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Analysis of Te and TeO_2 on CdZnTe Nuclear Detectors Treated with Hydrogen Bromide and Ammonium-Based Solutions

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Abstract

Surface defects caused during cutting and polishing in the fabrication of cadmium zinc telluride (CdZnTe) nuclear detectors limit their spectral performance. Chemical treatments are often used to remove surface damages and defects. In this paper, we present the analysis of Te and TeO_2 species on the surfaces of CdZnTe nuclear detectors treated with hydrogen bromide and ammonium-based solutions. The CdZnTe wafers were chemo-mechanically polished in a mixture of hydrogen bromide in hydrogen peroxide and ethylene glycol, followed by a chemical passivation in a mixture of ammonium fluoride and hydrogen peroxide solution. X-ray photoelectron spectroscopy showed significant conversion of Te to TeO_2, thus producing a more chemically stable surface. The resistivity of the CdZnTe samples is in the order of 10^{10} ohms-cm. The current for a given applied voltage increased following the passivation and decreased after a 3-hour period. Results from spectral response measurements showed that the 59.5-keV gamma-peak of Am-241 was stable under the same channel for the surface treatment processes.

Keywords

CdZnTe, Chemical Treatment, Nuclear Detectors, Surface Passivation, XPS

1. Introduction

Cadmium zinc telluride (CdZnTe) nuclear detectors have the advantage of oper-

ating at room temperature without cryogenic cooling [1] [2] [3]. The CdZnTe crystals are grown under tellurium-rich environments to attain high resistivity that is needed for the detector to operate at room temperature [4]. The major requirements need for detectors to operate at room temperature include high atomic number, large energy band gap, high density, and high electrical resistivity [2] [3]. The average atomic number of CdZnTe is (48 for Cd, 30 for Zn, and 52 for Te) high enough for room-temperature detector operation [3].

The development of room-temperate X-rays and gamma-rays semiconductor detectors is an advancement from silicon-based and germanium-based detectors that require cooling to cryogenic temperatures for them to operate effectively. The ability to operate at room temperature eliminates cooling and operational costs, and provides the fabrication of portable radiation detection devices. The application areas of CdZnTe detectors include nuclear security, environmental protection, medical imaging, and astrophysics [5] [6] [7].

The fabrication of CdZnTe nuclear radiation (X-rays and γ-rays) detector devices involves cutting wafers of desired sizes from the ingot or large slabs of the crystals. The wafers are then polished to smoothen their surfaces. The cutting and polishing processes often introduce surface damages and defects that could increase surface leakage currents and lead to the trapping of charge carriers generated by incident ionizing radiation. The contributions to surface and bulk currents by the fabrication-induced defects produce electronic noise, which in turn degrade the energy resolution of the detector [8] [9] [10]. There are three major steps taken to remove the fabrication-induced damages and defects. The first step is mechanical polishing to smoothen the surfaces of the CdZnTe wafers. This is followed by chemical etching (alternatively one could use chemomechanical polishing) to further smoothen the surfaces. The third stage is surface passivation using appropriate chemicals. In addition to reducing fabrication-induced defects, surface passivation also limits aging defects [11] [12] [13] [14].

In previous investigations, we compared the passivation of CdZnTe detectors using ammonium fluoride (NH_4F) in hydrogen peroxide and potassium hydroxide (KOH) in hydrogen peroxide solutions [11]. It was reported that the NH_4F-based solution is more effective than that of KOH at converting Te species on the CdZnTe wafer surfaces into a more stable TeO_2 layer [11]. It was observed that freshly passivated CdZnTe wafer in the NH_4F-based chemical contributed less to the leakage current compared to that passivated with the KOH-based solution [11]. In the present work, we present the analysis of Te and TeO_2 species on the surfaces of the CdZnTe wafers treated with hydrogen bromide and NH_4F-based solutions, and the effects of the chemical treatments on leakage current and gamma-energy peak position.

