LLNL-JRNL-404009

X-RAY PHOTOEMISSION ANALYSIS OF PASSIVATED Cd(1-x)ZnxTe SURFACES FOR IMPROVED RADIATION DETECTORS

A. Nelson, A. Conway, C. Reinhardt, J. Ferreira,
R. Nikolic, S. Payne

May 20, 2008

Materials Letters

Disclaimer

LLNL-JRNL-404009

X-RAY PHOTOEMISSION ANALYSIS OF PASSIVATED $Cd_{(1-x)}Zn_xTe$ SURFACES FOR IMPROVED RADIATION DETECTORS

A.J. Nelson, A.M. Conway, C.E. Reinhardt, J.L. Ferreira, R.J. Nikolic, and S.A. Payne
Lawrence Livermore National Laboratory, Livermore, CA, USA.

ABSTRACT

Surface passivation of device-grade CdZnTe was investigated using x-ray photoelectron spectroscopy in combination with transport property measurements after Br-MeOH (2% Br) and $KOH/NH_4F/H_2O_2$ solutions were used to etch and oxidize the surface. High-resolution photoemission measurements on the valence band electronic structure and core lines were used to evaluate the surface chemistry of the chemically treated surfaces. Metal overlayers were then deposited on these chemically treated surfaces and the I-V characteristics measured. The measurements were correlated to understand the effect of interface chemistry on the electronic structure at these interfaces with the goal of optimizing the Schottky barrier height for radiation detector devices.

The development of cadmium zinc telluride ($Cd_{(1-x)}Zn_xTe$, CZT) as a nuclear radiation detector material has progressed with advances in CZT crystal growth that minimizes bulk defects and precipitates.[1,2] With this progress, our focus is now on surface properties of CZT since the interfacial chemistry has a powerful influence on the electrical stability of ohmic and Schottky contacts to CZT. The performance of CZT as a room temperature radiation detector can thus be improved with careful attention to modification of the surface chemistry. Chemical treatments of the CZT surface prior to application of electrical contacts require comprehensive characterization to elucidate advantageous changes in surface electronic structure.

Mechanical polishing followed by bromine-based etching is routinely employed for CZT surface preparation prior to device fabrication. This treatment removes the native oxide but leaves a Te-rich surface resulting in metal/CZT interface degradation and excessive leakage currents. [1-3] Alternative surface preparation methods have been proposed for surface passivation [3-6] but have not been fully characterized nor implemented for practical device fabrication. A novel two-step chemical passivation process for CZT was reported in [4]. This paper further characterizes this chemical process in terms of the surface chemistry, surface morphology and electronic structure of chemically treated $Cd_{(1-x)}Zn_xTe$ and correlates the results with transport properties.

Device-grade unoriented p-$Cd_{(1-x)}Zn_xTe$ was polished and subjected to an initial 2 min Br-MeOH (2% Br) etch. Following Br:MeOH etching, the CZT was treated with KOH (15 % in water) for 40 min, rinsed with DI water, then subjected to NH_4F/H_2O_2 (10%/10% in water) for 45 min, rinsed again with DI water and blown dry. The resultant surface chemistry was characterized by x-ray photoelectron spectroscopy (XPS) after each process step.

XPS analysis was performed on a PHI Quantum 2000 system using a focused monochromatic Al Kα x-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 16-element multichannel detection system. A 200 μm diameter x-ray beam was used for analysis. The x-ray beam is incident normal to the sample and the x-ray detector is at 45° away from the normal. The pass energy was 23.5 eV giving an energy resolution of 0.3 eV that when combined with the 0.85 eV full width at half maximum (FWHM) Al Ka line width gives a resolvable XPS peak width of 1.2 eV FWHM. Deconvolution of non-resolved peaks was accomplished using Multipak 6.1A (PHI) curve fitting routines. The collected data were referenced to an energy scale with binding energies for Cu $2p_{3/2}$ at 932.72± 0.05 eV and Au $4f_{7/2}$ at 84.01± 0.05 eV. Binding energies were also referenced to the C 1s photoelectron line arising from adventitious carbon at 284.8 eV. Low energy electrons and argon ions were used for specimen neutralization.

