



Original Article

Effectiveness of parylene coating on CdZnTe surface after optimal passivation

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ABSTRACT

Parylene coating was adopted on CdZnTe (CZT) detector as a mechanical protection layer after wet passivation with hydrogen peroxide (H₂O₂) and ammonium fluoride (NH₄F). Wet chemical passivation lose their effectiveness when exposed to the ambient conditions for a long time. Parylene coating could protect the effectiveness of passivation, by mechanically blocking the exposure to the ambient conditions. Stability of CZT detector was tested with the measurement of leakage current density and response to radio-isotopes. When the enough thickness of parylene (>100 μm) is adopted, parylene is a promising protection layer thereby ensuring the performance and long-term stability of CZT detectors.

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1. Introduction

Cadmium zinc telluride (CZT) is a commercial material for X-ray and gamma-ray detectors operating at room temperature [1]. However, there are still some issues that need to be addressed to further improve detector performance. One of them is corresponding with the long-term stability after passivation [2].

Selective etching property of Br-based etchants leaves highly conductive Te-rich layers on the surface. These Te-rich layers act as a charge trapping center and degrade CZT detector performance. The most common way to solve this problem is to passivate the Te-rich layers through a wet or dry passivation process. In both passivation processes, Te atoms in Te-rich layers chemically react with oxygen and are then converted to TeO, TeO₂, and TeO₃. Typical wet passivation processes need chemical compounds rich in the oxygen, such as hydrogen peroxide (H₂O₂), ammonium fluoride (NH₄F) or ammonium sulfide ((NH₄)₂S) [2–7]. The main disadvantage of wet passivation is that chemicals are not pure compared to CZT material (6–7N purity). It can therefore contaminate the surface of CZT detector. Dry passivation requires thermal treatment with high temperature in oxygen atmosphere. When the CZT

material is exposed to 200 °C for more than 20 min, it loses its original high resistivity. Moreover, Te oxides initially form a stable state in both processes, however it gradually destabilizes over time in the ambient environment due to reacting with moisture and carbon dioxide [2].

To solve the problem, we added the parylene coating process after the conventional passivation processes. Parylene is an organic polymer with high resistivity, dielectric strength, and is waterproof. Moreover, it can form a uniform film on the surface of any sample despite having any unusual geometry, such as holes or bumps [8,9]. These are why the parylene has widely been used as a protective coating for challenging electronics, aerospace, and medical applications. Here, parylene coating was tested as itself or mechanical protection layer after wet passivation with hydrogen peroxide and ammonium fluoride.

2. Experiment

CdZnTe (Zn = 10%) ingots were grown by Bridgman method using a mixture of CdTe(6N), ZnTe(6N), and proper amounts of compensating dopant (indium). We prepared ten CZT samples for the experiments. Prepared samples are summarized in Table 1. Gold electrodes were formed by an electroless method using an AuCl₃ solution.

For wet passivation, CZT samples were immersed into hydrogen

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Table 1
Summary of CdZnTe detectors used in this research.

Sample	W × D × H (mm ³)	Resistivity (Ω · cm)	Passivant	Parylene (μm)
D1	5 × 5 × 2.4	1.2 × 10 ⁹	HPP	×
D2	5 × 5 × 3.6	4.7 × 10 ⁹	AFP	×
D3	5 × 5 × 2	3.1 × 10 ⁹	AFP	×
D4	5 × 5 × 2	3.0 × 10 ¹⁰	HPP	20
D5	5 × 5 × 2	3.1 × 10 ⁹	AFP	20
D6	6 × 6 × 12	8.9 × 10 ⁹	None	20
D7	5 × 5 × 12	1.0 × 10 ¹⁰	HPP	20
D8	5 × 5 × 12	1.2 × 10 ¹⁰	AFP	20
D9	6 × 6 × 10	1.0 × 10 ¹⁰	HPP	100
D10	6 × 6 × 10	1.7 × 10 ¹⁰	AFP	100

peroxide passivant (HPP) or ammonium fluoride passivant (AFP) at 25 °C. The HPP and AFP were made up of H₂O₂(30%) + H₂O, and NH₄F + H₂O₂ + H₂O (2.86 g, 8 mL, 17 mL), respectively [10,11]. The optimal immersion times of CZT on HPP or AFP were selected as the time exhibiting the highest resistivity in every 30 s steps. Electrical resistivity of CZT detectors was measured by the Keithley 237 source measure unit.

