

Surface Processing of CdTe Detectors Using Hydrogen Bromide-Based Etching Solution

著者 (英)	Madan Niraula, K. Yasuda, N. Takai, M. Matsumoto, Y. Suzuki, Y. Tsukamoto, Y. Ito, S. Sugimoto, S. Kouno, D. Yamazaki, Y. Agata
journal or publication title	IEEE Electron Device Letters
volume	36
number	8
page range	856-858
year	2015-06-29
URL	http://id.nii.ac.jp/1476/00006248/

doi: 10.1109/LED.2015.2450835(<http://dx.doi.org/10.1109/LED.2015.2450835>)

Surface Processing of CdTe Detectors Using Hydrogen Bromide-Based Etching Solution

M. Niraula, *Member, IEEE*, K. Yasuda, *Member, IEEE*, N. Takai, M. Matsumoto, Y. Suzuki, Y. Tsukamoto, Y. Ito, S. Sugimoto, S. Kouno, D. Yamazaki, and Y. Agata

Abstract—Chemical etching of CdTe crystals using hydrogen bromide (HBr)-based etchant was studied and its effectiveness in detector leakage current, gamma radiation detection performance was compared with that of a conventional Br-methanol (BM) etched detector. It was found that effect of surface leakage in total detector leakage current was lower in the HBr-processed detectors, and they also exhibited better radiation detection performances than that of the conventional BM-etched detectors. A slight variation in surface chemical states was found in these differently processed crystals which could be related to the observed differences in detector properties.

Index Terms— CdTe, Surface etching, Nuclear radiation detector, Spectroscopy

I. INTRODUCTION

CdTe and its alloy CdZnTe are now well recognized as the most promising materials for the development of nuclear radiation detectors operable at room temperature. Despite their suitable material properties, the widespread use of these detectors is hampered by the difficulties of the crystal growth as well as detector fabrication technique. Both the crystal quality and surface preparation during detector fabrication seriously influence the detector performance [1-3]. There has been a significant progress in the crystal quality improvements, however, the surface processing techniques have been remained essentially the same, which have impeded further detector performance improvements. Current surface processing procedure consists of mechanical polishing, followed by chemical etching using bromine-methanol (BM) solution to achieve a smooth surface [4-6]. Though this etching process results a comparatively smoother surface, however, it leaves behind regions of non-stoichiometric material and other undesirable surface features because of its non-uniform etch rate [4, 7-9]. These electrically active defects cause the surface conductivity increase leading to increased surface leakage currents and detector performance degradation [4,7-9]. These surface defects further affect the metal-semiconductor interface leading to the device to device performance variation and affecting their long term stabilities [8]. Hence, there is an urgent need to find a suitable surface processing technique that

would mitigate those problems.

In this study, we used a hydrogen bromide-based (HBr) etching solution to chemically etch the CdTe surface. This etchant offers highly stable etching where the etching rate could be varied by changing the solution composition. Moreover, it does not attack the positive photoresist making it suitable etchant in CdTe photolithography process. Our goal was to find its effectiveness in the surface processing of the crystal and study how it influences the detector leakage currents and the radiation detection performances. It was found that this etchant produce a uniform surface with small surface leakage currents, making it promising for highly efficient detector development. Here, we report on the properties of the HBr processed CdTe detectors, and compare them with that of conventional BM processed detectors.

II. EXPERIMENTAL DETAILS

Several 5 mm x 5 mm x 0.5 mm sized, (111)-oriented high resistivity detector grade CdTe crystals were used in this study. They were Travelling Heater Method (THM) grown crystals from ACRO RAD, Japan. As crystals cut from the same wafer were used for each set of experiments, we consider they have similar bulk material properties. The HBr-etchant consists of a mixture of hydrogen bromide, bromine and water at a volumetric ratio of 17:2:34, whereas the BM-etchant is a 0.5% Br-methanol solution. The samples were etched in respective etchants at room temperature without stirring and then rinsed thoroughly in methanol. The HBr and BM-solution etching rates were 0.4 $\mu\text{m}/\text{min}$ and 0.8 $\mu\text{m}/\text{min}$, respectively at room temperature. The crystals were immediately loaded into physical vapor deposition system after etching, where planar gold contacts were deposited on two opposite surfaces as in Fig. 1(b). For surface leakage current analysis solid circular contacts with different areas (radius varying from 100 to 600 μm) were deposited on one face of some crystals from each etch group, while planar type contacts on the opposite side, as shown schematically in Fig.1 (a). The process consistency was maintained to ensure that device properties do not get affected due to the crystal handlings and other process related factors.

