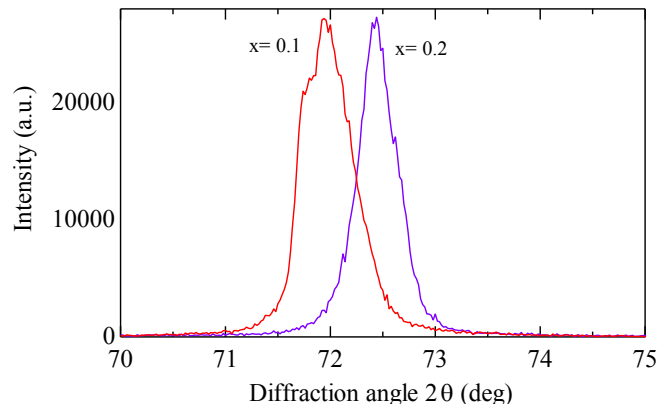

Fig. 3. The (422) diffraction peaks from the CZT layers grown with Zn-concentrations of 0.1 and 0.2. The Zn-concentrations in the epilayers were varied by controlling the supply ratio of DMZn, keeping the total supply rate of group II sources constant.

Table 1: Zn-concentration of the CZT 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

The results from the 4.2 K PL measurement of the CZT layers with different Zn-concentrations ($x = 0.07$ and 0.14, as determined from the XRD data) 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-concentration. Also,

due to the alloy broadening, width of the BE peak increases with the Zn-concentration [12]. 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^o,X) depending on the position and the shape of the peak [13]. However, (A^o,X) peaks in these epilayers are located at lower energies than their corresponding values in bulk crystals [14], [15]. This indicates there is residual tensile stress in these epilayers which arises due to the difference in the thermal expansion coefficients of the Si and the CZT [16].
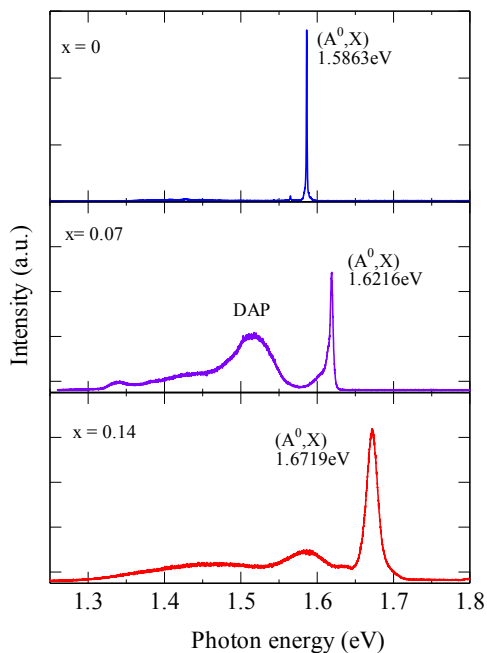

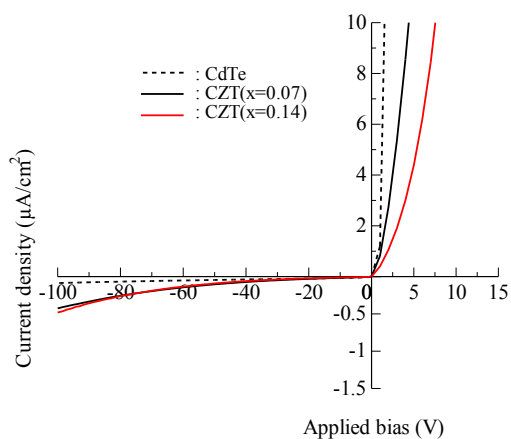Fig. 4. The 4.2K PL spectra of CZT layers with different Zn-concentrations, x= 0 (CdTe), 0.07 and 0.14.

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 (please notice the different axis divisions).