Prior to the parylene coating, plasma etching using a mixture of N₂ + O₂ + CF₄ (35, 315, 35 sccm) was done for 10 min to enhance the adhesion between CZT and parylene. The parylene coating machine consists of three main parts, namely the vaporizer, pyrolyzer, and deposition chamber. The parylene dimer, which is a source material, is vaporized at 180 °C in the vaporizer. When the parylene gas flows to the pyrolyzer, the dimer decomposes thermally to a monomer between 650 and 690 °C. The pyrolyzed parylene gas becomes polymerized at room temperature in the deposition chamber and is uniformly deposited on the CZT sample. The parylene was coated to the sample which is passivated with HPP or AFP.

The pulse height spectra of the passivated CZT detectors were measured by the CRZ-110 preamplifier (Cremat Inc.), CR-200 shaping amplifier (Cremat Inc.), and multichannel analyzer (MCA). The effect of temperature-induced changes in energy resolution and resistivity was excluded by maintaining the detector temperature at 25 °C throughout the whole experiment.

3. Results and discussion

The CZT sample whose surface has been treated with chemical etching based on Br-solutions exhibits lower resistivity than that of the mechanically polished CZT due to the selective etching property of Br. Özsan et al. [12] states that thin TeO₂ layer maintains high surface resistivity. In the case of Chen’s research [10], a TeO₂ layer of only 2–4 nm in thickness reduced the current density and improved spectroscopic properties of the specimen. Much research has successfully proved the effectiveness of the Te-oxide layer [4] [–] [7,13] [–] [15]. In addition, wet passivation is a typical method of oxidizing the CZT surface. However, the formation of the oxide layer was saturated at certain immersion times. Furthermore, the leakage current density may increase if the immersion time exceeds the saturation point. Consequently, an appropriate wet passivation time should be found depending on the Br contents and etching time, that is, Te-rich layer thickness.

Fig. 1 represents the leakage current density of D1 and D2 detectors that have been passivated after 2% Br–MeOH etching for 60 s depending on the immersion time in HPP and AFP. In the case of D1 which was passivated with HPP, the current density decreased while the immersion time increased up to 180 s (open circle in Fig. 1 (a)). The leakage current density of D1 detector did not change so much depending on the immersion time. On the other hand, the current density of D2 detector passivated with AFP