Diodes were fabricated by depositing platinum top contacts with guard rings and a gold backside contact. Current versus voltage measurements were performed on these diodes to determine the effect of contact interface chemistry on detector transport properties.

XPS survey spectra of the etched, reduced and oxidized surfaces of p-$Cd_{(1-x)}Zn_xTe$ were acquired to determine surface stoichiometry and impurity concentrations. The quantitative surface compositional analyses and elemental ratios are summarized in Table I. Cd/Te ratio indicates that (1) 2%Br:MeOH etch results in a Te-rich surface, and (2) KOH + NH_4F/H_2O_2 treatment results in a stoichiometric surface.

Figure 1 shows the shallow core-levels and valence band region for the as received, Br:MeOH etched, and KOH + NH_4F/H_2O_2 treated CZT surfaces. These spectra contain the Te 4d, Cd 4d and upper valence band, and provide unique information about the electronic structure and the nature of chemical bonding at the CZT surface. The evolution of the electronic structure at the surface is indicated by the transition of the valence band maximum (VBM).

In these spectra, the Te $4d_{5/2,3/2}$ core-level has two spin-orbit pairs. The higher binding energy spin-orbit pair at 43.8 eV and 45.0 eV represent an oxide (TeO_2/$CdTeO_3$) and the lower binding energy pair at 40.6 eV and 41.8 eV represents Te in CZT in agreement with literature values. [7] The Cd 4d spin-orbit pair cannot be resolved with our instrumentation, so the measured centroid of this peak is at 11.4 eV. In addition, the full width half maximum (FWHM) of the Cd 4d peak indicates the presence of a surface oxide ($CdTeO_3$) for as received CZT. Following the Br:MeOH etch the Te 4d oxide components disappear indicating removal of the native oxide. Also, Te $4d_{5/2,3/2}$ the spin-orbit pair and the Cd 4d peak shifts 0.4 eV to lower binding energy. In addition, the intensity of the Te 4d peaks increases relative to the Cd 4d intensity further supporting the presence of a Te-rich surface, possibly with the formation of Te islands. Formation of Te islands would account for the increased Te signal relative to the Cd signal due to the visibility of the substrate between the islands.

Following KOH + NH_4F/H_2O_2 treatment, the Te $4d_{5/2,3/2}$ core-level spectra show two component pairs and the Cd 4d core line broadens indicating oxide formation. The energy shifts observed for the Te $4d_{5/2,3/2}$ spin-orbit components following this peroxide treatment is similar to those observed for the Cd 4d core level. Also note that the relative intensity ratio of the Te 4d and Cd 4d has change. Recall that compositional analysis determined this to be a stoichiometric surface. Electrical contacts are deposited on this oxide surface for the following transport property measurements.

Measured current versus voltage curves for 500 μm diameter diodes with guard rings are shown in figure 2. Rectifying behavior was achieved for the device treated with the KOH +

NH_4F/H_2O_2 solution while the Br:MeOH sample shows ohmic behavior. We infer that the oxide layer created by the KOH + NH_4F/H_2O_2 solution is blocking current flow from the Pt contact into the semiconductor.

X-ray photoelectron spectroscopy has been used to determine the effects of wet chemical etching/treatment on the surface chemistry and surface electronic structure of CZT. Results show that 2% Br:MeOH removes the surface oxide and that the KOH + NH_4F/H_2O_2 treatment yields a well-behaved oxide surface. The I-V characteristics reveal that KOH + NH_4F/H_2O_2 treatment produces rectifying characteristics while the 2% Br:MeOH treatment results in ohmic behavior. Future work will include treating CZT with N_2H_4 and NH_4OH/thiourea solutions and measuring I-V and C-V characteristics.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

REFERENCES

1. T.E. Schlesinger, J.E. Toney, H. Yoon, E.Y. Lee, B.A. Brunett, L. Franks, and R.B. James, Materials Sci. Eng. 32, 103 (2001).

2. T. Takahashi and S. Watanabe, IEEE Trans. Nucl. Sci. 48(4), 950 (2001).

3. K.-T. Chen, D. T. Shi, H. Chen, B. Granderson, M. A. George, W. E. Collins, and A. Burger, J. Vac. Sci. Technol. A15(3), 850 (1997).

