

Novel Approach to Surface Processing for Improving the Efficiency of CdZnTe Detectors

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We emphasize an improvement of the surface processing procedures for cadmium zinc telluride (CZT) detectors, which is one of the principal problems limiting the technology. A rough surface enhances the leakage current into the medium, creating additional trapping centers and thereby degrading the detector's performance. Mechanical polishing followed by chemical treatment yields smoother surfaces as required, but chemical treatment, especially with bromine-based solutions, induces unwanted surface features, increases the surface conductivity, and generates chemical species that alter the material's surface and interfacial properties. It is essential to avoid such adverse consequences of surface etching in the manufacturing of highly efficient radiation detectors. We approached the problem of processing the crystals' surfaces by using two different solutions (a low-concentration bromine-based etchant mixture in conjunction with a surface-passivation reagent and a non-bromine-based etchant). The chemomechanical treatment yielded smooth nonconductive surfaces with fewer detrimental features, therefore allowing us to fabricate better devices. We determined the surface roughness using atomic force microscopy and optical profilometry (OP). We analyzed the surface structure, orientations of the crystals, and formation of chemical species by x-ray photoelectron spectroscopy techniques and delineated their effects on the devices' electrical properties and performance. Our experimental data revealed that our new chemical etching process produced nonconductive surfaces with fewer surface defects and so improved the detectors' charge transport and efficiency. We detail the results of our new etchants and compare them with those for conventional Br-methanol etchants.

Key words: CdZnTe, surface processing, chemical etchants, surface roughness, surface leakage current, spectral response

INTRODUCTION

Cadmium zinc telluride (CdZnTe, CZT) crystals are used extensively in x- and gamma-ray detection and imaging applications.^{1,2} Despite their demonstrated value, some problems related to their bulk and surface properties still remain unresolved.

Here, we focus on surface measurements to analyze surface properties (e.g., surface structure, orientations, and the formation of chemical species) and their dependence on processing conditions. Chemical reactions due to processing are major problems in fabricating high-efficiency radiation detectors because the crystal's surface properties control many aspects of the device's operation and performance. A rough surface enhances leakage current into the medium and creates additional trapping

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centers, thereby lowering the detector's performance.^{3,4} Surface processing usually encompasses two steps: (1) mechanical polishing that diminishes the damage on the crystal's surfaces caused by sawing and dicing, and (2) chemical etching that removes a certain amount of material from the top layers of the surfaces, thus leaving behind a comparatively smooth surface depending on the extent of damage incurred during the mechanical polishing.

Though chemical etchants help to reduce polishing-induced damage, resulting in a comparatively smooth surface, there is controversy about whether chemical etching improves or degrades the device's performance. Researchers generally accept that the combination of polishing and etching yields smoother surfaces, so mitigating the problem of charge trapping at surface defects.⁵ However, chemical etching can also cause large increases in the surface leakage current due to reaction by-products, which increases the noise in the device.

Among several widely used etchants, bromine-methanol (BM) solutions are the most popular for treating CdZnTe surfaces. However, they have high redox potential ($\text{Br}_2/2\text{Br} = 1.07 \text{ V}$), which yields Te-rich surfaces that are readily oxidized on exposure to air,^{6,7} and also can render them much more conductive than unetched ones. Also, employing bromine-based etchants generates some features on treated surfaces, and can leave behind some residues after chemical polishing that likely increase the surface conductivity and alter the properties of the metal–semiconductor interface. Therefore, it is vital to identify an etchant that gives a smooth nonconductive surface without having any adverse effect on device performance. Our goal is to reproducibly prepare surfaces with root-mean-square (rms) surface roughness $\leq 1 \text{ nm}$. We have worked systematically to find a suitable etchant for surface processing that will result in a high-quality surface by mitigating the existing problems. We report here our development of two new chemical etchants: (1) a variable ratio mix of hydrogen bromide, hydrogen peroxide, and ethylene glycol (solution A), and (2) a specific ratio of potassium dichromate, nitric acid, and ethylene glycol (solution B).

We analyzed the surface roughness and surface orientations of treated surfaces by atomic force microscopy (AFM) and optical profilometry (OP). Using an x-ray photoelectron spectroscopy (XPS) technique, we measured the elemental composition and the formation of chemical species on the treated surfaces, and compared the results from the new etchants with the conventional BM etchant. Finally, we deposited metal electrodes on the detector crystals and evaluated the electrical properties and device performance.

