



Original Article

Passivation effect on large volume CdZnTe crystals

B. Park ^{a, b}, Y. Kim ^{b, c}, J. Seo ^{a, b}, J. Byun ^{a, b}, K. Kim ^{d, *}^a Dept. of Health and Safety Convergence Science, Korea University, Seoul, 02841, South Korea^b Interdisciplinary Program in Precision Public Health, Korea University, Seoul, 02841, South Korea^c Marine Radioactivity Monitoring Group, Korea Marine Environment Management Corporation, Busan, 48931, South Korea^d School of Health and Environmental Science, Korea University, Seoul, 02841, South Korea

ARTICLE INFO

Article history:

Received 19 April 2022

Received in revised form

29 May 2022

Accepted 7 June 2022

Available online 18 June 2022

Keywords:

Passivation

Sodium hypochlorite

CdZnTe detector

Surface recombination velocity

ABSTRACT

Several cadmium zinc telluride (CZT) crystals were fabricated into radiation detectors using methods that included slicing, dicing, lapping, polishing, and chemical etching. A wet passivation with sodium hypochlorite (NaOCl) was then carried out on the Br-etched detectors. The Te-rich layer on the CZT surface was successfully compensated to the Te oxide layer, which was analyzed with X-ray photoelectron spectroscopy data of both a Br-etched crystal and a passivated CZT crystals. We confirmed that passivation with NaOCl improved the transport property by analyzing the mobility-lifetime product and surface recombination velocity. The electrical and spectroscopic properties of large volume detectors were compared before and after passivation, and then the detectors were observed for a month. Both bar and quasi-hemispherical detectors show an enhancement in performance after passivation. Thus, we could identify the effect of NaOCl passivation on large volume CZT detectors.

© 2022 Korean Nuclear Society, Published by Elsevier Korea LLC. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Cadmium zinc telluride (CZT) is a promising material for X- and gamma-ray detectors operating at room temperature [1]. However, it has an unresolved problem related to its surface treatment. Chemical etching with bromine, which is one of the fabrications on CZT, has a selective etching rate on each atom of CZT, resulting in the formation of a Te-rich layer on the CZT surface [2]. The Te-rich layer causes high conductivity on the CZT surface and acts as a trapping center. A representative method to solve the problem caused by the Te-rich layer is wet passivation, which has been investigated by many researchers [3–12]. Research shows a passivation effect mainly on the planar type CZT (or CdTe-based) detectors. There are few reports of a passivation effect on large-volume CZT detector (i.e., bar type or quasi-hemispherical). However, the passivation effect on large volume detectors will be more effective than passivation effect on small detectors, as they have wider surfaces and as the effect of passivation works at the surface of a specimen.

The chemical compounds rich in oxygen are used for passivation on the Te-rich surfaces of CZT crystals. Potassium hydroxide [3],

ammonium fluoride [4–9], ammonium sulfide [10,11], and hydrogen peroxide [4,12] epitomize chemical passivants. The passivant was proven to reduce the conductivity of the Te-rich layer and increase the spectroscopic performance of CZT detectors. However, wet-passivated detectors show degraded properties after a long time [8]. The phenomenon would occur gradually because of the passivated- and unstable CZT surface being exposed to ambient air or moisture. Thus, a novel passivant with long-term stability and an effective passivation ability (oxidation) needs to be found.

In this study, we investigated the effect of sodium hypochlorite (NaOCl) on bar and quasi-hemispherical CZT detectors which could effectively show the influence of passivation because of their wide surface area.

2. Experiment

The Cd_{0.9}Zn_{0.1}Te ingot was grown by the vertical Bridgman technique using CdTe(6N), ZnTe(6N), Te(7N) and 0.9 ppm of indium for compensation. We provide additional information about the growth of ingot in our previous article [13]. The grown CZT ingot was cut perpendicularly to the growth direction every 6.5 mm thickness. Seven CZT crystals were diced from wafers of the ingot, and crystals of the same characterization were cut from the same wafer. The CZT crystals were then lapped, mechanically polished by fine Al₂O₃ suspension upto 1 μm particle size, chemically polished

* Corresponding author.

