Development of Dry Processing Techniques for CdZnTe Surface Passivation

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A method for passivating the surface of $Cd_{1-x}Zn_xTe$ (CZT) x-ray and gamma ray detectors using relatively simple dry processing techniques has been developed. Leakage currents were significantly reduced for several processing methods. CZT samples were exposed to an oxygen plasma and/or coated with a reactively sputtered silicon nitride layer. Several parameters of the oxygen plasma step were found to be important for achieving enhanced surface resistivity. SiN_X has been previously characterized and was used because of its high dielectric quality and low deposition temperature. Reduction in leakage current after passivation by a factor of as much as twenty is demonstrated. Results are also presented which give a measure of the long-term stability of the passivating layers.

Key words: Cadmium zinc telluride, oxygen plasma, reactive sputtering, silicon nitride, surface passivation

INTRODUCTION

Cadmium zinc telluride (CZT) has shown great promise as a material to be used for the production of large-volume x- and gamma-ray spectrometers operating at room temperature. However, the performance of spectrometers fabricated from CZT crystals are often limited by leakage current in the devices. The leakage current acts as a source of noise which reduces the ability of the detectors to spectrally resolve the unique radiological emissions of a wide variety of isotopes. Current crystal preparation methods typically include a mechanical polish and a wet etch containing Br in methanol[3–9] or Br in ethylene glycol.[10] Although these etches can leave a smooth surface, this surface is not stoichiometric and has been shown to be Te-rich for CdTe[8] and CdZnTe.[3] As a result, the surface possesses a resistivity which is lower than the bulk resistivity of approximately 10^{11} Ω-cm. The current which passes through this low-resistivity region on the surface can be a large fraction of the total leakage current in the device. When a CZT crystal is fabricated into a device which functions in an enhanced mode called "electron-only,"[11–13] the design typically requires there to be closely spaced electrodes across which significant potentials are applied. Under such circumstances, the need to reduce surface leakage currents is increased. Specifically, a method is required to passivate, or reduce the conductivity of, the surface layer (Fig. 1). It is important that this passivation also be stable over time.

Previous methods of passivation include variations in the wet etch typically used after mechanical polishing, wet chemistry surface oxidation using peroxides,[1–3] and atomic oxygen bombardment.[14] In these studies, the increase in surface resistivity was attributed to the formation of thin layers (approximately 20Å) of Te oxides, primarily TeO_2. These methods typically result in surface leakage reductions of between 20 and 500%. One group reports reductions of factors greater than ten;[10] however, the passivation methods used in these studies have not as yet been discussed in detail. The methods listed above suffer from various drawbacks. Wet chemistry oxidation must typically be done before electrode deposition. As a result, these contacts are typically blocking because of the underlying oxide layer. The apparatus required for atomic oxygen bombardment is costly and the times required to obtain significant reduction in leakage currents are substantial.[14] Also, the long-term stability of the thin passivation layers

(Received November 5, 1998; accepted February 5, 1999)

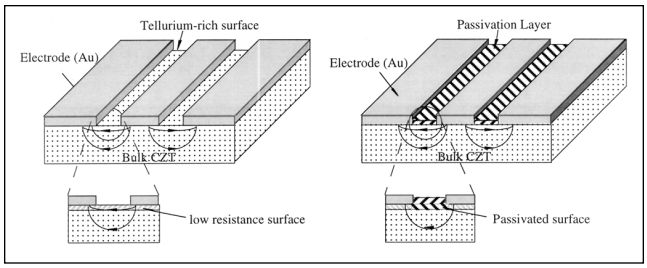

Fig. 1. Schematic showing effect of passivation on low-resistivity surface of patterned CZT surface.

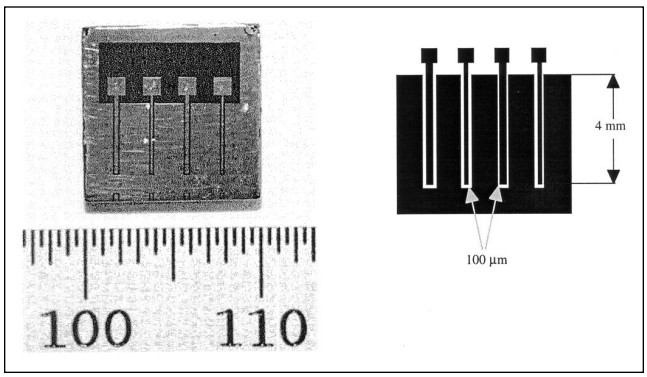

Fig. 2. Photograph of $10 \times 10 \times 2$ mm^3 CZT sample with patterned Au electrodes (left) and schematic showing dimensions of test structure used for I-V characterization (right).

resulting from these methods has not been carefully studied.