EXPERIMENTAL PROCEDURES

Six $8 \text{ mm} \times 8 \text{ mm} \times 2 \text{ mm}$ samples were chosen from a detector-grade CZT wafer for our experiments.

Mostly, the samples were mechanically polished with 800-grit and 1200-grit Al_2O_3 abrasive papers, followed successively by $3\text{-}\mu\text{m}$, $1\text{-}\mu\text{m}$, and $0.3\text{-}\mu\text{m}$ alumina powders. Finally, we chemically etched all polished surfaces, after which, in a multistep cleaning process, we removed the residual Br from the surfaces to diminish polishing damage and to generate nonconductive smooth surfaces. For this work, we used conventional bromine-methanol (BM) solution and a bromine-based passivated etchant, and also non-bromine-based etchants for treating the polished surfaces.

We also prepared a dual-contact sample with two different degrees of roughness on one surface: one half was polished with $3\text{-}\mu\text{m}$ grit and the other with $0.3\text{-}\mu\text{m}$ grit. We deposited Au contacts with guard rings within each area of the dual-finished surface and the entire area on the opposite surface.

XPS experiments were carried out using an RHK Technology UHV 7500 system in an ultrahigh-vacuum setup at pressure below $8 \times 10^{-10} \text{ Pa}$. The chamber was equipped with a dual Al/Mg x-ray gun and a source from an argon-ion sputtering system. We used an Al x-ray gun to acquire XPS measurements of the CZT samples immediately following their chemical treatment. Afterwards, we etched off the oxide layer via sputtering of their surfaces with 1-kV argon ions for 1 min.

To measure the surface and bulk leakage currents, and also to test the device's performance, we prepared a two-strip, small area with a guard ring and a regular planar-type contact. AuCl_3 solution was spread carefully on the detector's surface using a special pipette to avoid its spilling over onto the side surfaces. Some 15 s to 30 s later, the detector was dipped into deionized water to remove any excess solution, then quickly blow-dried with pressurized nitrogen gas.

We measured the surface and bulk currents against the applied voltage for the respective samples using a customized I – V probe coupled to a Keithley electrometer. To test the fabricated radiation detectors, we mounted them on a standard eV Product's brass holder, wherein a gold-plated spring contact held the detector against a beryllium window. The brass holder was connected to a multichannel analyzer (MCA) through a preamplifier and a shaping amplifier. The detector's surface against the beryllium window acts as a cathode. After irradiation from a sealed Am-241 gamma-ray source, the detector's response was recorded through the MCA and stored for further processing and analysis.

RESULTS AND DISCUSSION

Role of Surface Roughness

A rough surface enhances the leakage current into the medium and creates additional trapping centers, together resulting in degraded energy resolution and a larger low-energy tail of photopeaks.⁸ We