B. Heterojunction Diode Fabrication

The heterojunction diodes of cross-sectional diagram shown in Fig. 1 (b) were fabricated by growing about 80 μm-thick CZT epilayers, with Zn-concentrations of 0.07 and 0.14. Fig. 5 shows the typical *I-V* characteristics of the CZT diode at room temperature. For comparison, typical *I-V* characteristic of our CdTe heterojunction diode with a thickness similar to that of CZT is also presented. The results clearly show the rectifying behavior of the CZT heterojunction diodes, where a large current flows when a positive bias is applied on the electrode on CZT side, but the current is suppressed to a low value in the opposite case (reverse bias). 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 reverse bias, which is higher than that of the CdTe diode as seen from Fig. 5. The leakage current shows square root dependence with applied reverse bias up to 20 V, but the dependence becomes linear and then turns towards higher power dependence at higher biases. This implies generation current from the depletion layer is prominent at lower voltages, while the surface leakage currents and other current mechanisms become dominant at higher biases. It is most likely 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 the CZT diodes.
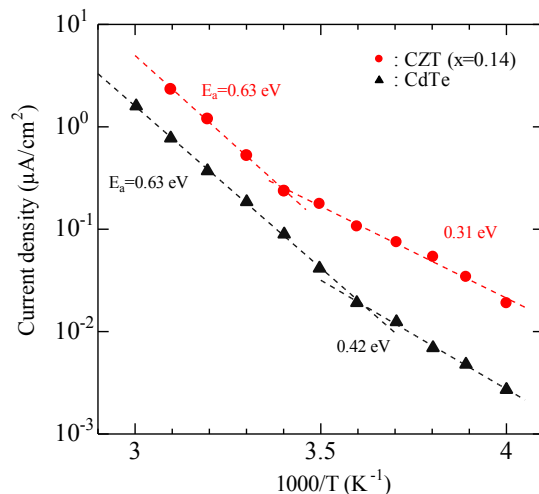

Fig. 6. Arrhenius plot of reverse leakage current density of CZT (x=0.14) and CdTe heterojunction diodes at 100 V applied bias.

In order to investigate the origin of the leakage currents in our CZT diodes and to compare them with CdTe diodes, we measured temperature dependence of the 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. The characteristics follow 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 associated with an acceptor complex involving native Cd-vacancy defect and an impurity [17]. However, 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 could be related to Zn-related defect [17]. The activation energy for CZT changes at around 21 ^{o}C, while that of CdTe at -3 ^{o}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 ^{o}C. A strict control of Zn-concentration in the grown epilayers was achieved by controlling the source materials flow rates and ratio. 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 are responsible for the high leakage currents in these diodes which should be minimized for their application as a radiation detector.

REFERENCES

[1] C. Szeles, S. A. Soldber, S. Vydrin, J. Graves, and D. S. Bale, "CdZnTe semiconductor detectors for spectroscopic x-ray imaging," *IEEE Trans. Nucl. Sci.*, vol. 55, pp. 572-582, 2008.

[2] S. Watanabe, S. Ishikawa, H. Aono, S. Takeda, H. Odaka, M. Kokubun, T. Takahashi, K. Nakazawa, H. Tajima, M. Onishi, and Y. Kuroda, "High energy resolution hard x-ray and gamma ray imagers using CdTe diode devices", *IEEE Trans. Nucl. Sci.*, vol. 56, pp. 777-782, 2009.

[3] K. C. Mandal, R. M. Krishna, P. G. Muzykov, and T. C. Hayes, "Fabrication and characterization of high barrier Cd$_{0.9}$Zn$_{0.1}$Te Schottky Diodes for high resolution nuclear radiation detectors," *IEEE Trans. Nucl. Sci.*, vol. 59, pp. 1504-1509, 2012.

[4] J. S. Iwanczyk, E. Nygard, O. Meirav, J. Arenson, W. C. Barber, N. E. Hartsough, N. Malakhov, and J. C. Wessel, "Photon counting energy dispersive detector arrays for x-ray imaging", *IEEE Trans. Nucl. Sci.*, vol. 56, pp. 535-542, 2009.

[5] K. Yasuda, M. Niraula, H. Kusama, Y. Yamamoto, M. Tominaga, K. Takagi, Y. Agata, and K. Suzuki, " Develeopment of nuclear radiation detectors with energy discrimination capabilities based on thick CdTe layers grown by metalorganic vapor phase epitaxy", *IEEE Trans. Nucl. Sci.*, vol. 52, pp. 1951-1955, 2005.

