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Abstract

Generally, mechanical polishing is performed to diminish the cutting damage followed by chemical etching to remove the remaining damage on crystal surfaces. In this paper, we detail the findings from our study of the effects of various chemical treatments on the roughness of crystal surfaces. We prepared several CdZnTe (CZT) and CdMnTe (CMT) crystals by mechanical polishing with 5 μm and/or lower grits of Al_2O_3 abrasive papers including final polishing with 0.05-μm particle size alumina powder and then etched them for different periods with a 2%, 5% Bromine-Methanol (B-M) solution, and also with an E-solution (HNO_3:H_20:$K_2Cr_2O_7$). The material removal rate (etching rate) from the crystals was found to be 10 μm, 30 μm, and 15 μm per minute, respectively. The roughness of the resulting surfaces was determined by the Atomic Force Microscopy (AFM) to identify the most efficient surface processing method by combining mechanical and chemical polishing.

Key words: CdZnTe, CdMnTe, chemical polishing, surface roughness, atomic force microscopy.

Introduction

The favorable properties of CdZnTe have made it the most promising material for room-temperature radiation detectors [1-2]. CdMnTe similarly has attracted attention due to its potentially useful characteristics and its similarities to CdZnTe [3-5]. However, for both materials, many drawbacks remain associated with the various steps from crystal growth to detector fabrication, which must be resolved to produce a good quality detector. We are particularly interested in the fabrication process wherein surface processing is an important step as it plays a critical role in determining the detectors' performance. Many studies have explored the surface processing of CdZnTe radiation detectors [6-10], but only a few have studied CdMnTe detectors. Studies show that surface properties can influence the electric field inside the device, and significantly affect charge transport and signal formation [11-12]. A rough surface enhances leakage current into the medium and creates additional trapping centers, thereby adversely affecting the detector's performance. Therefore, it is essential to evaluate the surface processing steps to identify those that deliver the best surfaces for developing good quality radiation detectors.

The crystal surfaces first are polished mechanically to diminish the damage from cutting, followed by chemical etching to remove any remaining damage from crystal cutting, and damage induced during mechanical polishing. Several etchants are suitable for chemically etching CdZnTe and CdMnTe crystal surfaces [13-15]; typically, a bromine-methanol (B-M) solution is used. Chemical etchants react with the crystal surfaces, remove a certain amount of material from the top layers, and leave behind a smoother surface. Each chemical has certain etching strength, and hence, the material-removal rate varies depending on the strength of the etchants and the material that is being etched. To ensure a reasonably good surface outcome, we need data to optimize the type of etchant, its concentration, and the etching time for particular crystal surfaces.

In this paper, we describe our study of the effects of various chemical treatments on the roughness of crystals' surfaces. We prepared several CdZnTe and CdMnTe crystals by mechanically polishing them with alumina powder of 0.05-μm particle size, followed by etching with a 2%, 5% Bromine-Methanol (B-M) solution and also with an E-solution (HNO_3:H_20:$K_2Cr_2O_7$), and a P-solution (HNO_3:HCl:H_20). We observed repeatedly that the P-solution reacted vigorously with the CdZnTe and CdMnTe surfaces, leaving highly non-uniform uneven surfaces; hence, we did not continue to work with it. We etched the samples with these different etchants for different periods, and recorded the removal trend with time. For both CdZnTe and CdMnTe the material removal rates in 2% B-M solution, 5% B-M solution, and the E-solution respectively, were about 10 μm, 30 μm, and 15 μm per minute. The etching rate of the B-M solution slowed down with time, but remained linear for the E-solution.

The roughness of the resulting surfaces was determined by the Atomic Force Microscopy (AFM) to identify the most efficient means of surface processing, using a combination of mechanical and chemical polishing to obtain a quality surface for fabricating radiation detectors.