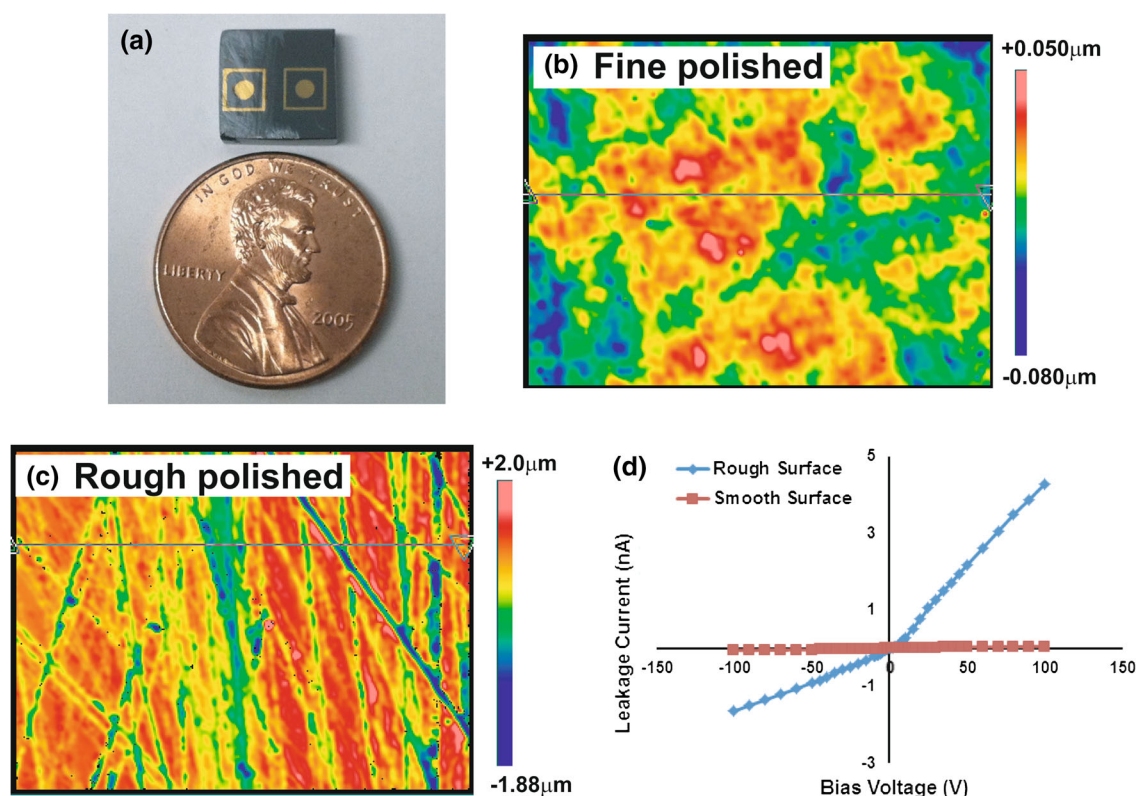


Fig. 1. Measurements of leakage current for rough and smooth CdZnTe surfaces. (a) Deposited contacts with a guard ring on both the rough and smooth areas. (b, c) Topographic images of surface profiles of rough and smooth surfaces taken by optical profilometer. (d) I - V plots for rough and fine-polished surfaces. The leakage current was about 20 times higher for the rough surface than for the smooth surface.

conducted a specific experiment with a dual-contact sample to observe the effects of surface roughness.

Figure 1a depicts the topographic features associated with the rough and smooth areas of the same surface of the detector. In a planar-type device, leakage current can occur both along the side surfaces and through the bulk. However, in this particular experiment, the surface current can be ignored as the contacts were confined by a guard ring. In addition, the dual contact on one surface of the single crystal normalizes the impact of bulk material defects. We measured the current-voltage curve across both surfaces separately. The leakage current was about 20 times higher for the rough surface than for the smooth surface.

Mechanical polishing removed some surface defects, but created new defects on the smoothly polished surfaces.^{9,10} Such defects act as trapping centers for the transport of charge carriers between the electrodes. Furthermore, with increasing roughness of the surface, more carriers contribute to the dark current, lowering the signal-to-noise ratio; hence, such degradation also lowers a device's spectral resolution due to noise, even rendering it unusable for gamma-ray spectroscopy for some samples. This conclusion supports our previous detailed explanation of the phenomenon,¹¹ wherein we offered some early experimental evidence on the effects of surface processing.

Effect of Chemical Treatment by Various Etchants

Chemical etchants help to reduce polishing damage and can leave behind comparatively smooth surfaces. However, such treatment induces features on the surfaces, rendering them more conductive. Our endeavor was to minimize the usage of bromine or to find an alternative etchant for preparing smooth, nonconductive surfaces. We treated our samples with solution A and solution B, and afterwards determined the surface roughness via AFM. We compared the results of our new chemical etchants with those of conventional ones.

Figure 2 depicts topographic images from different chemically treated and untreated surfaces. As is evident in Fig. 2a, the polished surface bore multiple scratches; its rms value was 5.9 nm. The BM solution removed the scratches incurred by mechanical polishing and reduced the rms value to 4.1 nm; however, the etching resulted in an overall bumpy surface that we believe reflects an inhomogeneous etching rate. We also conjecture that the bromine in the chemical etchant caused debris from the polishing to adhere to the surface. In both cases, the surfaces act as a source of leakage current into the fabricated devices, so directly influencing their energy resolution and charge collection efficiency. Figure 2c and d, respectively, display surfaces that