E-mail address: khkim1@korea.ac.kr (K. Kim).

Table 1
Summary of CdZnTe crystals used in this research.

Sample number	W × D × H (mm ³)	Passivation	Purpose
D1	5.0 × 5.0 × 2.0	×	XPS
D2	5.0 × 5.0 × 2.0	○	XPS
D3	6.0 × 6.0 × 3.0	○	SRV
D4	6.0 × 5.0 × 2.0	○	SRV
D5	6.0 × 5.0 × 2.0	○	SRV
D6	5.0 × 5.0 × 12.0	○	large volume*
D7	13.0 × 13.0 × 6.5	○	large volume*

* passivation effect on large volume CZT by observing electrical and spectroscopic properties.

with 1% Br-ethylene glycol, and etched using a 1% Br-MeOH solution. The physical dimensions and purposes of the CZT crystals are summarized in Table 1. Gold electrodes were formed at the crystals except for D1 and D2 by electroless method with 5% of an AuCl₃ solution.

Passivations with NaOCl were conducted for 90 seconds on crystals D2–7 after the prementioned fabrications. Protection of electrodes was not applied during passivation. The proper immersion time and long-term stability of NaOCl are ongoing experiments and will soon be reported.

To identify the formation of Te oxide layers, X-ray photoelectron spectroscopy (XPS) was done following passivation with NaOCl. Planar type detectors D3–5 were prepared to measure the mobility-lifetime product of electrons ($\mu\tau_e$) and surface recombination velocity (SRV). To calculate $\mu\tau_e$ and SRV, the bias voltages versus the peak channel number of three detectors were measured before and after passivation and then fitted by the modified Hecht's equation [14] below, where Q_0 is the maximum collected charge, s is the SRV, and L is the thickness of the sample:

$$\eta = \frac{Q}{Q_0} = \frac{1}{1 + s/\mu E} \frac{\mu\tau E}{L} \left[1 - \exp\left(-\frac{L}{\mu\tau E}\right) \right] \quad (1)$$

The leakage currents of detectors D6 and D7 were measured by two-probe current-voltage measurement using the Keithley 237 source measure unit. High voltage ranges from -1000 to 1000 V were applied. Before measuring the spectroscopic property, bar detector D6 was fabricated with a virtual Frisch grid, which is made up of an ultra-thin shrink tube (Norson MEDICAL) and an aluminum shielding electrode. The shielding electrode with 3 mm width was located adjacently to the cathode and grounded with aluminum tape. The pulse height spectra of detectors D6 and D7 were obtained with Cs-137 radio-isotope irradiated to the cathode side of the detectors. The signals were obtained from a positively biased anode electrode. The nuclear instruments used for detecting gamma-rays emitted from the Cs-137 were CRZ-110 preamplifier (Cremat Inc.), CR-200 shaping amplifier (Cremat Inc.), Easy-MCA-8k (Amptek), and Ortec 659 power supply. The shaping time of all measurements was 2 μ s. The electrical and spectroscopic properties of detectors D6 and D7 were observed for a month after passivation. All measurements were done within a range of 25 to 27 °C to exclude temperature-induced effects (Fig. 1).

3. Results and discussion

Te and Te oxide are dominant species that show the effect of passivation on the surface of CZT [3]; thus, Te peaks in XPS are proper to show whether the passivant works well. Fig. 2 represents the Te 3d peaks at binding energies of 583 eV and 573 eV and TeO₂ 3d peaks at binding energies of 586 eV and 576 eV [15]. The XPS spectrum of the Br-etched (without passivation) sample D1 shows a relatively small area of TeO₂ peaks (586, 576 eV). Contrastingly, the XPS spectrum of the passivated sample D2 displays a higher

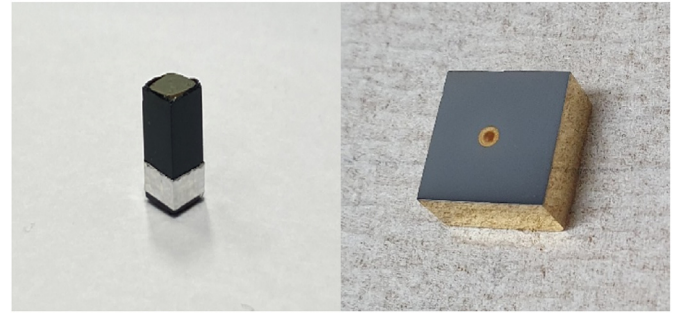


Fig. 1. Photograph of the bar type detector with virtual Frisch grid (left) and quasi-hemispherical type detector (right).