We have explored alternative methods of oxidizing a Te-rich surface via an oxygen plasma and passivation by reactively sputtered SiN_X which can yield superb passivating capability. In contrast to some of the drawbacks of other methods, our techniques require only standard vacuum equipment. They can also be done after electrode deposition and as a result the type of contact (blocking, Schottky, etc.) is not dependent on the passivation method. Finally, a thicker dielectric layer such as silicon nitride, which is resistant to a wide range of chemicals and has already been demonstrated as an effective passivating layer in Si, GaAs, and other material systems, seems a more likely candidate for maintaining high long-term performance.

EXPERIMENTAL PROCEDURE

Sample Preparation

Select counter-grade CZT samples (eVproducts, $10 \times 10 \times 2$ and $5 \times 5 \times 2$ mm^3) were mechanically polished with alumina powder (3.0, 0.3, and 0.05 µm grit sequentially) in water on a felt wheel. A solution of 48% HBr acid, 48% ethylene glycol and 5% bromine was used to chemically polish the surface (20 s). The addition of HBr acid appears to simplify controlling the surface roughness. The samples were then soaked in ethylene glycol (10 s), rinsed in deionized water, and dried with nitrogen. Lithography was used to define contact patterns. Lift-off after gold sputter deposition (1500Å) was done in an acetone solution with gentle agitation. A patterned test structure containing four separate test strips and a ground plane is shown in Fig. 2 along with a schematic illustrating the critical dimensions. Current-voltage measurements to quantify leakage currents before passivation were performed at room temperature using a Keithley source measurement unit (Model 237). The data was recorded using a PC via a GPIB interface. Resistances were extracted from the I-V curves by taking an average of the linear fits over the two voltage intervals (–100,–10) and (10,100) (to avoid nonlinear behavior at low bias.) An approximation of the sheet resistance was then calculated from $R_{sh} = R_m(W/L)$ where R_{sh} is the sheet resistance in ohms/square, R_m is the resistance as calculated from the above linear fit of the I-V curves, W is the width of the region between electrodes, and L is the spacing between electrodes. For example, in Fig. 2, the ratio (W/L) would be approximately (2*4 mm/0. 1 mm) = 80. Two other test structures used for resistivity characterization had (W/L) ratios of ten and three.

Table I. Conditions Used for Argon Milling Treatment of CZT Test Samples

Pressure	rf Power	Subst. Bias	Time
20.0 mTorr	50 Watts	–500 Volts	5–10 min

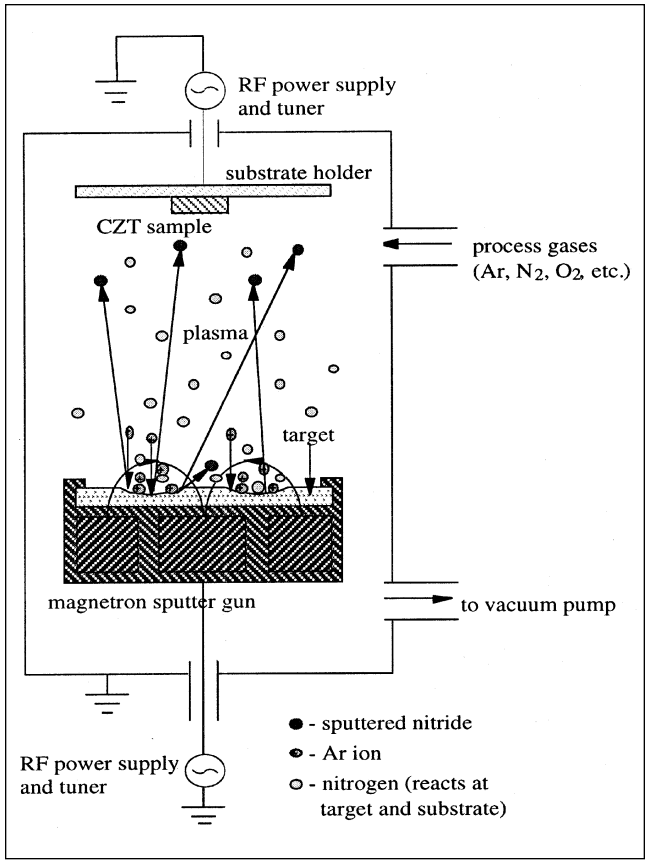

Fig. 3. Schematic of typical vacuum chamber equipped for reactive sputtering of dielectric compounds and plasma etching of substrates.