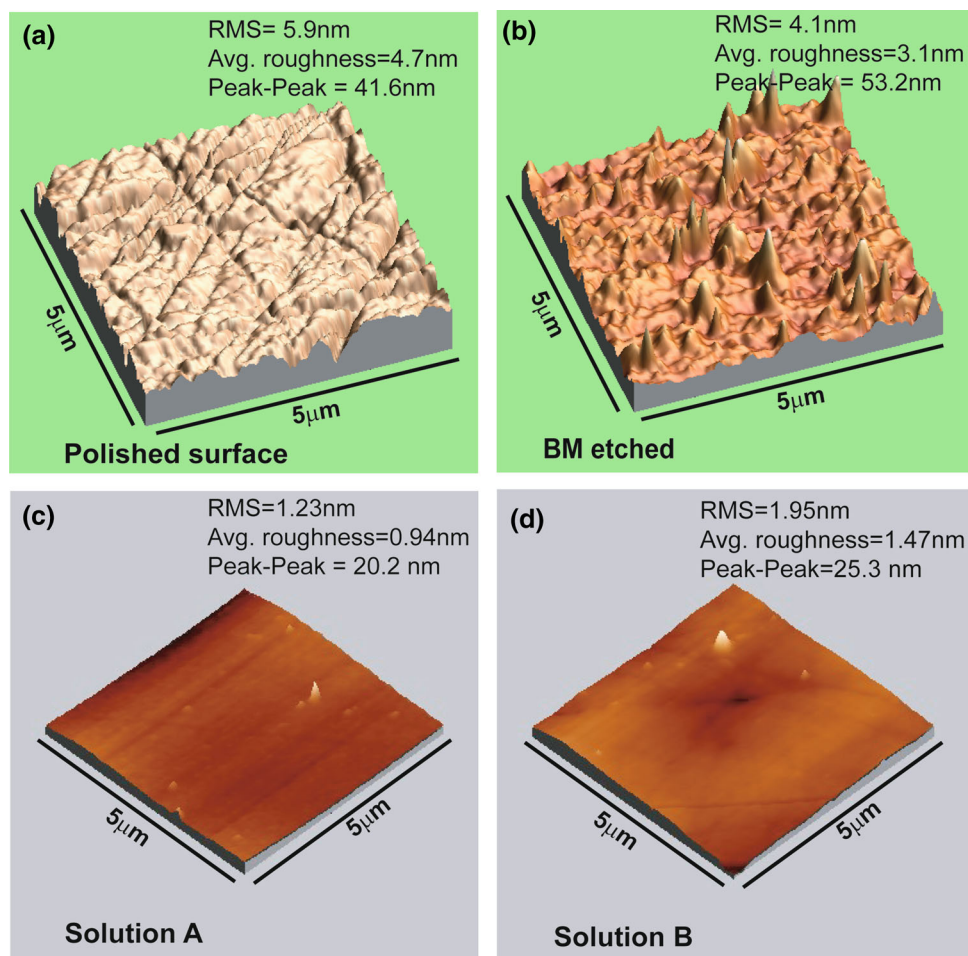


Fig. 2. AFM measurements of surface roughness of CZT crystal surfaces before and after chemical treatment: (a) mechanically polished surface, (b) surface etched by bromine-methanol solution, (c) surface polished chemomechanically by solution A, and (d) surface polished chemomechanically by solution B.

were chemomechanically polished using solution A and solution B. It is evident that both solutions yielded smoother surfaces than did the conventional BM etchant. The values of both the rms and average roughness are nearly 1 nm, highly comparable to values reported by others,¹² and more importantly, the bromine-related problems of the treated surfaces appear to be diminished. However, to confirm this, we need further information on the etching rate of oriented surfaces and the presence of any secondary phases on the treated surfaces. We selected two neighboring pieces of a CZT wafer, named sample #1 and sample #2, determined their orientation, and treated them separately with solution A and solution B.

Figure 3 displays AFM topographic images of the IIIA and IIIB surfaces of these two identical CZT crystals. Both solutions worked well and left behind smooth surfaces with satisfactory values of surface roughness. However, the etching rate of solution A varied with the sample's orientation. In Fig. 3a, b, it can be observed that the rms value (2.6 nm) of the

IIIB surface of sample #1 was high compared with that of the IIIA surface, for which the rms value was 1.9 nm. Also the nonuniform etching rate of surface IIIB resulted in a bumpy surface that reflected a high peak-to-peak value (17.1 nm). On the other hand, the rms values of both surfaces of sample #2 were <1 nm, and no significant features were observed on either surface (Figs. 3c, d).