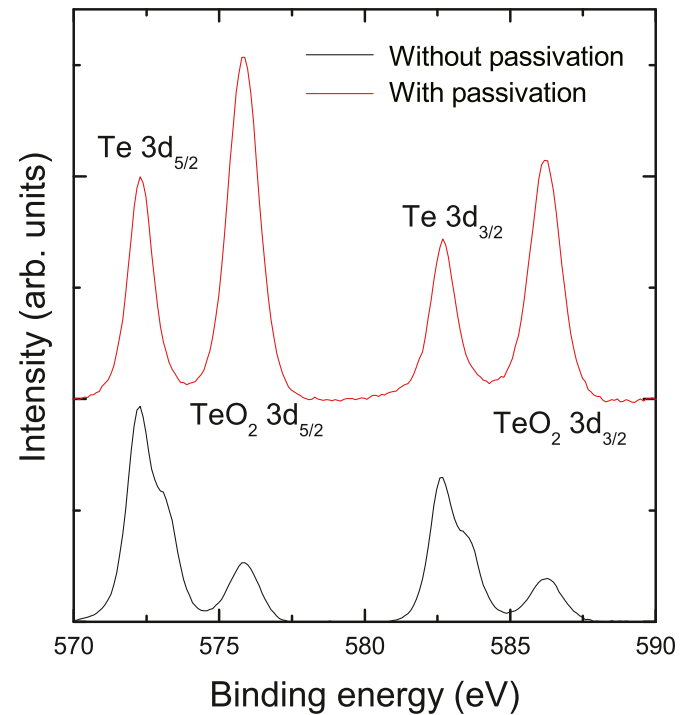


Fig. 2. XPS spectra of Te 3d levels of samples with/without wet passivation in sodium hypochlorite. Relative areas of Te or Te oxide 3d peaks are different as application of the wet passivation. Both the non-passivated and passivated samples were analysed 2 weeks after fabrications.

proportion of TeO₂ peaks than Te 3d peaks (583, 573 eV). This finding means that the NaOCl passivant is effective at forming the Te oxide on the surface of the as-grown and Br-etched CZT.

According to previous research [10,11], wet passivation with ammonium sulfide improves the transport property of CdTe-based semiconductor detectors. To see whether NaOCl has the same effect, samples D3–5 were prepared with planar dimensions. The bias voltage versus peak channel number of the detectors was measured for fitting using the modified Hecht's equation. Fig. 3 shows the charge collection efficiency of detector D3 before and after passivation with NaOCl. Following passivation, the induced charge slightly increased at the entire range of voltage. This finding means that trapping and recombination of charge carriers diminished following passivation. The difference between the induced charges before and after passivation converged to zero with increasing voltage. $\mu\tau_e$ was enhanced from 0.88×10^{-3} to 0.95×10^{-3} cm²/V following passivation. The transport properties according to the presence or absence of passivation in three detectors are shown in

