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Electrical Characteristics and Stability of Cu-electrode Cadmium Telluride Detectors

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In this paper, we report on the electrical stability of cadmium telluride (CdTe) detectors with metal-insulator-semiconductor (MIS) structures using a native oxide layer. Although such electrode structures are formed unintentionally owing to oxide formation during electrode processing, few studies have focused on the long-term stability of MIS structures on CdTe detectors. The CdTe detectors fabricated for evaluation were Cu-electrode detectors formed by the surface treatment of the bulk in atmospheric environments and subsequently evaporating copper on it. The fabricated detectors demonstrated excellent rectifying properties after electrical aging, indicating low electrical stability. In addition, their long-term electrical characteristics were unstable, as their properties change with storage. The direction of these changes was not constant, suggesting that the state of the chemical bond between the CdTe surface, the oxide layer, and the copper electrode can evolve, reflecting the multiple bonding possibilities offered by monovalent and divalent copper ions. These results suggest that other metals, including conventional electrode materials, may experience changes in electrode state over time if they are not completely free of a native oxide layer.

1. Introduction

Cadmium telluride (CdTe) has been used in X-/γ-ray detectors because of its high stopping power and band gap, which are significantly high for room-temperature operations. In practice, p-type CdTe bulk often uses Schottky-type electrodes (In, Al) for high-energy resolution[(1–3)] and Ohmic-type electrodes (Au, Pt) for stable operations.[(4,5)] These electrodes can be categorized into those with low and high Schottky barrier heights. However, rectifying properties can be obtained regardless of the metal work function using plasma treatment or metal-insulator-semiconductor (MIS) structures.[(6,7)] In particular, the formation of an unintended native oxide layer during the electrode process can result in MIS structures. However, few studies have

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focused on the long-term stability of MIS structures in CdTe. The long-term stability of CdTe, often referred to as polarization for historical reasons,[4,8] remains a challenge in practical applications and is a subject of ongoing debate. The mechanism of this phenomenon has been analyzed using the charge-accumulation[9,10] and Shockley–Read–Hall models,[11] which assume that the electrode-bulk junction is stable. Therefore, the stability of MIS structures containing native oxide layers must be evaluated. In this study, we used copper as an electrode, performed bulk surface treatment in an atmospheric environment, and evaluated the long-term stability of its electrical characteristics.

2. Materials and Methods

The Au/Cu//p–CdTe//Au (Cu–CdTe) detector was fabricated on a p-type CdTe crystal from Acrorad Co., Ltd. The crystal surface was initially treated with Br-methanol, which produces a Te-rich layer. [9,12] It is speculated that a native oxide layer subsequently formed on this surface upon exposure to air. The notation "//" in the device structure indicates this native oxide interface. Figure 1 shows the structure of the fabricated Cu–CdTe detectors. The planar copper electrode on the B-face of the crystal was coated with a gold layer. A 2 × 2 mm^2 gold electrode with a guard ring was formed on the opposite side by photolithography and vacuum deposition. The detector has 0.75 mm thickness (mmt). The electrical characteristics of the fabricated detectors were measured at room temperature using Keysight B1505A. The γ-ray spectra were measured at room temperature using ANSeeN CSP02 and ZMCAN-CH04-01.

Electrical aging was performed on the fabricated Cu–CdTe detectors, involving repeated cycles of applying a bias voltage for an extended period followed by a discharge phase. The steps of the aging process were as follows:

1. fabrication of the Cu–CdTe detector,
2. measurement of current–voltage characteristics,
3. application of reverse bias for 12 h, ensuring that the leakage current does not exceed a limit of 1 μA,
4. holding at 0 V bias for 10 min for discharge, and

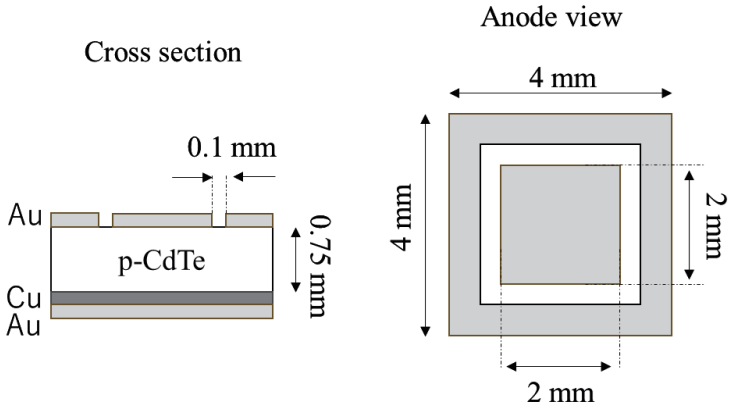

Fig. 1. Structure of fabricated Cu–CdTe detectors.