Chemical Composition of the Treated Surfaces

We conducted a study of the formation of chemical species on various chemically treated surfaces to identify the surface states and contaminants responsible for the surface conduction. The evaluation was made by XPS measurements immediately after chemical treatment and also after argon-ion sputtering.

Figure 4a, b shows the Te 3d region of the XPS spectra of CZT samples treated by different etchants. In the doublet structure of the Te 3d region, there are two peaks at approximately 572 eV

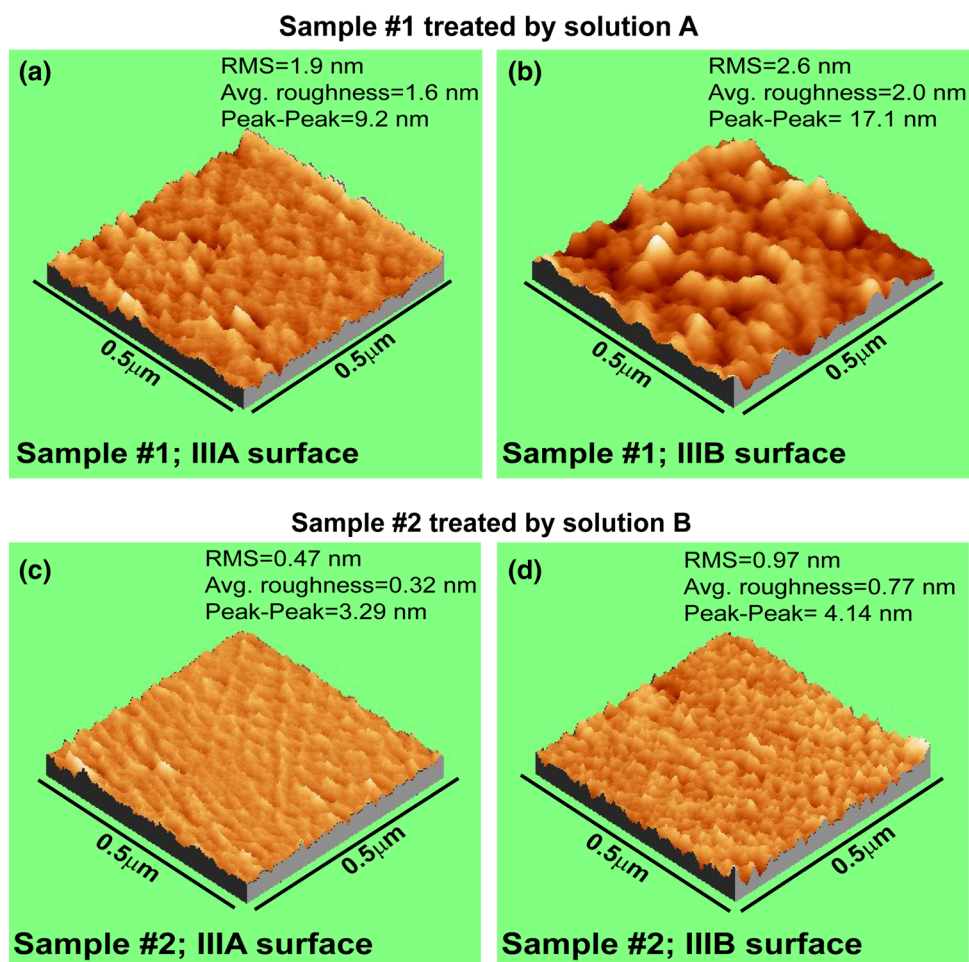


Fig. 3. AFM images of the IIIA and IIIB surfaces of two identical CZT crystals: (a, b) surfaces of sample #1 treated by solution A, and (c, d) surfaces of sample #2 treated by solution B. The etching rate of solution A seemingly depends on the surface orientation.

