Thermal Treatments of CdTe and CdZnTe Detectors

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ABSTRACT

An irreversible deterioration of CdTe and CdZnTe detectors after heat treatments in the temperature range of 150 - 200°C was reported by several authors; however, the nature of the processes responsible for the detector degradation and increased dark currents is not fully understood. In this study we have prepared CdTe and CdZnTe detectors equipped with Au contacts. The detectors were tested before and after thermal annealing under vacuum. Using combined measurements of current voltage characteristics, low temperature photoluminescence and nuclear spectroscopic measurements, we have attempted to differentiate between the various possible contributions to the detector degradation and elucidate the defect formation process involved.

Keywords: gamma ray detector, contact, barrier height, annealing treatment, interface diffusion

1. INTRODUCTION

CdZnTe and CdTe detectors exhibiting good spectral resolution are mostly fabricated from high resistivity materials ($\rho > 10^9 \Omega\text{-cm}$). The high electrical resistivity reduces the leakage current to values compatible with the low noise electronics used to process individual pulses. Proper contact design as well as the choice of the electrical contact material,¹ method of contact deposition,² interface control, surface treatment, and passivation^{3,4,5} are also extremely important in the fabrication of high energy resolution radiation detectors. In addition to surface passivation, which reduces the surface leakage current, an annealing treatment has been the choice of many researchers to increase the bulk resistivity of both CdZnTe^{6,7} and CdTe⁸ material and improve the detector performance. There have also been several reports on the effects of post annealing treatments on fabricated detectors. For CdZnTe strip detectors, this treatment improved the adhesion of the metal to CdZnTe⁹ for wire bonding and also increased the interstrip resistance. In CdTe detectors with Au contacts, it has been shown that annealing under hydrogen and vacuum leads to poor detector performance, while annealing gold contacts in air improved the detector quality.¹⁰ The objective of this paper is to understand the effects of CdTe and CdZnTe detectors due to annealing treatment in the temperature range of 150 - 200°C. By using combined measurements of current voltage characteristics, low temperature photoluminescence and nuclear spectroscopic measurements, we attempt to separate out the various possible contributions from the contact interface region and bulk to better understand the degradation of the detector performance.

2. EXPERIMENTAL

The $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and CdTe crystals used in this study were obtained from eV Products, Inc., USA and Acrotek, Japan, respectively. The samples were first polished on a mechanical polisher with 0.05 μm particle size alumina suspension and then rinsed with methanol. Next each sample was etched for 2 minutes in 5% Bromine in methanol (Br-MeOH) in order to remove the mechanically damaged layer, and then again rinsed in methanol. The detectors were fabricated with sputtered Au contacts

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immediately after the chemical treatment to minimize the effects of surface oxidation. After the metal deposition, Pt leads were attached to the contacts using a colloidal graphite suspension in water (Aquadag from Acheson Inc.). Finally, the device was covered with a protective coating (Humiseal from Chase Corp.) to help with surface passivation and also to improve the mechanical stability.

The detailed setup for the I-V, low temperature photoluminescence, and room temperature radiation spectral measurements have been reported earlier.⁷ For the detector performance study, an ^{241}Am source was used. After the measurements, the crystals were sealed in quartz ampoules and annealed at 150°C for 10 hrs under vacuum. The temperature was increased from room temperature to 150°C at a rate of $10^\circ\text{C}/\text{min}$, and it was also cooled down at approximately the same rate. All the measurements were repeated on the samples and compared with the results before annealing.

3. RESULTS AND DISCUSSIONS

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The I-V curves for CdZnTe and CdTe, before and after annealing, are shown in Figures 1 and 2, respectively. Both were fabricated

(a)

(b)

Figure 1. Comparison of the current voltage characteristics of CdZnTe before and after annealing from (a) 0 V to + 100 V, and (b) 0 V to + 5 V.

(a)

(b)

Figure 2. Comparison of the current voltage characteristics of CdTe before and after annealing from (a) 0 V to +100 V, and (b) 0 V to +5 V. with sputtered Au contacts and the current was measured from 0 V to +100 V. The resistivities before annealing in both the samples were of the order of 10^9 ohm-cm, and they were suitable for spectroscopy grade detector performance. We also measured the I-V characteristics of both samples in the low-voltage regime from 0 V to +5 V, as shown in Figures 1(b) and 2(b), in order to evaluate the surface contact resistance and the barrier height.