Surface chemical states of the HBr and BM-etched samples were analyzed in a PHI-500 (ULVAC-PHI) x-ray photoelectron spectroscopy (XPS) using monochromatic Al X-ray source. The current-voltage (I - V) measurements were performed in a manual probe station connected to an Agilent power device analyzer. Radiation detection tests were

This work was supported in part by the Japan Society for the Promotion of Science (JSPS) Grants-in-Aid for Scientific Research A-25242048.

The authors are with the Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan (e-mail: m.niraula@nitech.ac.jp).

performed in a standard set up consisting of a pre-amplifier, shaping amplifier and a multi-channel analyzer, using ^{241}Am gamma source.

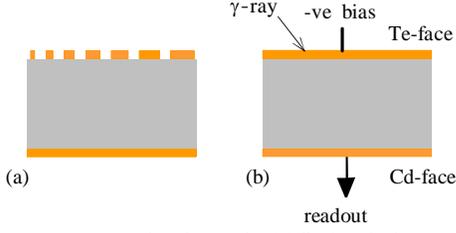


Fig. 1 Device structure used in this study. (a) Surface leakage current analysis, (b) radiation detection test.

III. RESULTS AND DISCUSSION

Fig. 2 shows the detector leakage current density at a fixed applied bias of 45V as a function of perimeter to area (P/A) ratio of the circular contacts. For a detector structure consisting of different sized circular contacts (Fig. 1(a)), the total leakage current density (J) which comprises the surface and the bulk components can be expressed in the following way [10]:

$$J = J_B + J_s (P/A) \quad (1)$$

where, J_B and J_s are the bulk and the surface components of the total detector leakage current. P and A are the perimeter and area of the circular contacts. For a fixed applied bias, total current density increases with the P/A ratio if the surface component is dominant, however, remains same when the bulk component is dominant [10]. Fig. 2 shows the current density changes with the P/A ratio for the BM-etched detector, however, it remains nearly the same for the HBr-etched one, which indicates the effects of surface leakage is small in HBr detector.

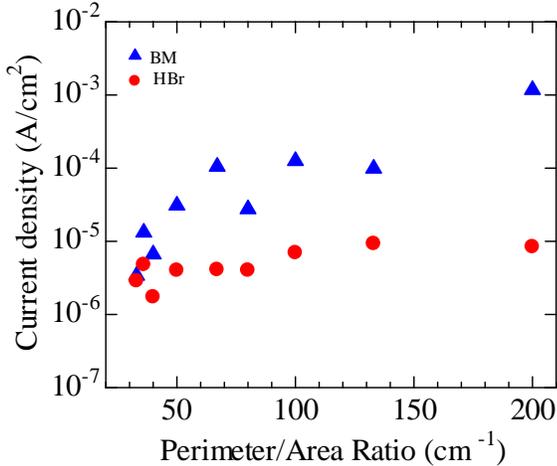


Fig. 2. Leakage current of the HBr and the BM-etched detectors measured at 45V bias as a function of perimeter to area (P/A) ratio of the circular contacts.

The total leakage currents of HBr and BM-etched detectors as a function of applied biases are plotted in Fig. 3. Current increases with applied biases in both detectors, however, the

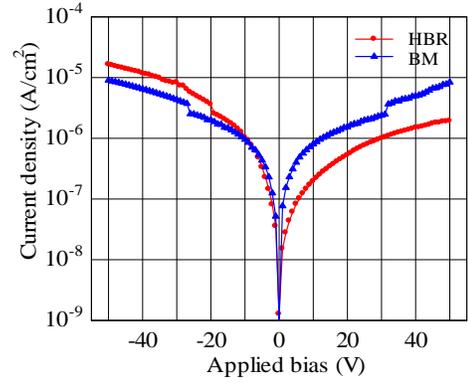


Fig. 3. Leakage current of the HBR and the BM-etched detectors as a function of applied bias, measured at room temperature.

characteristics show some asymmetries. The leakage current was lower when positive bias was applied to the Cd-face of the crystal. This type of characteristics in high resistivity p-type CdTe or CdZnTe is previously discussed in the literature [11,12]. The Au/CdTe/Au detector structure creates a blocking cathode when a negative bias is applied on the Te-face of the crystal, thereby restricting electron injection from the contact into the bulk, and the anode on the Cd-face less blocking (+ve voltage axis in Fig. 3). Thus currents will be controlled by holes entering from the anode contact. However, if the polarity is reversed, the Au-Cd cathode will be more injecting and Au-Te anode will be more blocking (-ve voltage axis). The higher current for the BM-processed detector in Fig. 2 could be due to higher concentrations of surface states formed on its surface (explained later in this paper), which lowers the barrier height at the Au-Te cathode, allowing electron injection [11,12].