Table II. Conditions Used for Oxygen Plasma Treatment of CZT Test Samples

	Pressure [mTorr]	O_2 Flow [sccm]	rf Power [Watts]	Subst. Bias [Volts]	Time [Min]
Nominal	16.0	95	30	–440	5
Range	12.0–16.0	70–95	20–100	–800– –300	2–10

Table III. Conditions Used for SiN_x Passivation Deposition

Pressure	N_2 Flow	Ar Flow	rf Power	Target Bias	Dept. Rate	Targ.-Sub.Space
5.5 mTorr	4.3 sccm	21 sccm	100 Watts	–300 Volts	100Å/min	8.0 cm

Argon Ion Etch

An attempt to "clean" the surface before passivation via an argon ion etch step was used for several samples, since this step uses the same apparatus as the oxygen plasma and does not require a vacuum break between steps. It was assumed that ion etching would remove any nonstoichiometric surface layer generated by the mechanical polish and wet etch preparation. The conditions used for this step are listed in Table I.

Plasma Oxidation

Oxygen plasma passivation was performed in a sputtering system equipped with a radio frequency (rf) (13.56 MHz) substrate etch power supply (Fig. 3). Samples were mounted on a 3″ Si substrate which was attached to the 4″ diameter substrate cathode. Samples were passivated using the conditions shown in Table II. The rf power was varied (with constant time) to determine the effect of total energy delivered to the substrate. However, because the substrate bias voltage is a strong function of plasma power (approximately –5 Volts/Watt in the power range explored for the system used), it was difficult to determine if the observed results were due to changes in power or voltage. As a result, other samples were run at low powers for longer times to deliver roughly the same energy but at lower bias voltages.

SiN_X Deposition

Deposition of reactively sputtered SiN_X ($1.3 < x < 1.4$, 1000Å thickness)[15] was performed in the same sputtering system (Fig. 2) using an elemental Si target and N_2 as a reactive gas. Details of the process are given in Ref. 15. The conditions for deposition are listed in Table III. These conditions yield films which have low stress (necessary for adhesion) and high resistivity (~ 10^{14} Ω-cm). Further, low temperature (<100°C) of the substrate can be maintained with this deposition process, unlike other dielectric film deposition methods (CVD, PECVD). This is important because degradation of the device will occur at elevated temperatures.

RESULTS

The test structures were passivated in three basic ways: oxygen plasma surface oxidation, SiN_X film deposition, or a sequential application of both processes without breaking vacuum. Parameters which were varied for the oxygen plasma passivation included plasma power, time, and bias voltage. All SiN_X films had thicknesses of approximately 1000Å and were deposited under the conditions in Table III. A summary of the result is shown in Fig. 4. The samples whose performance degrade due to the passivation step can be placed in four categories. The worst sample, which showed an increase in leakage current of a factor of 500 after the nominal oxygen plasma step (Table II) is an outlier which was probably contaminated with some material in the sputter chamber or reached elevated temperatures because of poor thermal contact with the substrate chuck. The next category of samples received the argon milling treatment before plasma oxidation. The marked increase in leakage current is probably due to preferential sputtering of the CZT surface, leaving it nonstoichiometric. This result is consistent with reports that argon milling before electrode deposition results in ohmic or at least very leaky Schottky contacts. The third category (two samples) in Fig. 4 received increased energy during the plasma oxidation (the power was increased in the

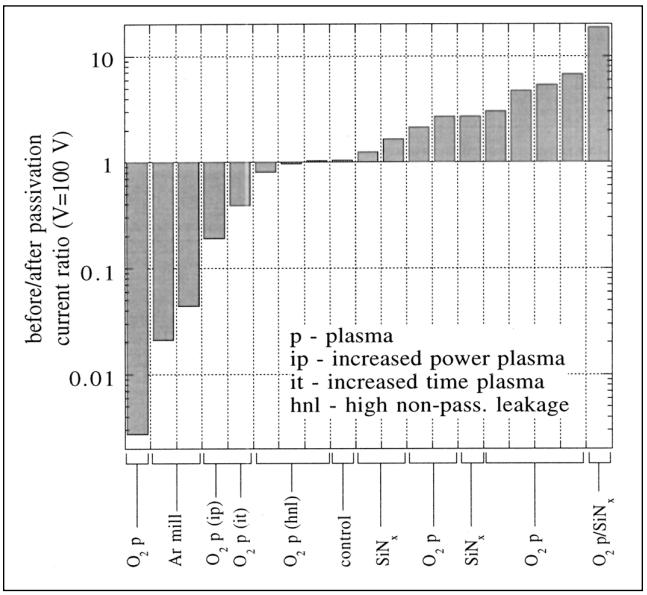

Fig. 4. Ratio of leakage current at applied bias of 100 V between before- and after-passivation I-V measurements. Values higher than one indicate a decrease in leakage current while values less than one indicate an increase in leakage current due to the passivation attempt.