Experimental procedures

We employed several different shaped and sized detector-grade CdZnTe and CdMnTe crystals in this experiment. The CdZnTe samples were bar shaped with dimensions of ~5x5x10mm^3, while the CdMnTe samples were planar with dimensions of ~8x10x2 mm^3. Three sets, each comprising one CdZnTe and one CdMnTe crystal, were mechanically polished with 5 μm and/or lower grits Al_2O_3 abrasive papers including final polishing with 0.05-μm particle size alumina powder and then rinsed in distilled water. To compare the surface roughnesses before and after chemical etching of identical surfaces, we first covered half of the polished surfaces of all crystals with nonstick insulating tape while the second half was chemically etched for 2 minutes with a 2%, a 5% B-M solution and with the E-solution, then rinsed with pure methanol and quickly blow dried with pressurized nitrogen gas.

We recorded infrared (IR) refection images before and after etching the surfaces. To measure the roughness of those surfaces, atomic force microscopy (AFM) was used to image the polished and etched area of each sample. AFM was used to image both the polished and etched areas of each sample. The instrument was an Innova Scanning Probe Microscope (SPM) with a nanodrive controller for an Innova large area single-tube piezoelectric scanner. A contact mode etched Silicon probe with symmetric tip of height of 15 microns and thickness of 4 microns was used.

Another two sets of CdZnTe and CdMnTe crystals were employed for a series of observations of the etchants actions, viz., the dissolution rate and a chemical aging experiment. We etched the crystals with the same three solutions for periods up to 10 minutes at room temperature. In each case before and after etching, we measured the crystal thickness with a micrometer to quantify the amount of material removed from each surface. We note that the entire crystal was dipped into the chemical solution to ensure the etchants uniformly acted on all the crystal surfaces.

Results and discussions

Fig. 1 shows two set of IR reflection images of six representative crystal surfaces. All samples were lapped and finally polished with 0.05-μm grit alumina powder. Half of each sample was etched with the three different etchants and other half remained as polished. We note that all CdZnTe crystals were from the same batches, and all CdMnTe crystals were from a single batch. They were all subjected to the same polishing procedure so that we could use one polished surface as a reference. From the IR images, it can be seen that chemical etching removed the surface damage significantly. Although the E- solution also removed the polishing damage, it created some pits so yielding a non-homogeneous surface. Longer etching times enhanced the number of pits and the unevenness of the surface. We were unable to generate a flat uniform surface in either CdZnTe or CdMnTe crystals by etching in the P solution, either for 30 sec or up to 2 minutes (Fig. 2). Longer etching also enhanced the roughness in this case. Seemingly, the concentrated nitric acid reacted with Cd(Zn/Mn)Te, left black tellurium layers on the etched surface, possibly the reason for the unevenness. This effect was reproducible in both the CdZnTe and CdMnTe crystal surfaces, so we ceased further work with it. However, we note that Inoue et. al. [16] used both the E and P solutions for chemical etching of CdTe crystals and obtained mirror-like surfaces.