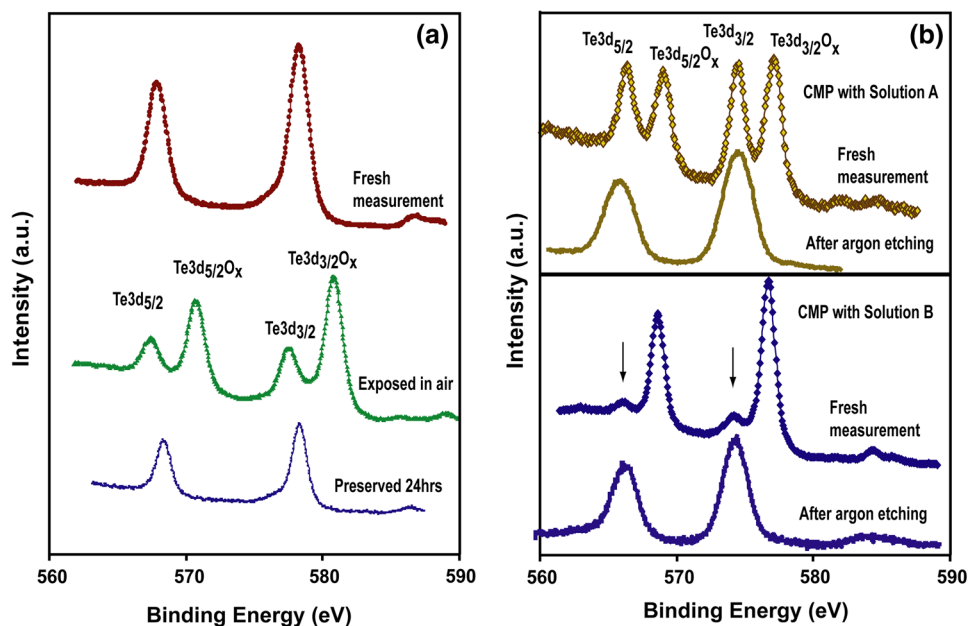


Fig. 4. Te 3d region of XPS spectra of: (a) three CZT samples treated by BM solution and processed differently before measurement, and (b) two CZT samples treated by solution A and solution B separately and measured freshly thereafter.

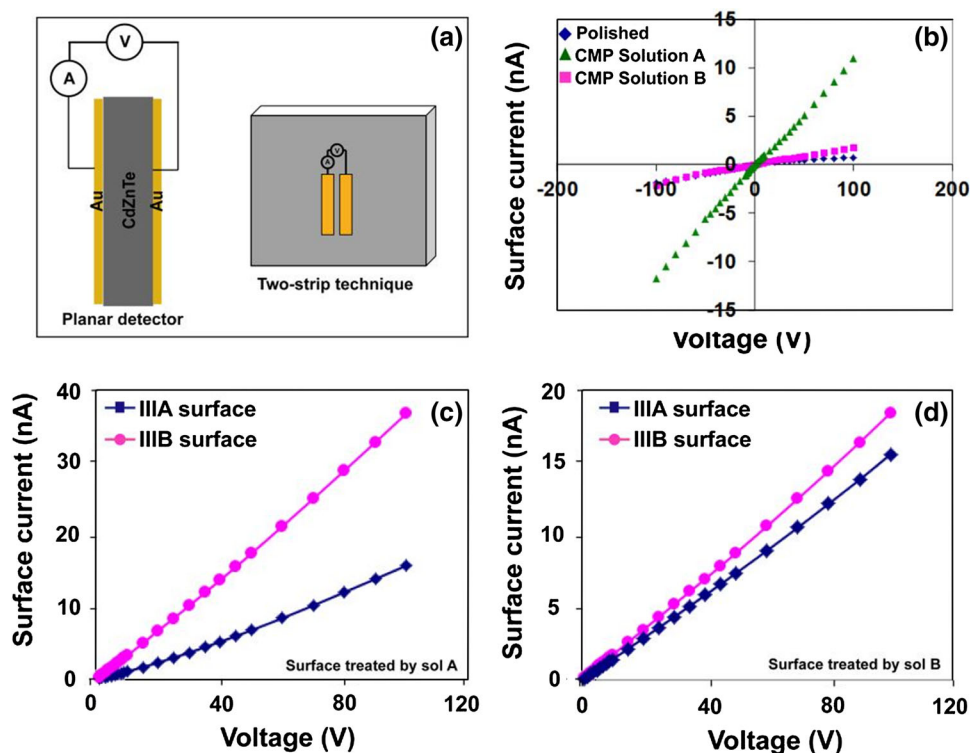


Fig. 5. (a) Drawings of contact configurations for current–voltage measurements. (b) Current–voltage measurements across the bulk of fabricated devices. (c, d) Plots from measurements of surface leakage current of CZT samples treated, respectively, by solution A and solution B.

and 583 eV that correspond to the Te elemental state; the two other peaks at approximately 576 eV and 587 eV reflect the production of the TeO_x state, as was clearly evident in a Te-rich etched surface exposed to air.¹³ Figure 4a reveals that a CZT surface etched by BM solution oxidizes over time upon exposure to air. So, to avoid oxidation of the surface before fabricating devices, either the metal contact must be deposited immediately or the surfaces must be protected from atmospheric exposure. On the other hand, It can be seen in Fig. 4b that the surfaces of our samples treated by solution A and solution B were also oxidized immediately after etching, and easily was removed by argon-ion sputtering.