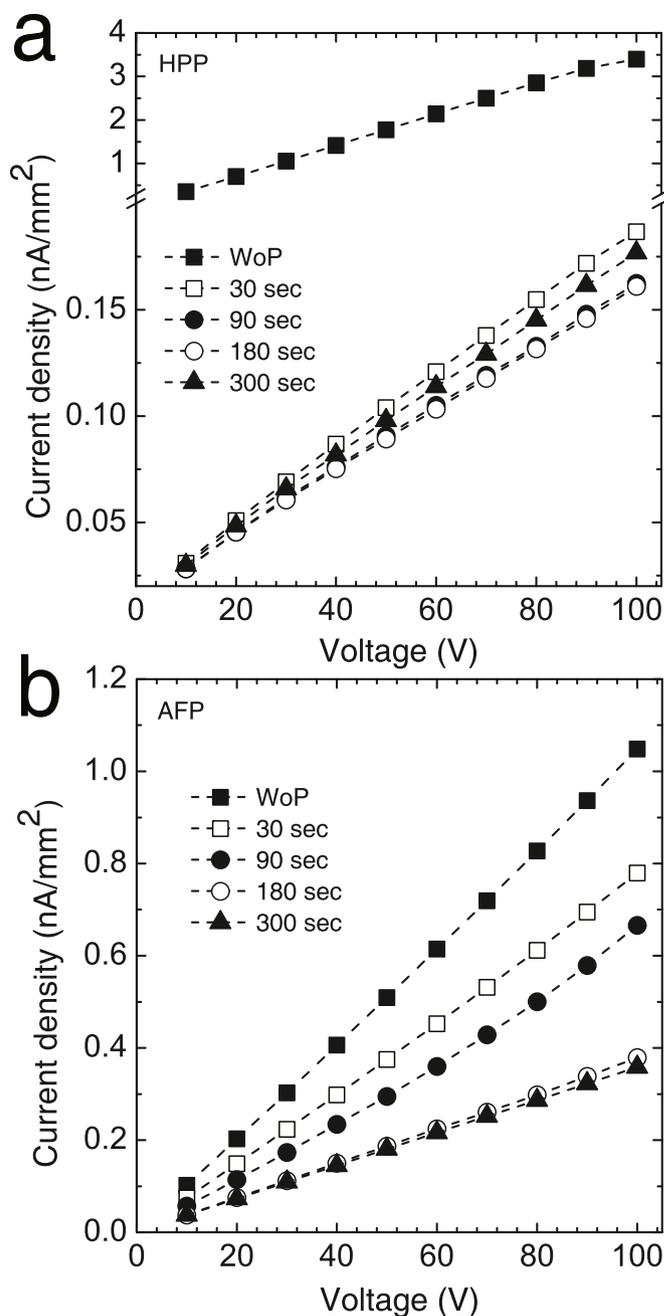


Fig. 1. Current density of D1 detector (a) and D2 detector (b) in the range of 10 ~ 100 V as an immersion time in each passivant. Wop means 'without passivation'.

decreased to 300 s of immersion time (close triangle in Fig. 1 (b)). The optimal immersion times in HPP and AFP are 180 and 300 s, respectively and valid only for CZT sample etched by 2 % Br–MeOH for 60 s.

To evaluate the stability of passivation, the leakage current density of D1, D2, and D3 detectors were observed for a month. D1 detector was republished and passivated again with HPP for 180 s. Also, a new detector D3 passivated with AFP for 300 s was added for evaluating stability. The reason for adding D3 detector was to figure out whether continuous and discontinuous processes affect the stability of passivation or not. All three detectors were kept in the ambient environment.

Fig. 2 shows the leakage current density of the three CZT detectors at 100 voltage over time. All detectors showed the lowest

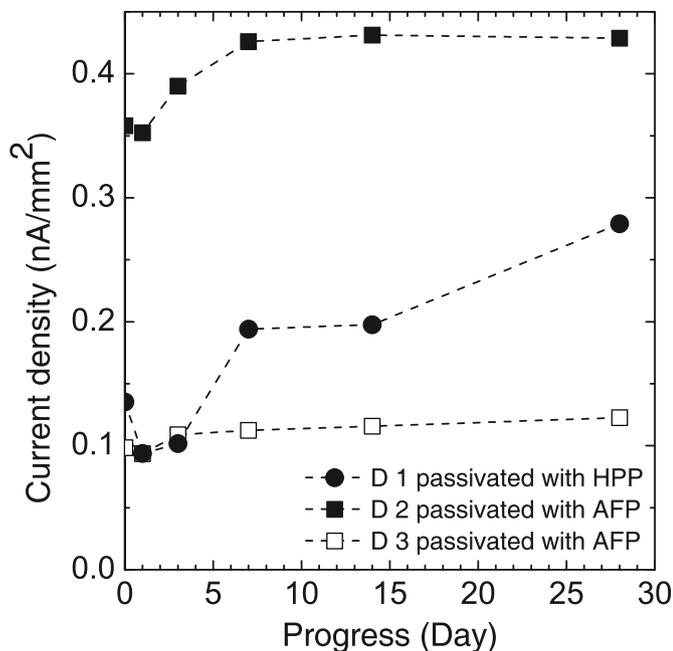


Fig. 2. Current density of D1, D2, and D3 detectors at 100 V for a month after the wet passivation. First symbols at each detector mean current density shortly after passivation, not before passivation.

leakage current density after 1 day and it increased gradually in time within a month. Although D1, D2, and D3 detectors had different absolute values of leakage current density, the values increased twice within a month of observation. Also, there was no significant difference in the continuous or discontinuous passivation processes. This means that if the total immersion time is the same, the same passivation effect is applied to the detector.

Fig. 3 shows the pulse height spectra of Am-241 taken with D1 and D3 detectors as a progress of time after passivation. Both detectors demonstrated the improved energy resolutions about 6–7% for Am-241 gamma peak of 59.5 keV after passivation. In addition, their energy resolution was kept stable for a month.

Parylene coating was implemented to improve the stability of wet-passivated (D4-5,7-10) or just Br-etched CZT detectors (D6). The dimensions of bar type (D6-10) were additionally introduced for easily identifying an impact of passivation due to their larger surface than planar type's (D4, D5). The stability of parylene coating was evaluated with leakage current density at 100 V.