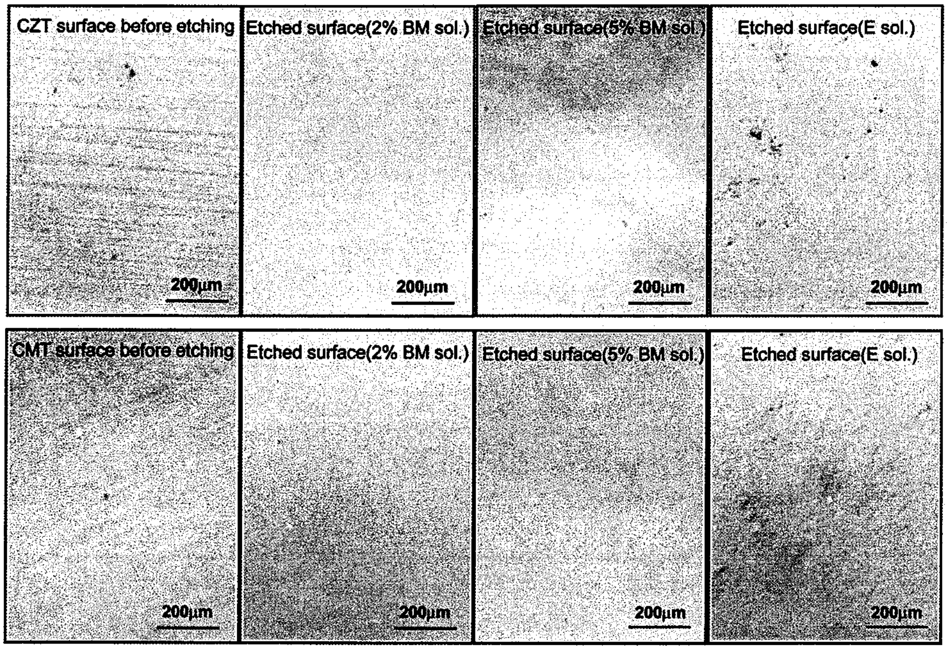

Fig. 1. 4x IR reflected images of the polished and etched surface of the crystals. The polishing damage was removed substantially by etching with different chemical etchants. The top row is images of the CZT crystals, and the bottom row those of the CMT crystals. Note the pits in the surfaces treated with the E solution.

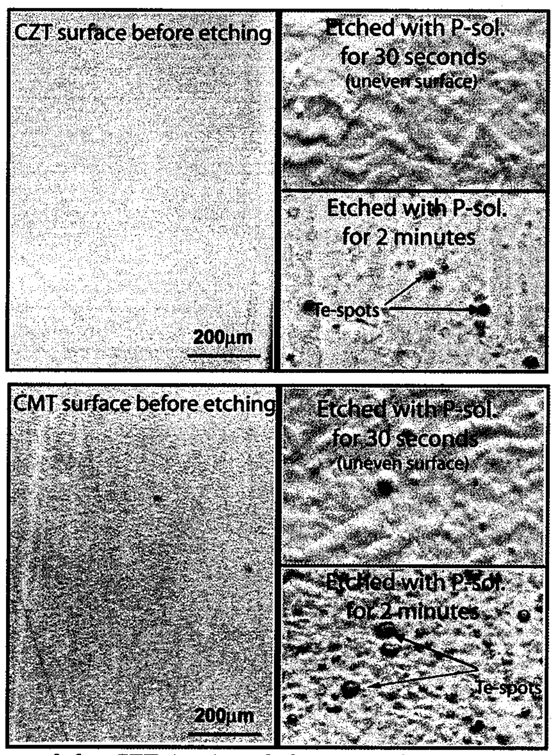

Fig. 2. 4x IR reflected image of the CZT (top) and the CMT (bottom) crystal surfaces before and after etching with the P-solution. 30 seconds etching left uneven surfaces, and 2 minutes etching left some Te-spots.

We carried out a series of experiments to demonstrate the etching rate of different chemical etchants after different exposure times. Fig. 3 plots the average amount of material removed from CdZnTe crystals after treating with different etchants for times from 30 seconds to 10 minutes. Etching with the 5% B-M solution removes an average layer of about 125 μm from the crystal's surface in 10 minutes; however, the removal rate is not linear, and gradually decreased with the time. The average etching rate was estimated to be about 30 μm per minute. Etching with a 2% B-M solution showed a similar trend, but the rate was 10 μm per minute and the etching rate of the E solution was estimated to be about 15 μm per minute. Burger et al. [17] reported an etching rate about 50 μm per minute for a 2-10% B-M solution. For our solution-aging experiments shown in Fig. 4, we prepared the 5% B-M solution and E-solution at room temperature and left them exposed to air for 2 hrs, 4 hrs, and 8 hrs before using them to etch the samples for 2 minutes slots. The samples exposed to fresh B-M solution had a higher etching rate than those treated with solutions aged for 4 hours, and even greater for those left 8 hours. Furthermore, the aged solutions left readily visible layers of black tellurium on the etched surfaces. However the reaction of E-solution was more or less linear over the aged period. The aging effect may reflect a change in the solution's pH. Rouse et al. [18] found that the acidity of etching solutions increase significantly over 8 hrs. The increasing acidity could be due to the uptake of moisture or CO_2 from air with time [19]. As the acidity of the solution increases, selectivity for cation etching increases, leading to an increasingly Te-rich surface.