2. Experiments

The samples used in this experiment were cut from CdZnTe ingot grown by the vertical Bridgman technique. In vertical Bridgman crystal growth technique, the start materials are loaded in a vertical cylinder which is lowered slowly from the

hot region of a furnace to the cold region. The Bridgman crystal growth of CdZnTe is described in several technical articles [15] [16] [17] [18]. The start materials are typically high purity cadmium telluride (CdTe) and zinc telluride (ZnTe) [17]. Typical data on $Cd_{1-x}Zn_xTe$, with x = 0.1, grown by Bridgman technique in our research group at Brookhaven National Laboratory is reported in [4] [17]. The CdTe and ZnTe start materials were commercially obtained with data on their composition. Time-of-flight secondary ion mass spectrometry (Tof-SIMS) experiments confirmed the CdZnTe composition and the impurities that originate from diffusion during the crystal growth process [18].

A special semiconductor cutting machine equipped with a wire saw and automated dimension-setting system was used to cut several CdZnTe wafers from the ingot. Three wafers (samples 1, 2 and 3) were selected from a set that were cut with a pre-set dimensions of 6.4 mm × 6.4 mm × 2.8 mm, similar to those used in our other investigations [11] [14] [15]. The fabrication steps for each sample are summarized in **Table 1**. The three wafers were mechanically polished, first with an 800-grit silicon abrasive paper and distilled water, followed by polishing in with a 1200-grit silicon abrasive paper.

To further smoothen the surfaces of the wafers they were polished on a MultiTex pad using distilled water and 3.0-μm alumina powder, and successively to 0.1-μm alumina powder. In CdZnTe nuclear detector fabrication, the mechanically polishing step is often followed by chemical etching on the wafer in bromine methanol (BME) solution. Chemical etching helps to further smoothen the wafer surfaces. Etching also reduces the problem of charge trapping [19] [20]. However, etching in BME generates low cadmium and high tellurium concentrations on the surfaces of the wafer. An alternative technique to chemical etching is chemo-mechanical polishing where the wafer is polished in a special pad using a chemical solution such as low concentration bromine-based solution [13] [15] [21]. In this experiment, we used a mixture of hydrogen bromide in hydrogen peroxide and ethylene to chemo-mechanically polish the two CdZnTe wafers.

After mechanical polishing of the three CdZnTe wafers, samples 2 and 3 were chemo-mechanically polished in a mixture of hydrogen bromide in hydrogen peroxide and ethylene solution. Next, sample 3 was passivated it immersing it in a mixture of ammonium fluoride in hydrogen peroxide solution.

We used X-ray photoelectron spectroscopy (XPS) to comparatively measure the Te and TeO_2 on the surfaces of the three samples. The XPS technique employed an RHK Technology UHV 7500 system that is mounted in an ultrahigh

Table 1. CdZnTe samples and chemical treatments.

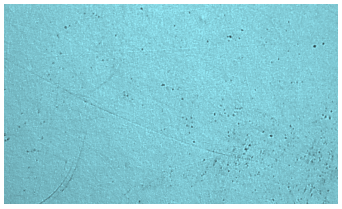
CdZnTe Wafer	Fabrication Processes
Sample 1	Mechanically polished on silicon abrasive paper and in alumina powder down to 0.9 microns.
Sample 2	Mechanically polished and chemo-mechanically polished with HBr + H_2O_2+ $C_2H_6O_2$ solution.
Sample 3	Mechanically polished, chemo-mechanically polished and passivated in NH_4F + H_2O_2 + H_2O.

vacuum chamber at a pressure below 8×10^{-10} Pa. An Al/Mg X-ray source of the XPS system was used to scan the samples. The energy peaks scanned for on the samples surfaces are those of cadmium, tellurium, and tellurium oxide. Prior to the measurement of response to a gamma-ray source, gold contacts were deposited on the opposite planner surfaces of each CdZnTe wafer using the electroless deposition method using drops of $AuCl_3$.

The current-voltage characteristics of each sample were recorded using a Keithley Picoammeter/Voltage Source, with the wafer mounted in customized metal box. The response of each CdZnTe wafer to gamma-rays was investigated by mounting samples on a standard eV Product's brass holder connected to a multichannel analyzer (MCA) via pre-amplifier and shaping amplifier. Am-241 gamma-ray sealed source was used.