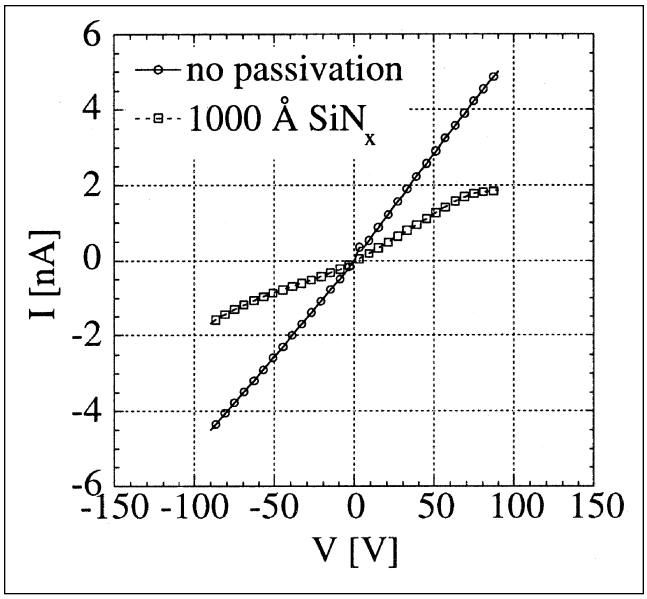

Fig. 5. I-V characteristics of sample passivated only with SiN_x layer.

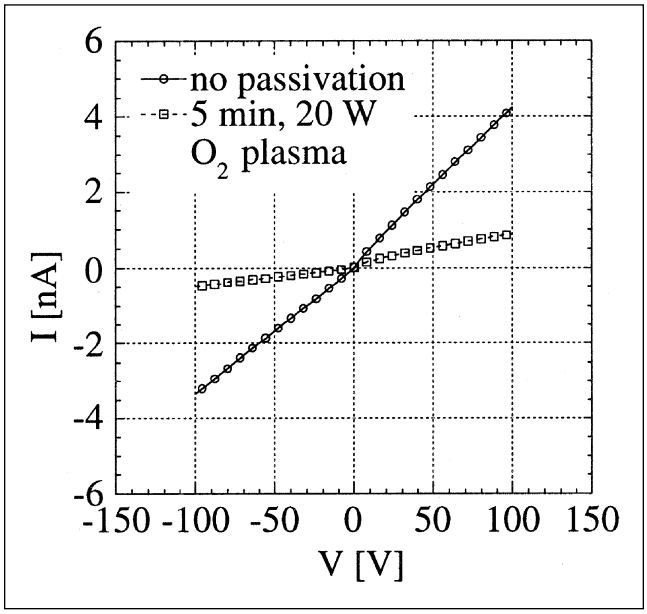

Fig. 6. I-V characteristics of sample passivated with nominal oxygen plasma process.

first and the time in the second.) It is probable that the performance degradation in these samples was caused by excessive heating during the passivation step. The fourth category which showed either degradation or essentially no improvement included three samples which received the nominal oxygen plasma treatment, but had excessively low sheet resistances (a factor of greater than 20 below typical measurements of approximately 20 GΩ/square) before passivation. This suggests that either the sample was of generally poorer quality or that the initial mechanical polish/wet etch preparation degraded the surface layer. With a thicker-than-average layer of low resistivity material on the surface, it is probable that the oxygen ions cannot penetrate the surface to the depth required

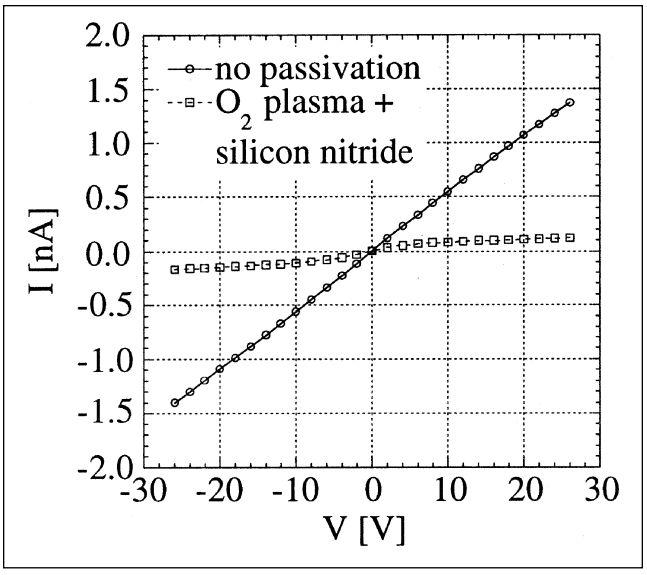

Fig. 7. I-V characteristics of sample passivated with nominal oxygen plasma process and coated with SiN_x.