5. repetition of steps 2–4 until the leakage current stabilized (i.e., showed no significant change between consecutive measurements).

The "absolute current density"–time (*J*–*t*) characteristics during aging at −300 V for 12 h are plotted in Fig. 2, corresponding to Step 3 of the aging process. The leakage current decreases exponentially with time, and this trend is expected to continue. Note that the leakage current decreases further when the detector is discharged after aging. This result is attributed to the negative charge accumulation, which contributes to the polarization. By discharging the detector, the accumulation is eliminated, and the "absolute current density"–voltage (*J*–*V*) characteristics return to their neutral state. Consequently, the aging process leads to instability in the electrical characteristics of the Cu–CdTe detector. Figure 3 shows the *J*–*t* characteristics of the fabricated detector during discharge at 0 V after long-term reverse bias application, corresponding to Step 4 of the aging process. The current remains stable after discharge for 400 s. Therefore, a discharge time of 600 s is sufficient to measure the *J*–*V* characteristics.

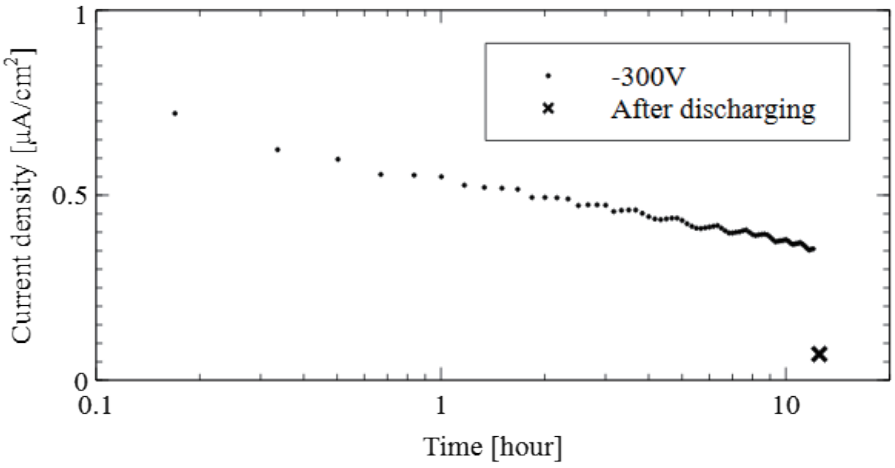

Fig. 2. *J*–*t* characteristics of Cu–CdTe detector during electrical aging at −300 V.

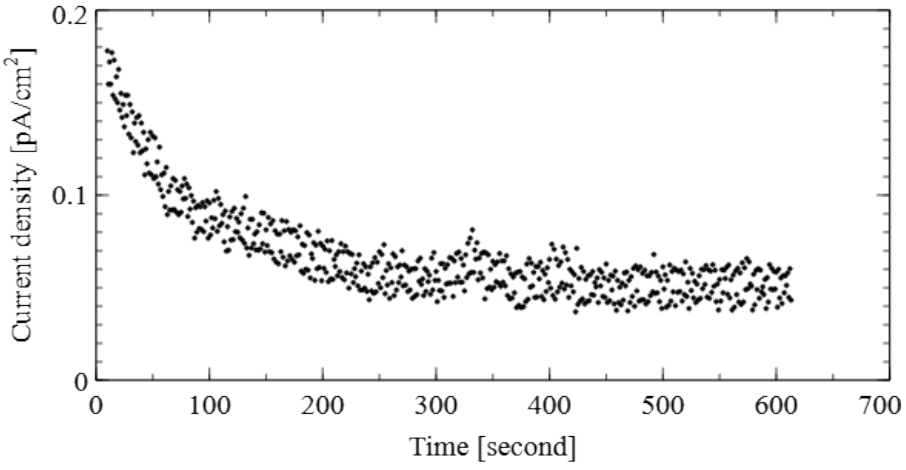

Fig. 3. *J*–*t* characteristics during discharge at 0 V.