3. Results and Discussion

Figure 1 shows the optical microscopy images CdZnTe surfaces for the types of surface treatment processes used in this study. The images were recorded using a Nikon industrial microscope Eclipse LV100 equipped with a CCD camera. Figure 2 shows the XPS results.

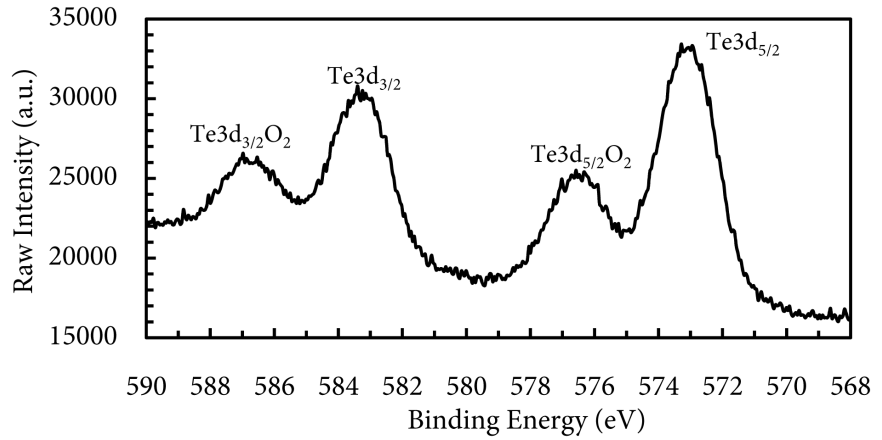


4000 μm × 2400 μm
(a)

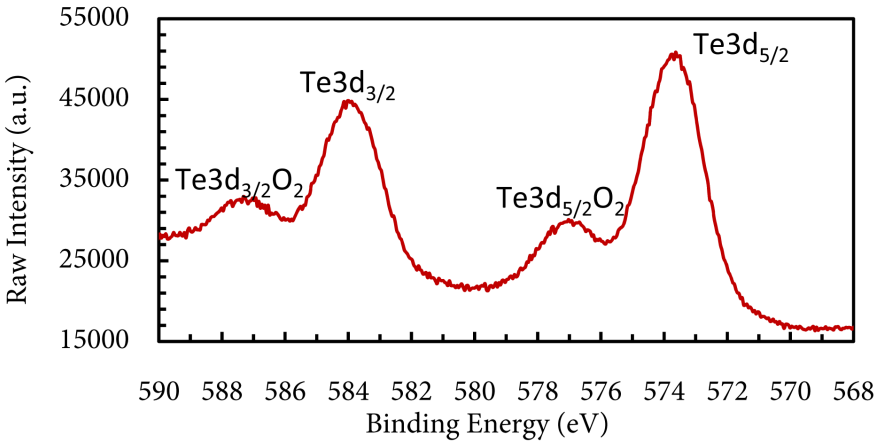
4000 μm × 2400 μm
(b)

4000 μm × 2400 μm
(c)

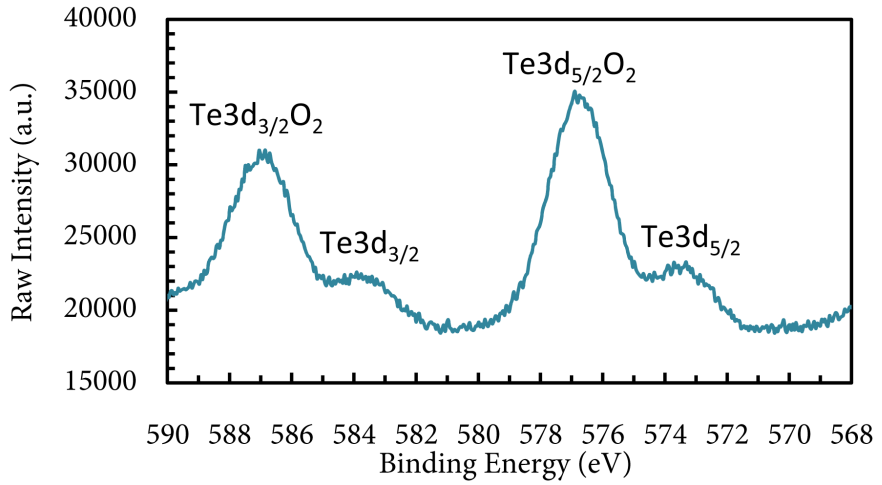
Figure 1. Optical images of CdZnTe surfaces mechanically polished, chemo-mechanically polished and chemically passivated. (a) Mechanically polished on silicon abrasive paper and in alumina powder; (b) Chemo-mechanically followed by chemo-mechanically polishing with HBr-based solution; (c) Mechanically polished, then chemo-mechanically polished with HBr-based solution followed by passivation in the NH4F-based solution.