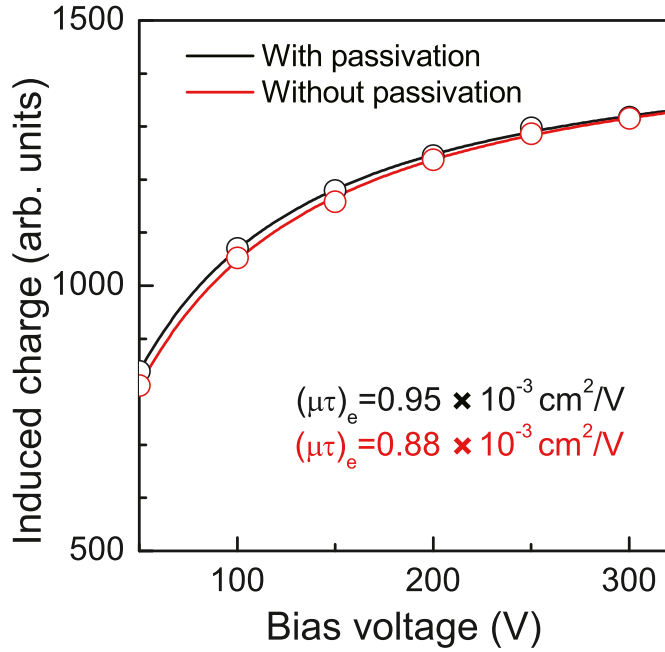


Fig. 3. A plot of bias voltages vs. induced charge from 59.5 keV gamma-ray in planar detector D3. Solid line is the fitting the experimental data with the modified Hecht's equation.

Table 2

$\frac{s}{\mu}$ and $\mu\tau_e$ values of detectors before/after passivation. All values were calculated with the modified Hecht's equation.

Sample	$\mu\tau_e$ value		s/μ value	
	Before	After	Before	After
D3	0.88×10^{-3}	0.95×10^{-3}	37.8	36.3
D4	0.96×10^{-3}	1.07×10^{-3}	63.6	55.3
D5	1.29×10^{-3}	1.56×10^{-3}	35.4	28.5

Table 2. The $\mu\tau_e$ of detectors D4 and D5 improved following passivation, which was the same result as that of detector D3.

Table 2 shows the s/μ values of detectors D3–5 fitted with eq. (1). Calculating the exact SRV (s) value with eq. (1) is challenging because mobility and lifetime cannot be, respectively, divided and identified in the equation. However, we can infer the variation of SRV (s) before and after passivation through the s/μ value. Mobility (μ) is constant in the s/μ value before and after passivation because passivation does not influence the mobility of CZT. In all detectors, s/μ decreased, meaning the SRV values of detectors D3–5 decreased because of passivation. The results in **Table 2** prove that the NaOCl passivant can improve the transport property of CZT the way a conventional passivant can [10,11].

A passivation on large-volume detectors D6 and D7 was carried out. After passivation, electrical and spectroscopic properties were measured and compared with the results before passivation. **Fig. 4** shows the leakage current of detectors D6 and D7 at a voltage range from -1000 to 1000 V. The leakage current of both detectors dramatically reduced following passivation and were then kept stable for a month.

Fig. 5 shows the spectroscopic properties of detectors D6 and D7 in regard to gamma-rays emitted from Cs-137 for a month following passivation. For every measurement, the electrical field was set the same and the virtual Frisch grid of detector D6 was equally