There is a large increase in the leakage current as is evident from the I-V curves. The barrier height of the metal-semiconductor contact for both CdZnTe and CdTe, is obtained by fitting a theoretical model to the experimental data as shown in Figures 3(a) - 3(d).

Figure 3. $\ln(J) - V$ curves for (a) CdZnTe: before annealing, (b) CdZnTe: after annealing, and (c) CdTe: before annealing and (d) CdTe: after annealing. The solid lines are the theoretical fits to the experimental data used for the calculation of barrier heights (ϕ). R_c is the specific contact resistivity.

The values obtained show a reduction in the barrier height due to annealing. In case of CdZnTe the barrier height is lowered from

0.938 eV to 0.725 eV, whereas for CdTe the reduction is from 0.844 eV to 0.766 eV. At the above mentioned annealing temperatures, Au diffuses into CdTe and CdZnTe and locally dopes the samples which changes the electrical properties of the interfacial layer. This change in the electrical properties results in a reduction of the barrier height.

Figures 4(a) and (b) show the spectral response to ^{241}Am for CZT and CdTe before and after annealing, respectively. It is quite evident that there is a deterioration of the detector performance after the annealing treatment. The barrier height is lowered by heat treatment and this increases the noise in the device, which results in the poor performance of the detectors.

(a)

(b)

Figure 4. Room temperature ^{241}Am spectrum of (a) CdZnTe detector ($A = 0.12 \text{ cm}^2$, $V = 200 \text{ V}$), and (b) CdTe detector ($A = 0.03 \text{ cm}^2$, $V = 100 \text{ V}$). The measurements were obtained before and after annealing. The accumulation time for all the measurements was 250s.

If the changes were confined to the electrode and electrode/semiconductor interfacial layer, then repolishing, etching and refabricating the detectors with new contacts should have enabled us to get back the original detector performance. Since we were unable to retrieve our original detector performance, we believe that the bulk was also modified.

We used low temperature PL measurements to better understand the nature of the processes responsible for the detector degradation. The PL spectra in Figure 5 show that the annealing treatment introduced deep level defects in the crystal. It is generally accepted that

Figure 5. Low temperature photoluminescence spectra of CdZnTe after annealing in vacuum for 10 hrs at 150° C, showing the deep level defects. The PL measurements were taken through the transparent Au electrode.

a larger intensity ratio of $I_{\text{bound exciton}}/I_{\text{defect}}$ indicates a lower density of detrimental carrier traps.¹¹ The $I_{(D^0, X)}/I_{\text{def}}$ value drops from 7 to 1.4 after annealing. The broad band centered at 1.50 eV may be donor-acceptor pair recombination with deeper acceptor impurities (e.g., Cu) or with vacancy impurity complexes ($V_{\text{Cd}}\text{-D}_{\text{Cd}}$, D=Group III or VII element) known as A-centers. IMARAD CdZnTe crystals which were doped with In showed similar features around 1.45 eV.¹² Earlier work on annealing of gold deposited contacts on CdTe¹⁰ at around a temperature of 140° C suggested that this treatment increased the cadmium vacancies (V_{Cd}) due to cadmium sublimation. There is also a possibility that the deep level defects may be due to Cu impurities, since the Au target has 0.0004% of Cu. We believe that the deep level defects at about 1.50 eV introduce more trapping centers in the bulk of the crystal, which hinders the charge collection efficiency and thus results in the degraded performance of the detectors.

4. CONCLUSION

This paper attempts to elucidate the effects of post annealing treatment on the performance of CdZnTe and CdTe radiation detectors. The annealing treatment affects the contact and interface layer, as well as the bulk properties of the material. There is a lowering of the barrier height due to the diffusion of Au in the interfacial layer. This results in an increase in the surface and bulk leakage currents and degrades the detector performance. We have seen that when the annealing only effects the near surface region, one can retrieve the original spectrum by removing a few microns from the surface and refabricating the detectors. When the annealing is performed for a longer time or at a higher temperature, an increase of deep level defects is observed which is accompanied by an irreversible deterioration of the detectors. We would like to mention here that in this case irreversible deterioration implies that in order to regain the detector quality of the material an appreciable amount of material has to be removed by polishing.

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