to oxidize all of metallic constituents of the thick low-resistivity layer.

The samples which showed improvement due to passivation processing can be divided into three groups. The first includes samples which did not receive the oxygen plasma step but were coated with a layer of sputtered SiN_x. This passivation technique showed modest improvements of less than a factor of four reduction in the leakage current. The I-V characteristics for one sample passivated with only SiN_x are shown in Fig. 5. The calculated sheet resistance for this sample was approximately 460 GΩ/square after passivation.

The second set of samples showing improved characteristics after passivation are those which received the nominal oxygen plasma treatment. These samples showed improvement ratios of between two and six. The I-V curves for such a sample are shown in Fig. 6. The calculated sheet resistance for this sample was approximately 1200 GΩ/square.

Finally, the last sample was processed with the nominal oxygen plasma step and then coated with SiN_x. This sample yielded an improvement ratio in leakage current of approximately 20. The I-V curves for this sample are shown in Fig. 7. The calculated sheet resistance for this sample was approximately 1500 GΩ/square.

The long-term stability of this sample was also examined, and I-V characteristics taken at three different times spanning roughly 1.5 months are shown in Fig. 8. The results indicate that in fact the leakage currents decreased over time. Further study over longer time intervals and under harsher conditions (large applied biases, etc.) is required to fully characterize the long-term stability.

CONCLUSIONS

Several techniques for passivating the surface of CZT after electrode deposition using dry processing

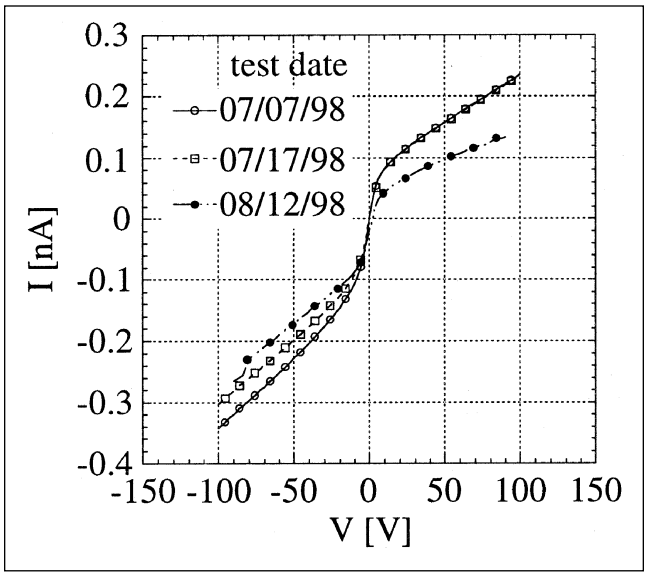

Fig. 8. I-V characteristics of sample passivated with nominal oxygen plasma process and coated with SiN_X taken over 1.5 month interval. No bias voltage was applied during the intervals between I-V tests.

steps were examined. Argon milling degrades the surface resistivity, presumably by generating a nonstoichiometric and/or damaged surface via differential sputtering. We have also found that samples must be prepared in such a way that the initial sheet resistance before passivation is roughly 20 GΩ/square or greater if the proposed passivation techniques are to be successful. High power and/or long oxygen plasma exposure times also degrade the surface state. However, oxygen plasmas under the appropriate conditions can yield significant improvements in the surface leakage properties of CZT samples. Reactively sputtered SiN_X can also be used to passivate the surface of CZT; however, by itself it appears to provide only modest improvements in surface resistivity. Finally, a combination of oxygen plasma and SiN_X coating yields excellent improvements in the surface resistivity, and also seems likely to be able to provide long-term passivation given the stability of silicon nitride. Further study is required to determine if stored charge in the nitride layer generates a depleted region near the CZT surface or if the passivation process is instead chemical in nature.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of the U.S. Department of Energy, Office of Research and Development, Office of Nonproliferation and National Security, NN-20.

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