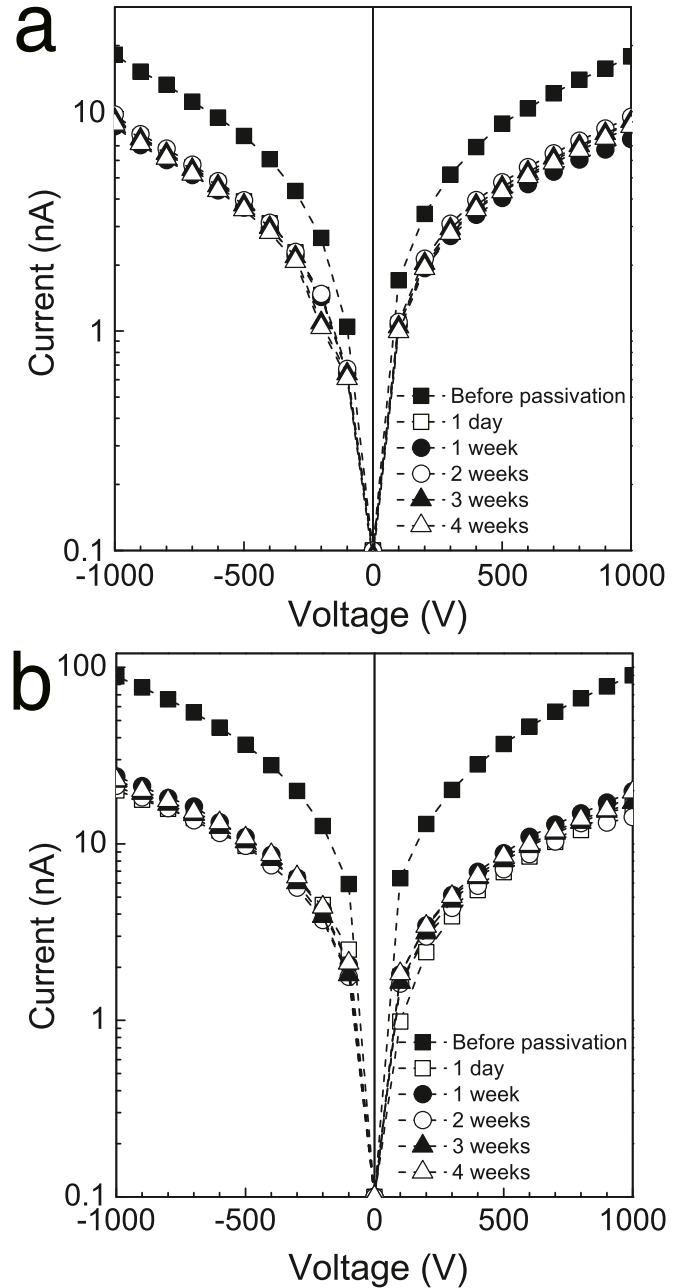


Fig. 4. Leakage current of (a) the bar type detector D6 and (b) the quasi-hemispherical type detector D7 in the range of -1000 ~ 1000 V as a progress of passivation.

fabricated. In **Fig. 5** (a) and (b), the as-grown state displays a worse shape of spectra than after passivation. Even the quasi-hemispherical type D7 detector did not have any Compton edge at the as-grown state. However, the spectroscopic properties of both detectors were restored after passivation, and their improved properties were then maintained for a month. **Table 2** shows that passivation with NaOCl can improve carrier transport properties by reducing the SRV. High SRV causes carrier loss with ease, resulting in charge loss or count loss. In addition, recombination causes an incomplete charge collection, thereby causing a lost charge and a broadened peak [16]. Thus, the deteriorated shape of photo-peak in the as-grown D6 detector and Compton edge of as-grown D7 detector would be due to the recombination from a high SRV. Because