(a)



(b)



(c)

Figure 2. XPS spectra showing Te and TeO_2 peaks for the three samples: mechanically polished, chemo-mechanically polished, and chemically passivated. (a) Sample 1. Mechanically polished on silicon abrasive paper and in alumina powder; (b) Sample 2. Mechanically polished followed by chemo-mechanically polishing with HBr + H_2O_2+ $C_2H_6O_2$ solution; (c) Sample 3. Mechanically polished, then chemo-mechanically polished with HBr + H_2O_2+ $C_2H_6O_2$ solution followed by passivation in NH_4F + H_2O_2 + H_2O.

The optical images in **Figure 1** show that the chemomechanical polishing and surface passivation processes smoothen the surfaces of the CdZnTe wafers. In previous experiments, we studied the smoothness of the CdZnTe wafers using polishing, chemical etching, chemo-mechanical polishing techniques, and surface passivation [11] [13]. Atomic force microscopy (AFM) measurements showed that chemo-mechanical polishing in hydrogen bromide in hydrogen peroxide solution produced smoother CdZnTe surfaces (1.97 nm root-mean-square roughness) than chemical etching in bromine–methanol–ethylene (BME) glycol solution surfaces (37.35 nm root-mean-square roughness) [11].

In the XPS results are shown in **Figure 2**, the data for sample 1 was obtain from the dataset reported in [11] since that wafer was also used as a reference sample in this experiment. The binding energies for the Te elemental states appear for the $3d_{3/2}$ and $3d_{5/2}$ doublets at approximately 583.5 eV and 573.1 eV respectively [22]. The binding energies for the TeO_2 species for the $3d_{3/2}$and $3d_{5/2}$doublets are approximately 586.5 eV and 576.1 eV respectively [22]. These binding energies were reported by Bahl *et al.* [22] with and estimated error of ±0.2 eV, and by Egarievwe *et al.* [11] with an estimated error of ±0.4 eV. We can see from Figure 2that TeO_2 species were formed during the surface passivation stage. The Te peaks, which were much higher than those of TeO_2 in sample 1 (mechanical polishing only) and Sample 2 (mechanically and chemo-mechanically polished) have been reduced to relatively smaller peaks in sample 3.

The reduction in the peak heights for Te species by the passivation process are due to the conversion of Te to TeO_2. **Table 2** shows the quantification of the peak height ratios. The surface damages and defects created during cutting and mechanical polishing, are decreased by the formation of TeO_2 species which appear as cluster-like features the form into granular shapes [23]. The formation of TeO_2 species was reported to come from H_2O_2 in the processing solution [23], which are HBr + H_2O_2 + $C_2H_6O_2$ for chemo-mechanical polishing NH_4F + H_2O_2 + H_2O for chemical passivation in the present study. A surface roughness decrease from 2.3 nm to 1.3 nm, which confirms decrease in surface damages by H_2O_2, was report in [23]. Thicknesses of TeO_2 greater than 2 nm were recorded in [23].

The current-voltage characteristics of the samples are shown in **Figure 3**. The resistivity of the samples is of the order of 10^{10} Ω-cm. The chemo-mechanical polishing process increased the measured bulk leakage current due to increase in surface current [11]. The contributions from the surface currents are much higher for freshly passivated samples, and continue to reduce afterwards as shown by the current-voltage curve recorded 3 hours later.