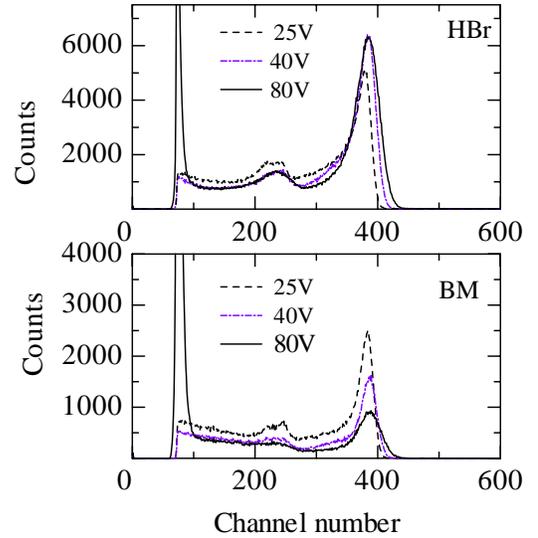


Fig. 4. A comparison of the spectroscopic performances of the HBr and the BM-etched detector measured at room temperature with different biases.

Fig. 4 compares spectroscopic performances of these detectors at three different applied biases. The measurements were carried out at room temperature using ^{241}Am gamma source in

exactly identical conditions, with measurement configuration shown in Fig. 1(b). The 59.5keV photopeak obtained from the HBr-etched detector shows higher total counts and the peak shape improves with the bias. The BM-etched detector, on the other hand, has lower photopeak counts and its shape is inferior. This indicates trapping and recombination of generated carriers before they are collected at the contacts. The difference in the surface conditions of these differently processed detectors could be the reason for the observed difference in the detector properties. In order to verify this surface chemistry of these differently etched crystals was studied using XPS. Care was taken while preparing and loading the samples into the XPS chamber so that their exposure to the ambient air was maintained at very short and exactly the same duration.

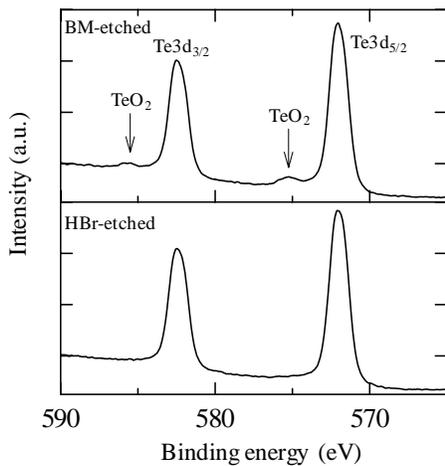


Fig. 5. XPS spectra of the Te3d peak of (top) BM-etched and (bottom) HBr-etched CdTe surface.

The result of XPS analysis in Fig. 5, which was performed without sputtering the surface with Ar-ion, showed that surface of BM-etched sample had a small but distinct peak of tellurium oxide, however, no such peak was observed in the HBr-etched sample. Also the peak intensity of the elemental oxygen (O1S) was stronger and Cd-related peak was slightly weaker in the BM-sample than in HBr-sample (not shown here). The TeO_2 peak was mostly removed with a 1-min sputtering of the BM-sample. However, in contrast to HBr-sample traces amount of oxygen was still present in it. The BM-etching of CdTe has been described by oxide-dissolution reaction, which proceeds by oxidation of the surface atoms followed by chemical dissolution of the oxidized product [13]. Similar mechanism can be expected for the HBr-etchant. However, the observed difference of TeO_2 and the elemental oxygen contents suggests that they are responsible for the formation of surface states in the BM-etched samples affecting the detector performances. However, it needs further verification and details on these are in progress.

IV. CONCLUSION

Chemical etching of CdTe crystals using HBr-based solution was studied and its effectiveness in detector leakage current and gamma radiation detection performance was compared with that of a conventional Br-methanol (BM) processed detector. The result showed that the HBr-etched detector exhibits lower surface leakage current than the BM etched, and also offers better radiation detection property. XPS results showed small but distinct TeO_2 peak and higher elemental oxygen from the BM-etched CdTe surface, however no TeO_2 peak was observed in the HBr-etched surface. We suggest that larger surface states on the BM etched crystal possibly due to partial TeO_2 formation is responsible for its inferior performance, thus making HBr-etchant a better choice.