4. S. Wenbin, W. Kunshu, M. Jiahua, T. Jianyong, Z. Qi and Q. Yongbiao, Semicond. Sci. Technol. **20 ,** 343 (2005).

5. V. G. Ivanitska, P. Moravec, J. Franc, Z. F. Tomashik, P. I. Feychuk, V. M. Tomashik, L. P. Shcherbak, K. Masek, and P. Hoschl, J. Electron. Mater. 36(8), 1021 (2007).

6. L. Qiang and J. Wanqi, Surface states and passivation of p-Cd0.9Zn0.1Te crystal, Nucl. Instrum. Methods A 562(1), 468 (2006).

7. P. John, T. Miller, T.C. Hsieh, A.P. Shapiro, A.L. Wachs, and T.-C. Chiang, Phys. Rev. **B34**, 6704 (1986).

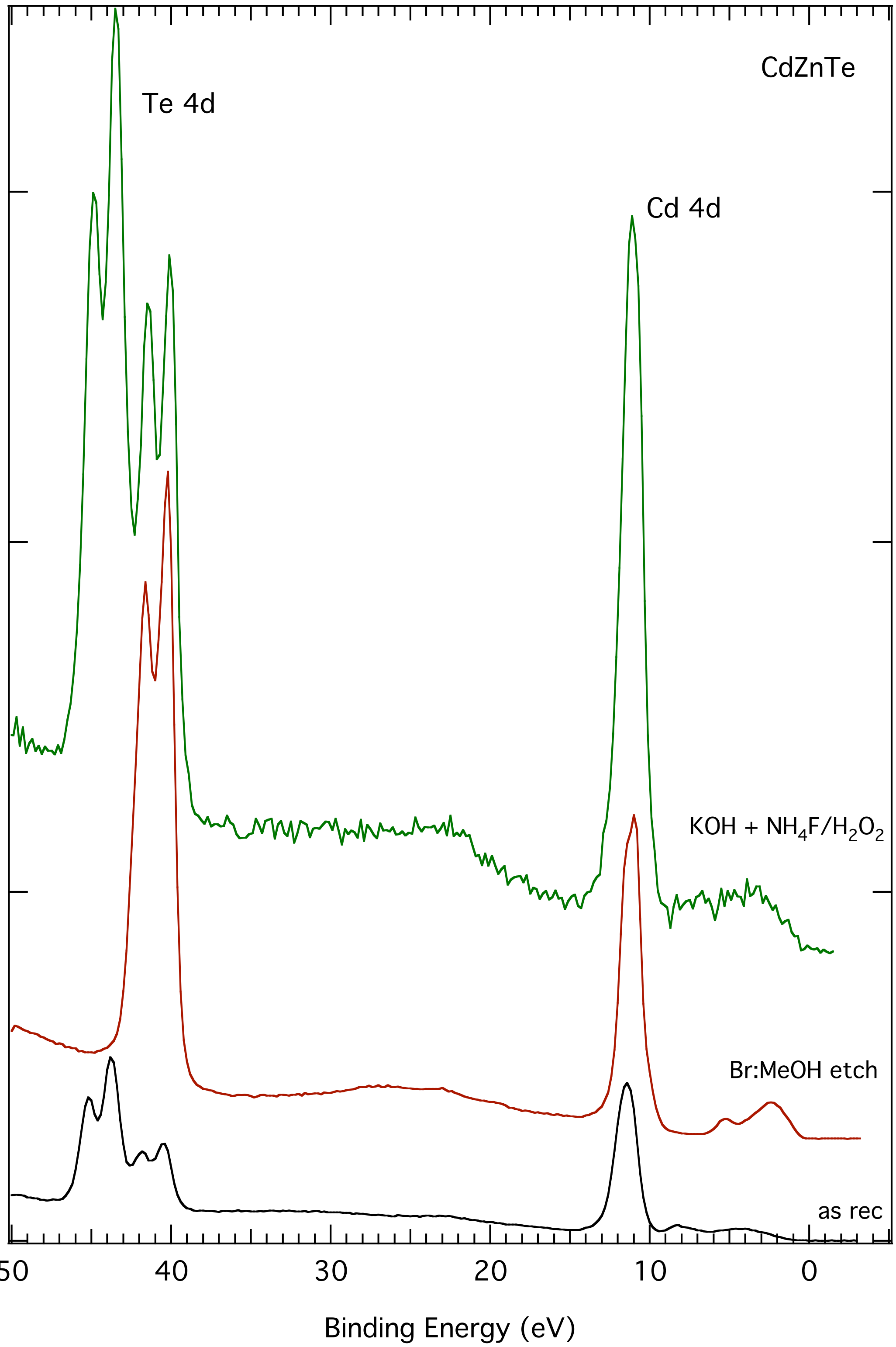
FIGURES

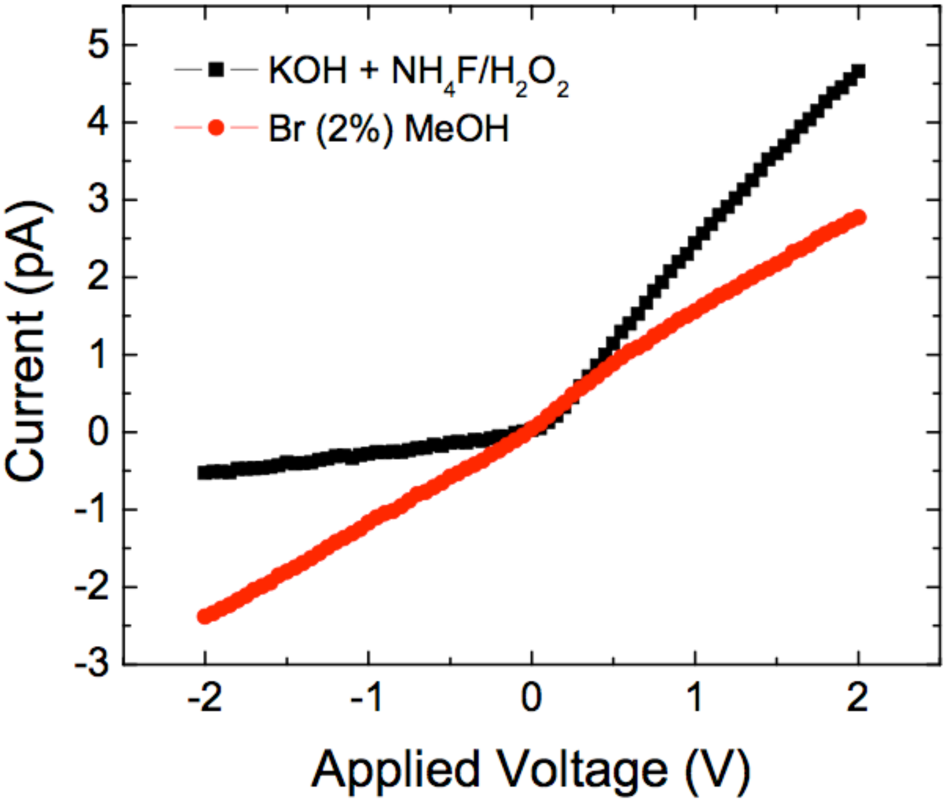
Figure 1. XPS core-level and valence band spectra for the etched and treated CZT surfaces.

Figure 2. Measured current versus voltage response for 500µm diameter diodes with guard rings.

Table I. Relative XPS Surface Compositional Analysis (atomic %) of the Chemically Treated $Cd_{(1-x)}Zn_xTe$

Sample	**Cd**	**Zn**	**Te**	**Cd/Te**
CZT, as received	50.7	2.0	47.3	1.07
CZT – 2%Br:MeOH etch	31.6	2.0	66.4	0.48
CZT - KOH + NH_4F/H_2O_2 treatment	50.5	-	49.5	1.02


CdZnTe
Te 4d
Cd 4d
KOH + NH_4F/H_2O_2
Br:MeOH etch
as rec
15
10
5
0
50
40
30
20
10
0
Binding Energy (eV)


KOH + NH_4F/H_2O_2
Br (2%) MeOH
Current (pA)
5
4
3
2
1
0
-1
-2
-3
-2
-1
0
1
2
Applied Voltage (V)