The responses of the three CdZnTe detectors to the 59.5-keV gamma peak of Am-241 sealed source showed that the peak was stable under the same channel [14]. The energy resolutions, measured in percent full-width-at-half-maximum (%FWHM) are 8.83 for the mechanically polished wafer, 9.71 for the chemo-mechanically polished wafer, and 9.83 for the wafer passivated in NH_4F-based solution [23].

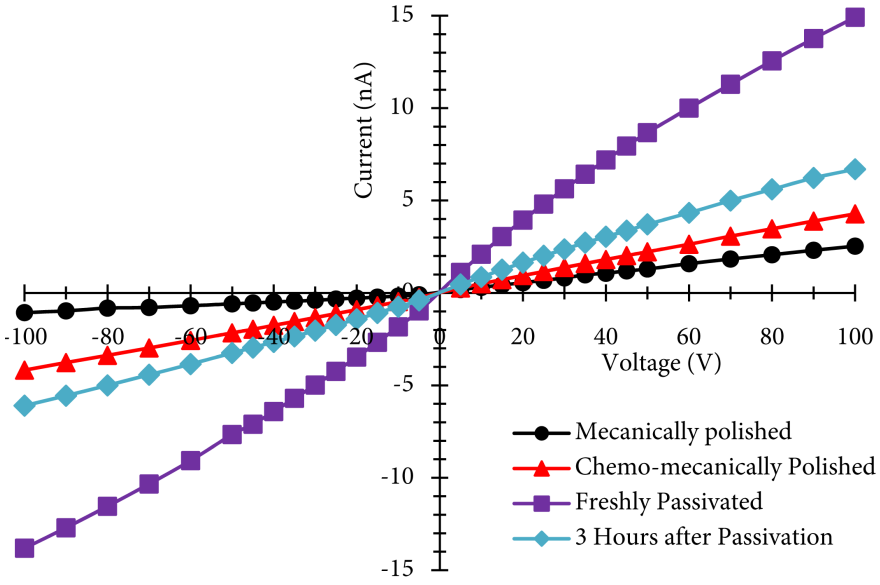


Figure 3. Current-voltage characteristics of the samples: mechanically polished, chemo-mechanically polished, and chemically passivated.

Table 2. Peak ratios of the XPS spectra.

CdZnTe Wafer	Fabrication Processes	Te3$d_{3/2}$O$_2$/Te3$d_{3/2}$ Ratio	Te3$d_{5/2}$O$_2$/Te3$d_{5/2}$ Ratio
Sample 1	Mechanically polished on silicon abrasive paper and in alumina powder	0.869	0.759
Sample 2	Mechanically polished and chemo-mechanically polished	0.725	0.593
Sample 3	Mechanically polished, chemo mechanically polished and passivated	1.370	1.518

4. Conclusions

We have analyzed the Te and TeO_2species on the surfaces of CdZnTe nuclear detectors treated with hydrogen bromide and ammonium-based solutions. The CdZnTe wafers were chemo-mechanically polished in a mixture of hydrogen bromide in hydrogen peroxide and ethylene glycol, followed by a chemical passivation in a mixture of ammonium fluoride and hydrogen peroxide solution. The X-ray photoelectron spectroscopy results showed that there were conversions of Te to TeO_2. This conversion produced a more chemically stable surface. The measured resistivity of the CdZnTe samples is in the order of 10^{10} ohms-cm. The current for a given applied voltage increased rapidly following the passivation and decreased steadily after 3 hours.

The high resistivity of TeO_2 on CdZnTe contributes to decrease in the surface leakage current [23] [24] [25]. Thus, it is expected that increasing the thickness of TeO_2 layer would lead to reducing the surface leakage current until one reaches insignificant levels. In future studies, we plan to find the largest thickness of TeO_2 layers that could be attained and how much reduction in surface leakage current could result. Results from spectral response measurements

showed that the 59.5-keV gamma-peak of Am-241 was stable under the same channel for the mechanically polished surface and the two treatment processes. In future studies, we plan to correlation the TeO_2 layer thickness to the energy resolution of the CdZnTe detectors.

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