Fig. 4 shows the leakage current density of D4 and D5 detectors to which parylene coating was adopted after Br–MeOH etching and each passivation. After a month, two detectors showed the higher current density more than 2 times of the primary value. This tendency appeared at D6-8 detectors in Fig. 5 regardless of the passivants type. The current density of D6 detector started to increase rapidly from 7 days after applying parylene coating and reached 700 nA/mm² after 42 days. Also, the leakage current density of D8 detector started to increase from 7 days later and reached about 15 nA/mm² after 42 days. The leakage current density of D7 detector was kept at 0.15 nA/mm² for 7 days, however, it slightly started to increase within a month.

D4-8 detectors received thermal treatment at 65°C for 3 h to remove moisture that would be present on their surfaces. Half-closed symbols in Figs. 4 and 5 mean the current density after thermal treatment. All the thermally treated samples showed the decreased leakage current density compared to previous values but were not restored to the initial values. It indirectly shows that the parylene coating (20 μm) cannot prevent moisture effectively in the

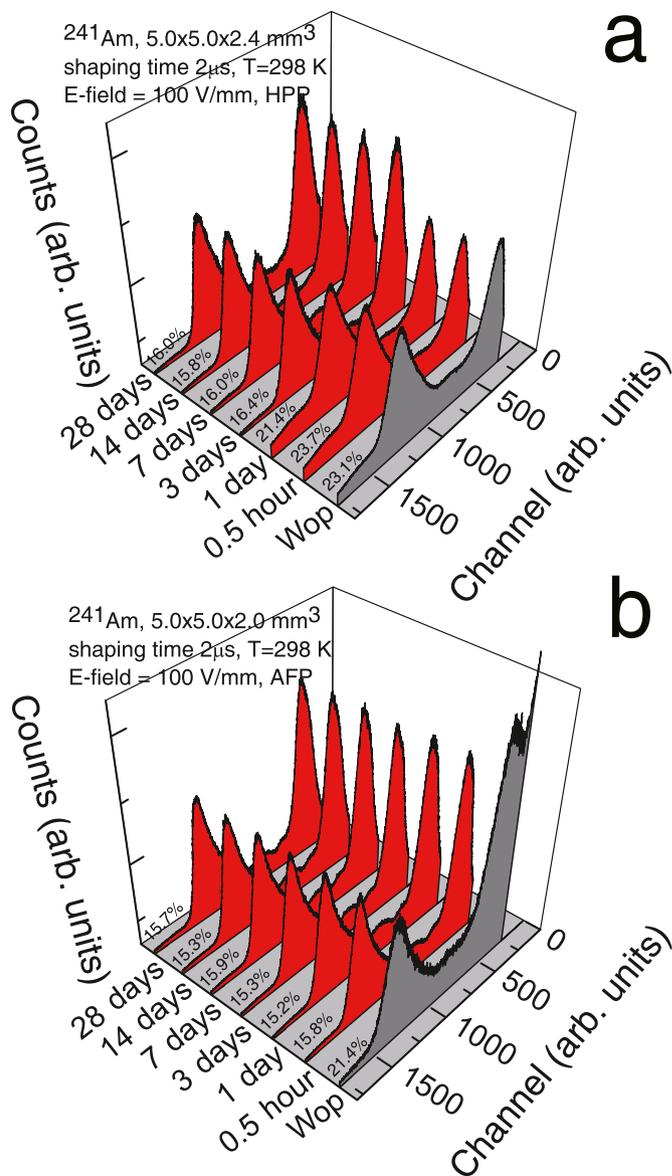


Fig. 3. Pulse height spectra of Am-241 taken with D1 detector (a) and D3 detector (b) as a progress of time after each passivation. Wop means 'without passivation'. Each spectrum has the same photoelectric peak maximum corrected.

ambient condition. The thickness (20 μm) of parylene coating adopted to the D4-8 detectors was much thinner than previous (150 μm [8]) although the paper was not focused on the protection of the surface. Therefore, the moisture and carbon dioxide penetrated the thin parylene layer in the ambient air and reacted with the passivation layer.