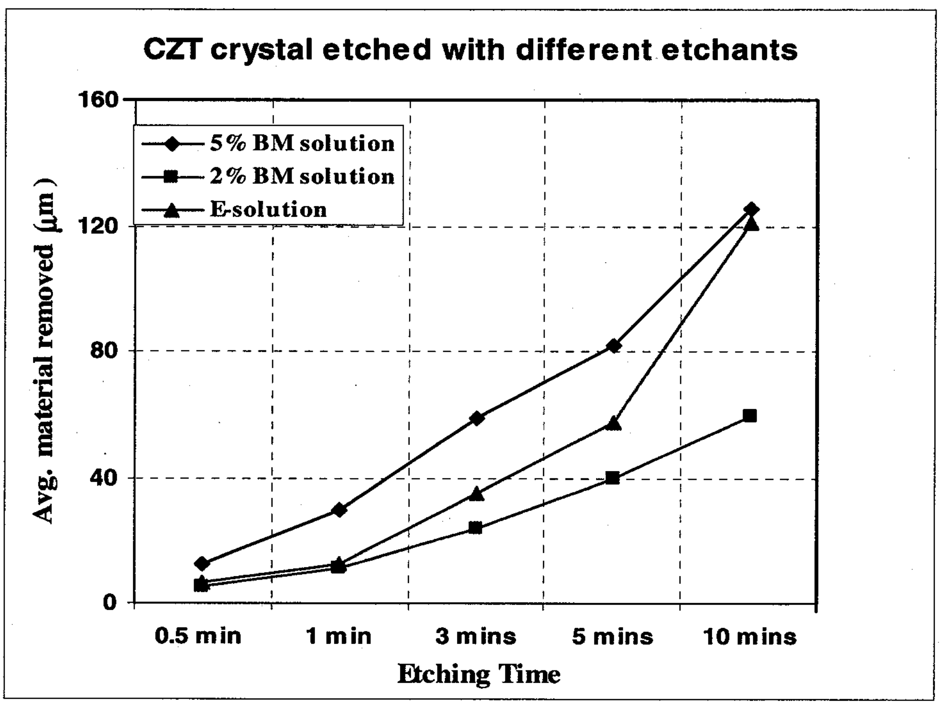

Fig. 3. Plot of the effect of different chemical etchants on CdZnTe crystals. The etching rate of the 2%-, 5%- B-M solutions and the E solution is about 10 μm, 30 μm, and 15 μm, respectively.

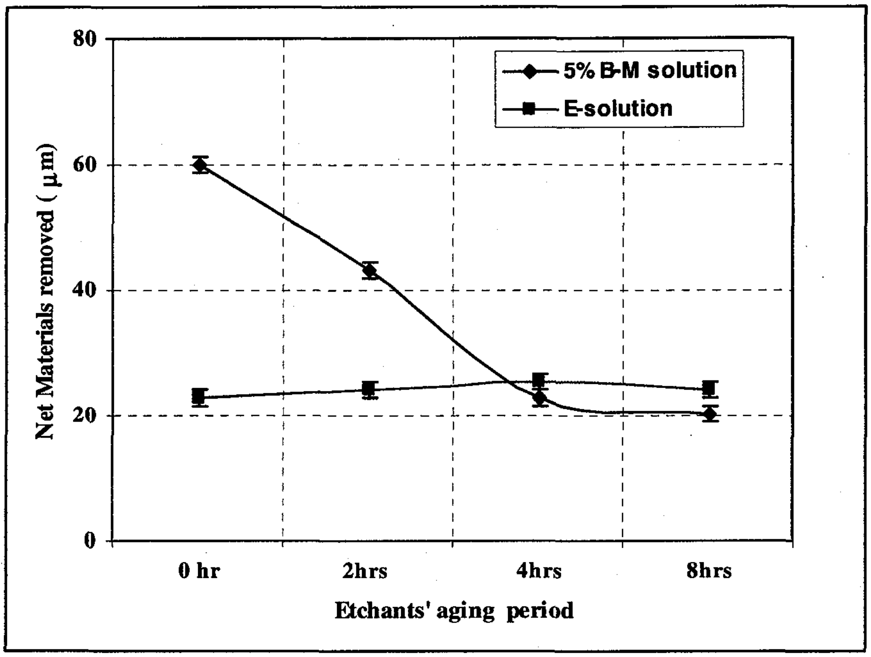

Fig. 4. Graph of the effect of aging the etchants in air on the removal of materials from two crystals. The etching rate of 5% B-M solution decreased with increasing exposure time, but remained more or less linear for E-solution over the aged period.