Device Performance

Surface conductance becomes an important factor for contact patterns with steering (biased) electrodes, e.g., in coplanar-grid or pixel devices. A comparatively high surface conductance in CZT detectors apparently reflects the presence of a lower-resistivity surface layer with different stoichiometry and defect structure than the bulk CZT band structure. We measured the current–voltage characteristics of various CZT samples across their bulk and individual surfaces.

Figure 5a illustrates two contact configurations for the current–voltage measurements. Figure 5b

shows a current–voltage plot for the bulk current measurement of treated surfaces; Fig. 5c, d shows similar plots of the surface current measurements of the corresponding samples. It can be seen that the sample treated by solution A had higher leakage current in both bulk and surface measurements than the sample treated by solution B. Seemingly, solution A produced a smooth surface with rms value ≤ 1 nm, but the bromine in solution A most likely reacted vigorously with the IIIB surface. Such a reaction yielded a Te-rich surface that readily oxidized; we also believe that it induced thereon some random bumps that acted as charge-trapping centers. These bumps in the surface enhance the surface leakage current, which degrades the efficiency of fabricated devices and can affect the internal electric fields due to space-charge buildup.

Using a sealed Am-241 source, we recorded the spectral responses of two detectors (named D1 and D2) fabricated before and after chemical polishing. It can be clearly seen from Fig. 6a, b that the charge collection efficiency and energy resolution of detector D2 improved substantially after the chemical treatment compared with detector D1. The energy resolution was determined to be 20% and 19% for D1 and 23% and 17% for D2, before and after chemical treatment. Though the energy resolution of detector D1 improved slightly, a tail appeared at the low-energy side due to the enhanced leakage current.

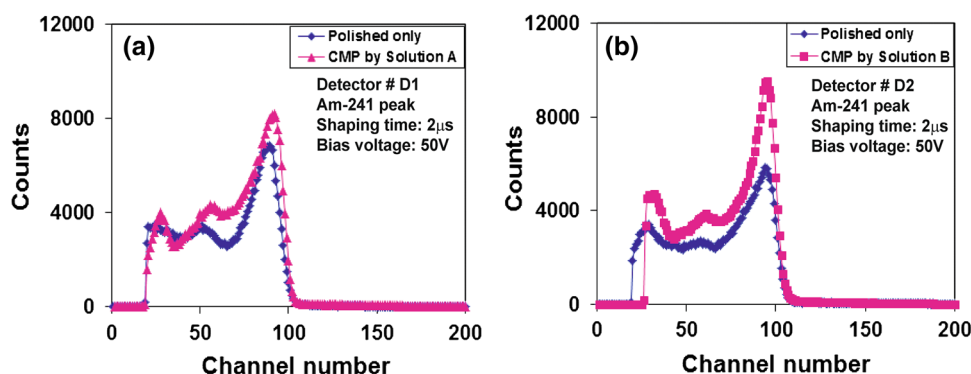


Fig. 6. Spectral response of two CZT planar detectors using a sealed Am-241 source. Responses were recorded from chemically untreated and treated detectors: (a) detector D1, whose surfaces were treated by solution A; (b) detector D2, whose surfaces were treated by solution B.

CONCLUSIONS

Chemical treatment helps to improve the surface quality of CZT crystals, but the usage of etchants, especially bromine, engenders secondary problems that degrade the detector's performance. We demonstrated that surface quality can be improved by both solution A (bromine-based passivation solution) and solution B (potassium dichromate and nitric acid), but the latter, a non-bromine-based solution, significantly improves the charge collection efficiency and energy resolution of the fabricated detector. However, further studies are needed on these etchants to determine the long-term stability of the resulting surfaces and the reproducibility of the processing steps for different surface orientations and pre-etching surface processing conditions.

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