Closed symbols in Fig. 5 represent the leakage current density of D9 and D10 detectors to which we additionally carried out parylene coating process with thickness of 100 μm after passivation in HPP or AFP. The results of thin parylene coating show the increase of leakage current density within 2 weeks, so the observation of the thick parylene coating for 2 weeks can prove the effectiveness of thick parylene. Leakage current density of D10 detector slightly increased in the early part of progress, however it reached a lower leakage current density than the first value within 1 week and was kept stable. Leakage current density of D9 detector shows a new trend of the continuously decreased leakage current density. In consequence, the thick parylene coating of 100 μm well protected

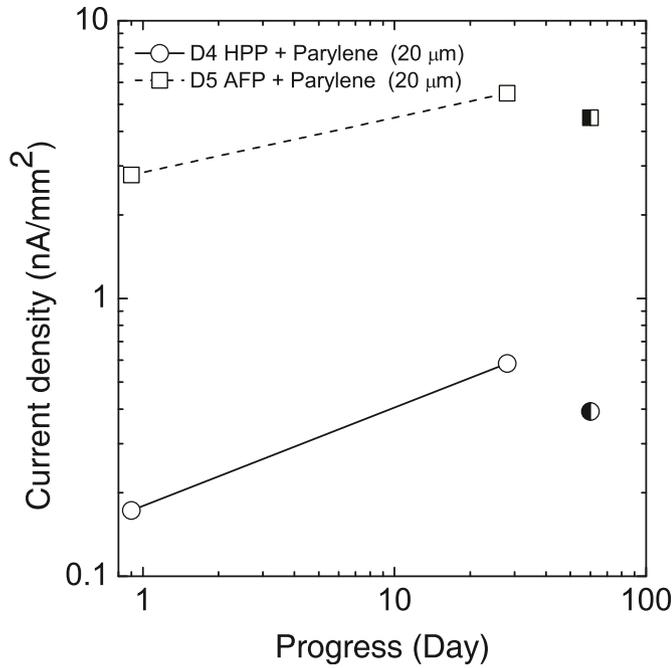


Fig. 4. Current density of planar detectors at 100 V in the progress of time after the parylene coating (20 μm). First data in the x-axis were taken shortly after parylene coating and Half-closed symbols mean that the sample was annealed with temperature of 65°C for 3 h.

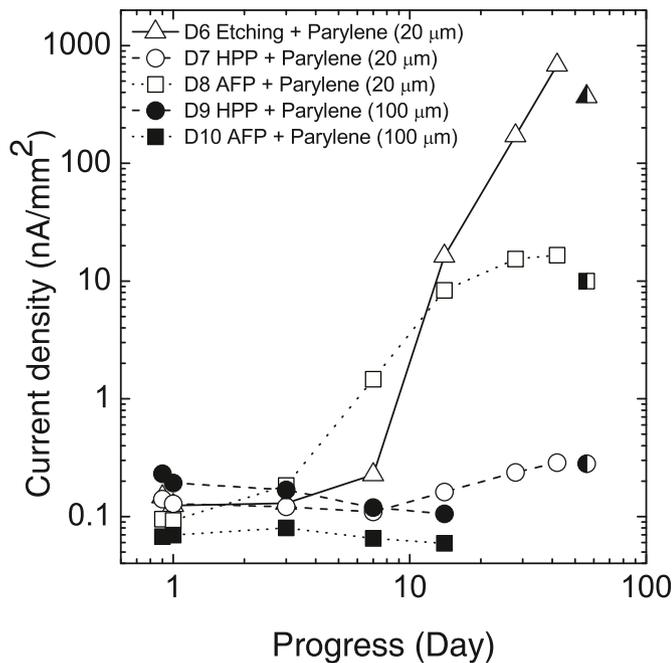


Fig. 5. Current density of bar detectors at 100 V in the progress of time after the parylene coating (20 or 100 μm). First data in the x-axis were taken shortly after parylene coating and half-closed symbols mean that the sample was annealed with temperature of 65°C for 3 h. While thin parylene coating could not protect the surfaces of CZT, thick parylene coating succeeded in keeping the current density stable in spite of exposure to the ambient air.

the wet-passivated surface from degradation taken by reaction with moisture and carbon dioxide.

For further proof of the thick parylene coating effect, the spectroscopic property of D10 detector was measured as shown in Fig. 6.