We found that it is hard to evaluate the uniformity as well as the roughness of the etched surfaces by IR images. Therefore, we have used the AFM method to study more precisely the surface roughness of those polished and etched surfaces. We chose areas for imaging from the polished and etched portion of each crystal. As in Fig. 1 we displayed one polished surface of each type of crystal as a reference. Fig. 5 shows AFM images of one polished surface and three different etched surfaces of CdZnTe crystals. The rms roughness of the polished surface was estimated to be around 9 nm. Etching with 2% B-M solution lowered the rms roughness value to about 2.5 nm, while etching with 5% B-M solution reduced the rms roughness to about 1.3 nm. From AFM images it can be seen that etching with 5% B-M solution has removed the surface damage that can be estimated to be about 88%, whereas 74% with 2% B-M solution and 35% with E-solution.

Fig. 6 shows the same measurement for CdMnTe crystals. Chemically etching these crystal surfaces provided even better rms roughness values than did the CdZnTe surfaces. Starting with an rms roughness of polished surface of around 7 nm, etching with 2% B-M solution lowered it to about 2 nm, and to 0.9 nm with the 5% B-M solution. Etching CdMnTe crystal's surface with the E solution left a comparatively rougher surface than did the B-M solution at either concentration.

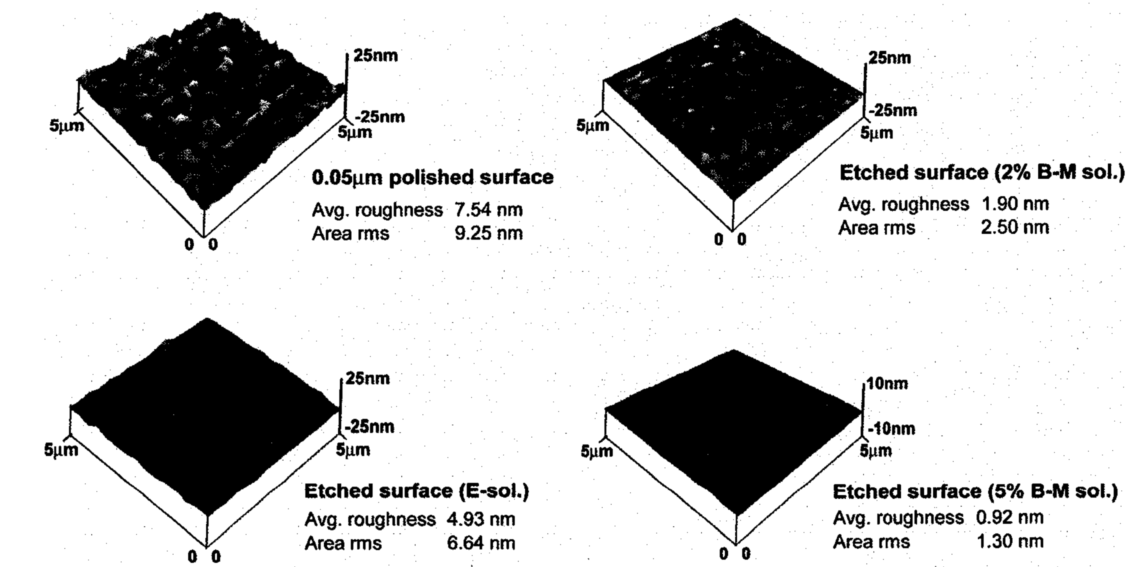

Fig. 5. AFM images of polished and etched surfaces of the CdZnTe crystals. The lowest rms roughness was obtained after etching with 5% B-M solution followed by the 2% B-M solution; the E- solution was not as efficacious.