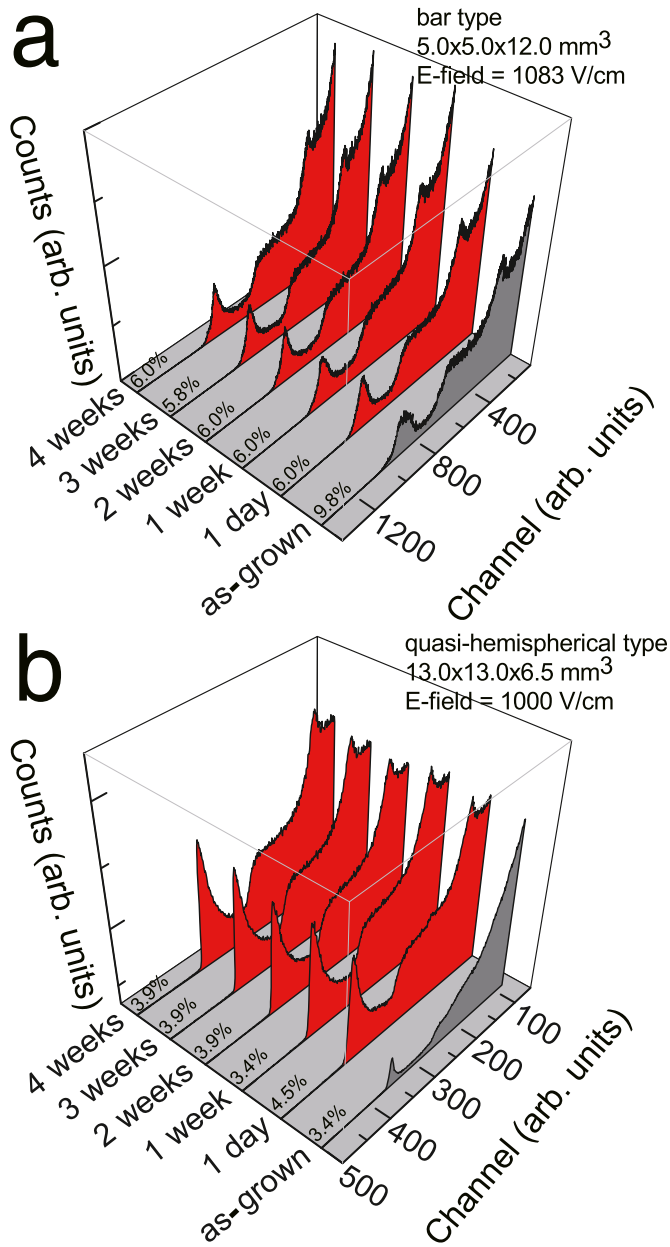


Fig. 5. Variation of spectroscopic property for Cs-137 obtained with (a) the bar type CZT detector D6 and (b) the quasi-hemispherical type CZT detector D7 for a month. High voltage was not adopted to each detector before passivation, so relatively low voltage was selected and biased to the detectors.

the SRV decreased after wet passivation, the photo-peaks in Fig. 5 (a) became sharp with an energy resolution (ER) from 9.8 % to 5.8 % at maximum. In the same concept, the backscatter peak of 184 keV and Compton edge of 477 keV in Fig. 5 (b) did not appear clearly because their signals were distorted by the charge loss from the high SRV. However, following passivation, the Compton edge and backscatter peak appeared and then preserved their restored shapes for a month.

After passivation, detectors D6 and D7 became acceptable for the higher bias voltage than what had been applied at the as-grown state. Fig. 6 shows the obvious stability of passivation with pulse height spectra at a higher electric field than previously. In Fig. 6 (a), the improved ER of detector D6 was kept stable for a month, fluctuating only from 4.5% to 5.2%. This degree could result from the