3. Results and Discussion

Figure 4 shows the *J–V* characteristics of the fabricated Cu–CdTe detector. The initial reverse-bias current (dotted line) was significantly higher than that of conventional In-/Al-Schottky CdTe detectors. Conventional leakage currents were plotted by calculating the current density from the values published by Acrorad,[13] considering the difference in detector thickness. Electrical aging was performed on this detector multiple times in 12-h increments while gradually increasing the voltage from −400 to −900 V. The leakage current after this operation (dashed line) decreased to the conventional Schottky level. Moreover, no significant changes in forward current were observed. The current of the fabricated detector was greater than that of the effective detector resistivity of conventional Ohmic types (solid-line), 2×10^9 Ωcm.[14] However, it was lower than the forward current of a conventional In-Schottky detector (circles), measured with a 2 mm × 2 mm × 0.75 mmt-sized detector without a guard ring from Acrorad. This tendency is attributed to the presence of an insulator.[7]

Figure 5 shows the *J–V* characteristics of the aged Cu–CdTe detector after four months of storage. The withstand voltage decreased from 1000 to approximately 600 V. This implies that the aged and thermal equilibrium states differ. Figure 6 shows the *J–V* characteristics of another Cu–CdTe detector before and after aging. The aging process for this sample was terminated at −200 V because the leakage current flowing into the guard ring reached the predefined limit of 1 μA. The freshly fabricated detector changed in the direction of decreasing leakage current after being stored for one and two weeks. During subsequent electrical aging, the current decreased further. However, the current increased toward the pre-aging value after being stored for two months. This means that the thermal equilibrium state of Cu–CdTe detectors is relatively close to the initial state and is clearly different from the aged state.

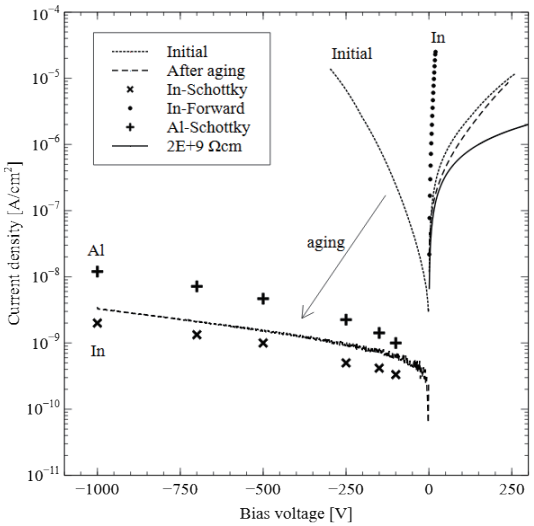

Fig. 4. *J–V* characteristics of Cu–CdTe detector before and after electrical aging.

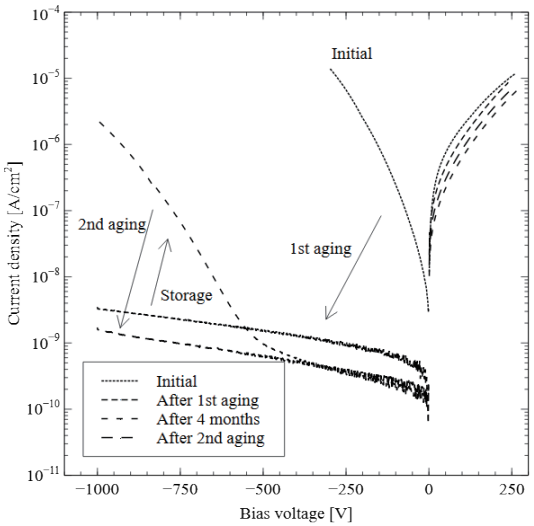

Fig. 5. *J–V* characteristics of Cu–CdTe detector after four months of storage and after second aging.

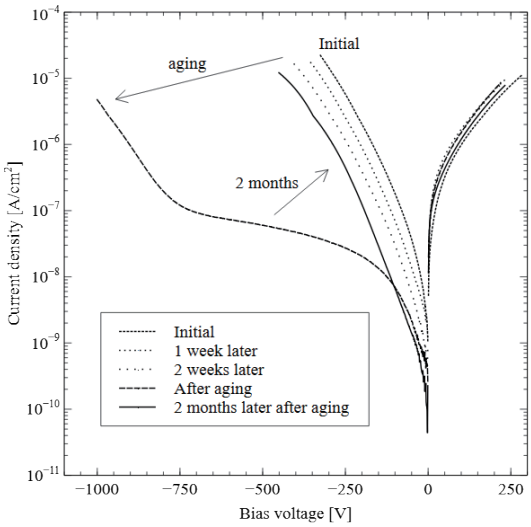

Fig. 6. *J–V* characteristics of another Cu-CdTe detector before and after aging.