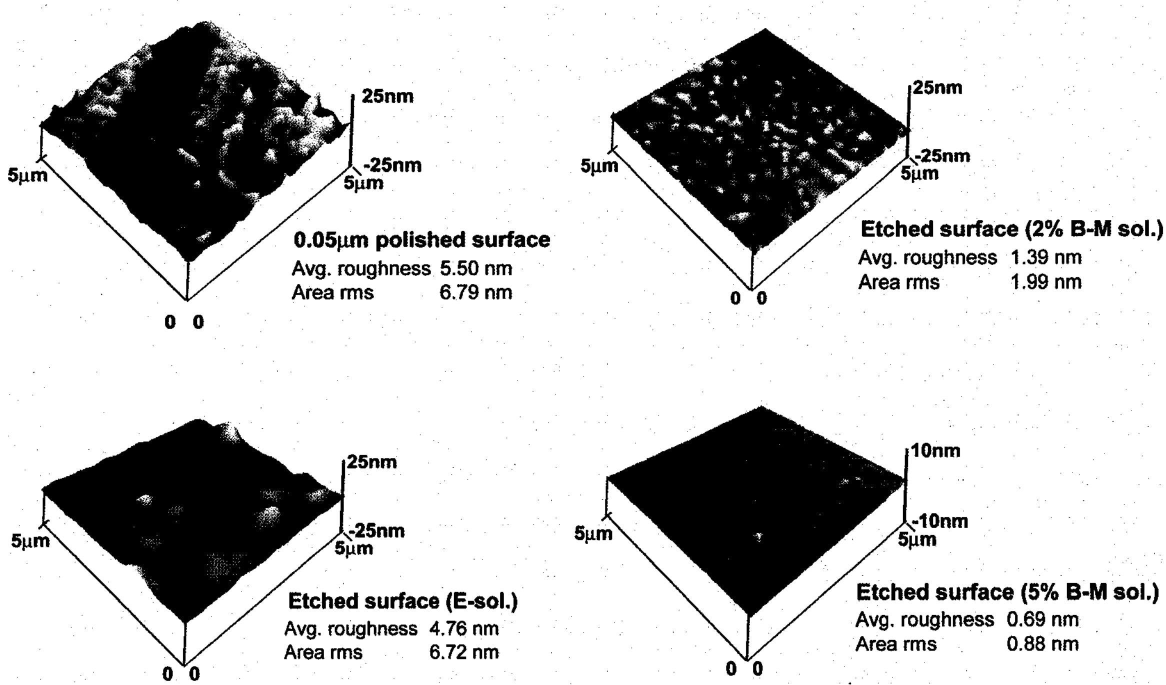

Fig. 6. AFM images of the polished and etched surfaces of CdMnTe crystal. The lowest rms roughness was attained after etching with 5% B-M solution as compared to a 2% B-M solution and the E solution.

Conclusions

We demonstrated that polishing damage can be substantially removed by chemical etching with either type of chemical etchant i.e., a B-M solution at different concentration, and an E solution, although to different extents. We estimated the amount of material removed with different concentrations of these etchants and different immersion times. We believe this information will help to enhance the process of preparing smooth crystal surfaces. As we have understood from this study, it can be assumed that higher percentage of B-M solution with shorter etching time can be helpful to yield a smoother surface, which is suitable for detector fabrication. We have also found that E- and P-solutions are not useful for etching of CdZnTe and CdMnTe crystals in this particular study. However we need further investigation to understand the reason behind it. We used AFM to obtain detailed information about the topography of the etched surfaces, especially roughness and uniformity, which will help in selecting the appropriate surface-etching preparations for making good detectors. We showed the effects of different chemical etchants on the surfaces of CdZnTe and CdMnTe detectors, and the differences in etching rates between the E solution and the B-M solution that reduced with time over 10 minutes. However, further investigation is needed to optimize conditions, using the smallest sized polishing grit and the subsequent most suitable chemical etchant. In combination with other surface processing, this may yield a crystal surface of suitable quality for fabricating a good detector.

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