[6] K. Yasuda, M. Niraula, K. Noda, M. Yokota, H. Ohashi, K. Nakamura, M. Omura, I. Shingu, S. Minoura, R. Tanaka, and Y. Agata, "Development of heterojunction diode-type gamma ray detectors based on epitaxially grown thick CdTe on n$^+$-Si substrates", *IEEE Elect. Dev. Lett.*, vol. 27, pp. 890-892, 2006.

[7] M. Niraula, K. Yasuda, A. Watanabe, Y. Kai, H. Ichihashi, W. Yamada, H. Oka, T. Yoneyama, H. Nakashima, T. Nakanishi, K. Matsumoto, D. Katoh, and Y. Agata, "MOVPE growth of CdTe on Si substrates for gamma ray detector fabrication", *IEEE Trans. Nucl. Sci.*, vol. 56, pp. 836-840, 2009.

[8] M. Niraula, K. Yasuda, N. Fujimura, T. Tachi, H. Inuzuka, S. Namba, T. Kondo, S. Muramatsu, and Y. Agata, "Development of spectroscopic imaging arrays using epitaxially grown thick single crystal CdTe layers on Si substrates", *IEEE Trans. Nucl. Sci.*, (2012) early access available online, DOI: 10.1109/TNS.2012.2215628.

[9] W. L. Ahlgren, S. M. Johnson, *et al*., "Metalorganic chemical vapor deposition growth of Cd$_{1-y}$Zn$_y$Te epitaxial layers on GaAs and GaAs/Si substrates", *J. Vac. Sci. Technol. A*, vol. 7, pp. 331-337, 1989.

[10] M. Carmody, S. Mallick, J. Margetis, R. Kodama, T. Biegala, D. Xu,, P. Bechmann, J. W. Garland, and S. Sivananthan, " Single-crystal II-VI on Si single-junction and tandem solar cells", *Appl. Phys. Lett.*, vol. 96, pp. 153502(1)-153502(3), 2010.

[11] K. Yasuda, M. Niraula, H. Kusama, Y. Yamamoto, M. Tominaga, K. Takagi,a nd Y. Agata, "Control of Zn composition (0<x<1) in Cd$_{1-x}$Zn$_x$Te epitaxial layers on GaAs substrates grown by MOVPE", *Appl. Surf. Sci.*, vol. 244, pp. 347-350, 2005.

[12] D. J. Olego, J. P. Faurie, S. Sivananthan, and P. M. Raccah, "Optoelectronic properties of Cd$_{1-x}$Zn$_x$Te films grown by molecular beam epitaxy on GaAs substrates", *Appl. Phys. Lett.*, vol. 47, pp. 1172-1174, 1985.

[13] S. P. Tobin, J. P. Tower, *et al*., "A comparison of techniques for nondestructive composition measurements in CdZnTe substrates", *J. Electr. Mat.*, vol. 24, pp. 697-705, 1995.

[14] K. Suzuki, S. Seto, T. Sawada, K. Imai, M. Adachi, and K. Inabe, "Photoluminescence measurements on undoped CdZnTe grown by the high-pressure Bridgman method", *J. Electr. Mat.*, vol. 30, pp. 603-607, 2001.

[15] T. E. Schlesinger, J. E. Toney, R. B. James, L. Franks, and H. Yoon, "Cadmium Zinc Telluride and its use as a nuclear radiation detector material", *Mat. Sci. Engg R*, vol. 32, pp. 103-189, 2001.

[16] M. Niraula, K. Yasuda, H. Ohnishi, K. Eguchi, H. Takahashi, K. Noda, and Y. Agata, "Direct growth of high-quality CdTe epilayers on Si (211) substrates by metalorganic vapor-phase epitaxy", *J. Cryst. Growth*, vol. 284, pp. 15-19, 2005.

[17] A. Castaldini, A. Cavallini, B. Fraboni, P. Fernandez, and J. Piqueras, "Deep energy levels in CdTe and CdZnTe", *J. Appl. Phys.*, vol. 83, pp. 2121-2126, 1998.