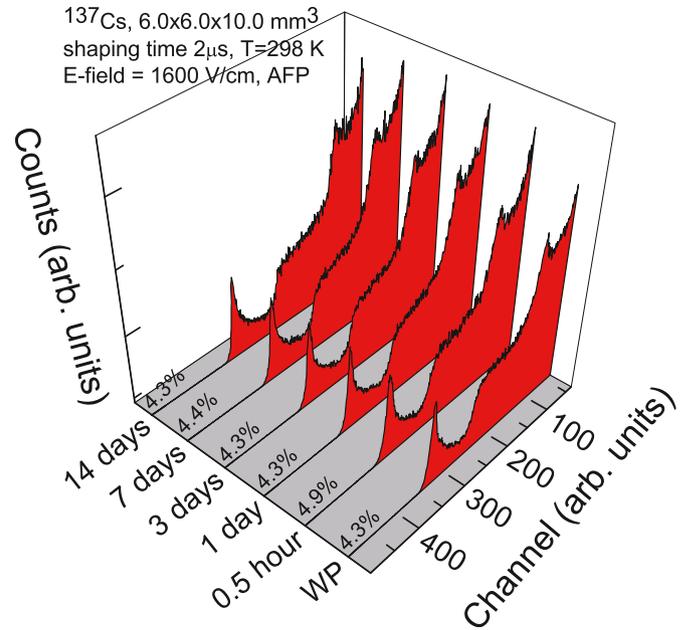


Fig. 6. Pulse height spectra of Cs-137 taken with D10 detector as a progress of the thick parylene coating after wet passivation with AFP. For the measurements, a virtual Frisch grid was fabricated to D10 detector. WP means 'with passivation', and before parylene coating.

If the moisture penetrates the parylene coating, the spectroscopic property will be degraded over time. However, the energy resolution for Cs-137 gamma peak of 662 keV was kept stable within measurement error for 2 weeks. Adding to the result of electrical property, the result of the spectroscopic property proved that the parylene coating (>100 μm) could protect the wet-passivated surface of CZT layer. Also, it was confirmed that the parylene could be a good dielectric layer, which is a part of VFG fabrication [8].

4. Conclusions

We carried out the wet passivations with HPP and AFP for 2% Br-etched CdZnTe(CZT) crystal for 60 s to identify the optimal wet passivation time. The optimal immersion time of HPP and AFP were 180 and 300 s, respectively. In wet passivations, current density was low and exhibited the improved pulse height spectra within 24 h after passivation. While thin parylene coating after optimal wet passivation failed to maintain the improved physical properties of CZT, the thick parylene coating succeeded in maintaining the properties. The parylene coating with thickness of 100 μm could protect the wet-passivated surface of CZT from reaction with moisture and carbon dioxide.

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.

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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] 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.
- [3] 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.
- [4] 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 (2008) 317.
- [5] J. Zázvorka, J. Franc, M. Statelov, J. Pekárek, M. Veis, P. Moravec, K. Mašek, Optical and electrical study of CdZnTe surfaces passivated by KOH and NH₄F solutions, *Appl. Surf. Sci.* 389 (2016) 1214.
- [6] 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.
- [7] S.U. Egarievwe, U.N. Roy, C.A. Goree, B.A. Harrison, J. Jones, R.B. James, Ammonium fluoride passivation of CdZnTeSe sensors for applications in nuclear detection and medical imaging, *Sensors* 19 (2019) 3271.
- [8] M.J. Harrison, A. Kargar, A.C. Brooks, K.H. Carpenter, D.S. McGregor, Improved techniques for the fabrication of Frisch collar CdZnTe gamma ray spectrometers, *IEEE Trans. Nucl. Sci.* 56 (2009) 1671.
- [9] Y.S. Shin, K.C. Cho, S.H. Lim, S. Chung, S.J. Park, C.I. Chung, D.C. Han, J.K. Chang, PDMS-based micro PCR chip with parylene coating, *J. Micromech. Microeng.* 13 (2003) 768.
- [10] 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.
- [11] 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.
- [12] M.E. Özsan, P.J. Sellin, P. Veeramani, S.J. Hinder, M.L.T. Monnier, G. Prekas, A. Lohstroh, M.A. Baker, Chemical etching and surface oxidation studies of cadmium zinc telluride radiation detectors, *Surf. Interface. Anal.* 42 (2010) 795.
- [13] 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.
- [14] 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.
- [15] 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.