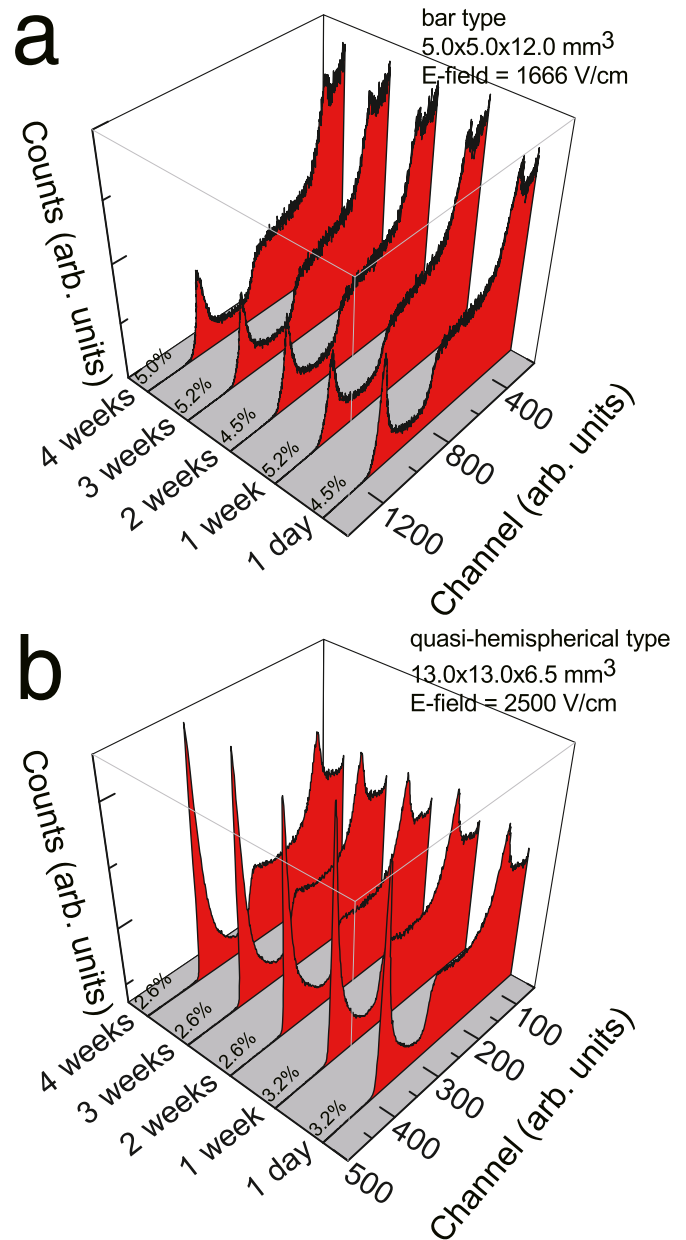


Fig. 6. Variation of spectroscopic property for Cs-137 obtained with (a) the bar type CZT detector D6 and (b) the quasi-hemispherical type CZT detector D7 for a month.

temperature which varied from 25 to 27 °C for the period of observation. In Fig. 6 (b), the ER of detector D7 ranged from 2.6% to 3.2%. In both detectors, the spectroscopic properties were kept stable for a month with high ER, as the tendency of leakage current in Fig. 4 did. Consequently, wet passivation with NaOCl was effective improving the spectroscopic performance of large-volume CZT detectors. In this study, the effect of passivation on large-volume CZT detectors was investigated. Passivation with NaOCl enhanced the resistivity of the samples by forming Te oxide on the CZT surface. Moreover, an improvement in transport properties and a reduction in surface recombination were also identified following passivation. The spectroscopic properties of passivated detectors D6 and D7 improved. Wet passivation with NaOCl is a good method for compensating the Te-rich surface of large volume CZT detectors, thereby improving spectroscopic performance.

4. Conclusion

A novel NaOCl passivant was introduced in this study. It shows the increased intensity of TeO₂ peaks in XPS, meaning successful passivation. In the bias voltage versus induced charge graph, the full collected charge at 300 V did not change despite passivation. However, the induced charge increased at lower bias voltages after passivation. This finding means that charge loss and defect density were reduced possibly because of the Te-rich layer, as passivation influences only the CZT surface. In conclusion, passivation with NaOCl could compensate for the Te-rich layer and improve the electrical, transport, and spectroscopic properties of large-volume CZT detectors. These results correspond with the compensation of the Te-rich layer and can, thus, be applied to the other CdTe-based semiconductor detectors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2021R1A2C1012161), by Ministry of Environment as "the Graduate school of Particulate matter specialization" and by Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government (MOTIE) (20214000000070, Promoting of expert for energy industry advancement in the field of radiation technology).