Note that γ-ray measurements can be performed normally even after electrical aging. Figure 7 shows the measurement result of the γ-ray spectrum of ^{241}Am using an aged Cu–CdTe detector biased at −900 V. The energy resolution at 60 keV is 2.5 keV full width at half maximum.

As described above, the fabricated Cu–CdTe detector achieved excellent rectifying properties through electrical aging. However, changes in electrical characteristics due to the application of bias voltage and storage reveal that the detector has low electrical stability. Gold has a significantly lower diffusion coefficient in CdTe[15] and a lower ionization tendency than copper. Therefore, copper is assumed to be the primary species responsible for the observed changes in the fabricated detector. Furthermore, the reversibility observed after electrical aging and long-term storage (Fig. 5 and Fig. 6), coupled with the detector's normal operation post-aging (Fig. 7), suggests that copper did not diffuse into the CdTe bulk. Instead, it likely diffused into the native oxide layer and interacted at the CdTe surface.

The resulting MIS structure, where the native oxide containing diffused copper acts as the insulator, effectively explains the measured electrical properties. The insulator provides rectifying properties regardless of the work function of the metal[16] and leads to forward currents lower than those of conventional Schottky detectors.[7] In addition, the observed fluctuations in rectifying properties suggest that the insulator has two or more states, which are formed by the chemical bond between the CdTe surface, the oxide layer, and the copper electrode, particularly multiple chemical bonding modes based on monovalent (Cu^{+}) and divalent (Cu^{2+}) copper ions corresponding to the states of reverse current. Another possible structure is the acceptor concentration at the interface due to copper diffusion, as used in the back contact of solar cells.[17,18] However, such a highly doped layer leads the Cu electrode to the ohmic contact, and this structure cannot explain the two states of rectifying properties. Consequently, the MIS structure better explains the measured electrical characteristics. Nevertheless, it should be emphasized that this represents only one possible model to account for observed characteristics. Elucidating the underlying physical behavior of the electrode through detailed physical analysis remains a crucial objective for future studies.

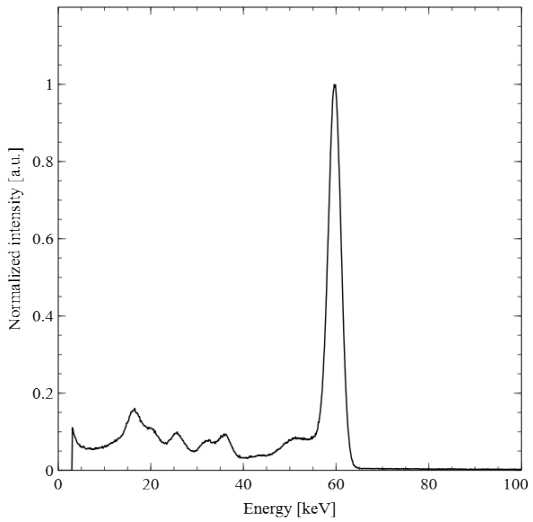

Fig. 7. Measurement result of γ-ray spectrum of ^{241}Am using aged Cu–CdTe detector biased at −900 V.

5. Conclusions

In this study, we evaluated the electrical characteristics and stability of CdTe detectors subjected to surface treatment in atmospheric environments. Our findings indicate that electrical aging leads to rectifying properties that are independent of the work function. In addition, the long-term electrical characteristics are unstable, as they change with the storage duration, indicating low electrical stability. The significant changes observed in this study suggest the multiple chemical bonding modes based on monovalent and divalent copper ions within the Cu electrode. Considering that most metals, including conventional electrode metals, can exist in at least two states (oxidized and reduced), it is suggested that other metals may also change the electrode state over time if they are not completely free of the native oxide layer. Conversely, the excellent rectifying properties obtained via the interaction between the metal and a simple native oxide layer by electrical aging indicate that a wider variety of metals can be used as electrodes for improved energy resolution.

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