REFERENCES

- [1] C. Szeles, S. A. Soldner, S. Vydrin, J. Graves, and D. S. Bale, "CdZnTe semiconductor detectors for spectroscopic x-ray imaging", *IEEE Trans. Nucl. Sci.*, vol. 55, no. 1, pp. 572-582, Feb. 2008.
- [2] A. V. Rybka, S. A. Leonov, I. M. Prokhoretz, A. S. Abyzov, L. N. Davydov, V. E. Kutny, M.S. Rowland, and C. F. Smith, "Influence of detector surface processing on detector performance", *Nucl. Instrum. Meth. in Phys. Res. A*, vol. 458, pp. 248-253, 2001.
- [3] R. B. James, *et al.*, "Material properties of large-volume cadmium zinc telluride crystals and their relationship to nuclear detector performance", *J. Electron. Mat.*, vol. 27, no. 6, pp. 788-799, 1998.
- [4] A. A. Rouse, C. Szeles, J-O. Ndap, S. A. Soldner, K. B. Parbham, D. J. Gaspar, M. H. Engelhard, A. S. Lea, S. V. Shutthanandan, T. S. Thevuthasan, and D. R. Baer, "Interfacial chemistry and the performance of bromine-etched CdZnTe radiation detector device", *IEEE conference record*, pp. 2459-2463, Nov. 2001.
- [5] A. Burger, H. Chen, K. Chattopadhyay, J-O. Ndap, S. U. Egarievwe, and T. B. James, "Cadmium zinc telluride high resolution detector technology", *SPIE Proceed.*, vol. 3446, pp. 154-158, Jul. 1998.
- [6] K. C. Mandal, R. M. Krishna, P. G. Muzykov, and T. C. Hayes, "Fabrication and characterization of $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ schottky diodes for high resolution nuclear radiation detectors", *IEEE Trans. Nucl. Sci.*, vol. 59, no. 4, pp. 1504-1509, Oct. 2012.
- [7] M. J. Mescher, J. F. Hoberg, T. E. Schlesinger, and R. B. James, "Analyses on the measurement of leakage currents in CdZnTe radiation detectors", *IEEE Trans. Nucl. Sci.*, vol. 46, no. 6, pp. 2289-2296, Dec. 1999.
- [8] A. Hossain, A. E. Bolotnikov, G. S. Camarda, Y. Cui, D. Jones, J. Hall, K. H. Kim, J. Mwachhi, X. Tong, G. Yang, and R. B. James, "Novel approach to surface processing for improving the efficiency of CdZnTe detectors", *J. Electron. Mat.*, vol. 43, no. 8, pp. 2771-2777, 2013.
- [9] S. Tari, F. Aqariden, Y. Chang, A. Ciani, C. Grein, J. Li, and N. Kioussis, "Structural and electronic properties of gold contacts on CdZnTe with different surface finishes for radiation detector applications", *J. Electron. Mat.*, vol. 43, no. 8, pp. 2978-2883, 2014.
- [10] V. Bhagwat, Y. Xiao, I. Bhat, P. Dutta, T. F. Refaat, M. Nurul Abedin, and V. Kumar, "Analysis of leakage currents in MOCVD grown GaInAsSb based photodetectors operating at $2\mu\text{m}$ ", *J. Electron. Mat.*, vol. 35, no. 8, pp. 1613-1617, 2006.
- [11] H. Chen, S.A. Awadalla, P. Marthandam, K. Iniewski, P. H. Lu, and G. Bindley, "CZT device with improved sensitivity for medical imaging and homeland security applications", *SPIE Proceeding*, paper 7449-1 (2009).
- [12] J. Crocco, H. Bensalah, Q. Zheng, V. Corregidor, E. Avles, A. Castaldini, B. Fraboni, D. Cavalcoli, A. Cavallini, O. Vela, and E. Dieguez, "Study of asymmetries of Cd(Zn)Te devices investigated using photo-induced current transient spectroscopy, Rutherford backscattering, surface photo-voltage spectroscopy, and gamma ray spectroscopies", *J. Appl. Phys.*, vol. 112, pp. 074503-1-9, 2012.
- [13] V. Srivastav, R. Pal, and H. P. Vyas, "Overview of etching technologies used for HgCdTe", *Opto-electronics Rev.*, vol. 13, pp. 197-211, 2005.