References

- [1] R.B. James, T.E. Schlesinger, J. Lund, M. Schieber, *Semiconductors and Semimetals Semiconductors for Room Temperature Nuclear Detector Applications*, Elsevier, New York, 1995.
- [2] A.J. Nelson, A.M. Conway, C.E. Reinhardt, J.L. Ferreira, R.J. Nikolic, S.A. Payne, Study of surface passivation and Contact Deposition Techniques in CdZnTe X-Ray and gamma-ray detectors, *Froc. MRS.* 1038 (2008), <https://doi.org/10.1109/NSSMIC.2012.6551942>.
- [3] S.U. Egarievwe, A. Hossain, I.O. Okwechime, A.A. Egarievwe, D.E. Jones, U.N. Roy, R.B. James, Effects of chemical treatments on CdZnTe X-ray and gamma-ray detectors, *IEEE Trans. Nucl. Sci.* 63 (2016) 1091, <https://doi.org/10.1109/TNS.2016.2527779>.
- [4] G.W. Wright, R.B. James, D. Chinn, B.A. Brunett, R.W. Olsen, J. Van Scyoc, M. Clift, A. Burger, K. Chattopadhyay, D. Shi, R. Wingfield, Evaluation of NH₄F/H₂O₂ effectiveness as a surface passivation agent for Cd_{1-x}Zn_xTe crystals, *Proc. SPIE* 4141 (2000) 324, <https://doi.org/10.1117/12.407594>.
- [5] S.U. Egarievwe, U.N. Roy, C.A. Goree, B.A. Harrison, J. Jones, R.B. James, Ammonium fluoride passivation of CdZnTe sensors for applications in nuclear detection and medical imaging, *Sensors* 19 (2019) 3271, <https://doi.org/10.3390/s19153271>.
- [6] L. Marchini, A. Zappettini, E. Gombia, R. Mosca, M. Pavesi, Study of surface treatment effects on the metal-CdZnTe interface, *IEEE Trans. Nucl. Sci.* 56 (2009) 1823, <https://doi.org/10.1109/TNS.2009.2022831>.
- [7] K.H. Kim, V. Carcelén, A.E. Bolotnikov, G.S. Camarda, R. Gul, A. Hossain, G. Yang, Y. Cui, R.B. James, Effective surface passivation of CdMnTe materials, *J. Electron. Mater.* 39 (2010) 1015, <https://doi.org/10.1007/s11664-010-1090-y>.
- [8] K.H. Kim, R. Tappero, A.E. Bolotnikov, A. Hossain, G. Yang, R.B. James, P. Fochuk, Long-term stability of ammonium-sulfide-and ammonium-fluoride-passivated CdMnTe detectors, *J. Korean Phys. Soc.* 66 (2015) 1532, <https://doi.org/10.3938/jkps.66.1532>.
- [9] D.E. Jones, S.U. Egarievwe, A. Hossain, I.O. Okwechime, M.L. Drabo, J. Hall, A.L. Adams, S.O. Babalola, G.S. Camarda, A.E. Bolotnikov, W. Chan, R.B. James, Study of surface passivation and Contact Deposition Techniques in CdZnTe X-Ray and gamma-ray detectors, *IEEE Nucl. Sci. Conf. R.* (2012) 4124, <https://doi.org/10.1109/NSSMIC.2012.6551942>.
- [10] K. Kim, J.H. Won, S.H. Cho, J.H. Suh, P.K. Cho, J. Hong, Y.R. Han, S.U. Kim, Passivation of semi-insulating polycrystalline CdZnTe films, *J. Korean Phys. Soc.* 53 (1) (2008) 317, <https://doi.org/10.3938/jkps.53.317>.
- [11] K.H. Kim, G.S. Camarda, A.E. Bolotnikov, R.B. James, J. Hong, S. Kim, Improved carrier-transport properties of passivated CdMnTe crystals, *J. Appl. Phys.* 105 (2009), 093705, <https://doi.org/10.1063/1.3121502>.
- [12] K.T. Chen, D.T. Shi, H. Chen, B. Granderson, M.A. George, W.E. Collins, A. Burger, Study of oxidized cadmium zinc telluride surfaces, *J. Vac. Sci. Technol. A* 15 (1997) 850, <https://doi.org/10.1116/1.580719>.
- [13] S.J. Hwang, H.S. Yu, A.E. Bolotnikov, R.B. James, K.H. Kim, Anomalous Te inclusion size and distribution in CdZnTeSe, *IEEE Trans. Nucl. Sci.* 66 (2019) 2329, <https://doi.org/10.1109/TNS.2019.2944969>.
- [14] Y. Cui, M. Groza, D. Hillman, A. Burger, R.B. James, Study of surface recombination velocity of Cd_{1-x}Zn_xTe radiation detectors by direct current photoconductivity, *J. Appl. Phys.* 92 (5) (2002) 2556, <https://doi.org/10.1063/1.1497696>.
- [15] <http://srdata.nist.gov/xps/>.
- [16] Y. Eisen, Y. Horovitz, Correction of incomplete charge collection in CdTe detectors, *Nucl. Instrum. Meth. A* 353 (1994) 60, [https://doi.org/10.1016/0168-9002\(94\)91603-9](https://doi.org/10.1016/0168-9002(94)91603-9).