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Special Issue Paper

Growth of Thick Epitaxial CdTe Films by Close Space Sublimation

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This paper reports on a detailed study of the development of the close space sublimation method, which has been widely used in the preparation of polycrystalline CdTe/CdS solar cells, as an epitaxial method for the growth of thick CdTe single crystal films over 200 μm on GaAs and Ge substrates for high-energy radiation detectors. The resulting microscopic growth phenomena in the process are also discussed in this paper. High-quality single crystalline CdTe thick films were prepared with x-ray rocking curves full width at half maximum (FWHM) values, which were ~100 arcsec on Ge substrates and 300 arcsec on GaAs substrates. The quality of thick films on Ge(100) showed a substantial improvement with nucleation in a Te-rich growth environment. No Te inclusions in the CdTe films grown on GaAs(211)B and Ge(100) were observed with IR transmission imaging. Photoluminescence of CdTe/Ge shows a large reduction in the 1.44 eV defect energy bands compared with films grown on GaAs substrates. The film resistivity is on the order of 10^{10} Ω cm, and the film displayed some sensitivity to alpha particles.

Key words: CdTe, detector, epitaxy, thick film

INTRODUCTION

There is a growing interest in epitaxially grown thick semiconductor films (0.1–1 mm) that may be used in room-temperature γ-ray and x-ray radiation detection as an alternative to bulk crystal CdTe and CdZnTe, which often contain various structured defects.[1] An epitaxial growth method for the preparation of such single crystalline thick films should have the following characteristics: (1) the growth rate should be variable from 1 μm/h to ~100 μm/h, i.e., a lower growth rate for the nucleation stage in the hetero-epitaxy process and a higher growth rate for increasing the thickness efficiently; (2) the growth setup, as well as the source materials, should be cost effective so that the thick films are competitive with the bulk materials available in the market; (3) a homogeneous and stable growth interface in both its composition and temperature, to ensure uniformity and, ideally, freedom from defects that would severely degrade the performance of the device. Well-established epitaxial methods, such as molecular beam epitaxy and hot wall epitaxy (HWE), suffer from low growth rates, and, while metal organic vapor phase epitaxy is capable of high growth rates, it requires substantial amounts of expensive source materials for prolonged growth.

In contrast, close space sublimation (CSS) is both comparatively inexpensive and capable of high deposition rates and, as a result, has been widely used in the preparation of poly-crystalline CdTe for solar cells.[2] As its growth interface is subject to a high vacuum environment, the mass transport may become very dynamic, and the problem of composition changes at the interface after a long period of growth, which occurs in most of the semi-open or enclosed physical vapor transport (PVT) systems, is less of an issue. Thus, the growth interface is less

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favorable for the formation of Te inclusions. However, this may lead to non-uniform and unstable mass transport patterns at the low growth rates that are necessary for the critical nucleation process, which can then easily become out of control and promote the formation of polycrystalline films. Therefore, there have been few reports on the growth of single crystal films by CSS. Recently, we have developed the CSS method into a viable method for the epitaxial growth of CdTe films,[3] hereafter, modified close space sublimation (MCSS). This paper reports on the growth and characterization, including the structural perfection, reduction of the number of Te inclusions, and electrical properties.

EXPERIMENTAL

In the MCSS method, two pyrolytic boron nitride heaters were clamped by hot-pressed boron nitride blocks. The flat surfaces of the blocks ensured uniform temperature distribution across both substrates and source materials. The mass flow pattern was constrained by reduction of the source–substrate distance to ~1 mm, together with the use of substrate and source heaters. The improved confinement on mass transport allowed a growth rate as high as 50 μm/h to be established. Different substrates have been used for the demonstration of epitaxy growth by MCSS and include multigrain CdTe seeds with a primary orientation of [311] for homo-epitaxial growth and high-mismatched (>12%), mis-oriented GaAs(100), GaAs(211)B, 6° mis-oriented Ge(100) toward (111), and 4° mis-oriented Ge(100)/Si(100) toward (111) for hetero-epitaxy. A similar etching process to that reported by Tatsuoka et al.[4] was used for GaAs substrates, but the Ge substrates were treated with either diluted HCl (17%) or H_2O_2 (30%) followed by thermal etching in the growth system. All the wafers were immediately loaded into the growth chamber, which was pumped to $\sim10^{-6}$ mbar, without any background gas. The substrate temperatures ranged from 350°C to 500°C, and the source temperature was tuned between 500°C and 600°C for optimization of the growth rate. It has been suggested that the initial reaction between Te and Ge atoms may help the formation of high-quality epilayers through the reduction of anti-phase domain defects.[5,6] Thus, Te-rich CdTe polycrystalline sources were also used in comparison with the usual stoichiometric ones, as the former may promote an efficient Te–Ge bonding process at the initial nucleation stage. The surface morphology was inspected by scanning electron microscopy (SEM), while film quality was further assessed by high resolution x-ray diffraction (HRXRD) using a Bede D1 (Cuα1, beam diameter 3 mm). Photoluminescence spectra were recorded with an Ar^+ laser (λ = 514.5 nm, 10–20 mW). The resistivity was measured by the *I–V* method using a Keithley source meter.

The substrates, as well as the highly strained CdTe–substrate interface, were carefully removed for the measurement of electrical properties and the inspection of Te inclusions. After an as-grown surface had been hydroplane polished in a bromine–methanol solution (1.5%), a gold contact was evaporated onto the mirror-like surface without any treatment or passivation. This was then bound to a stainless-steel disk using a silver-loaded epoxy and buried in resin, leaving the substrate for mechanical removal. Finally, the substrate was carefully polished, while the resin block and the epoxy protected the CdTe layer from any mechanical shock. Once again, the polished surface was etched with bromine–methanol solution and coated with a thin gold layer that acted as another electrode. In preparing the samples for observing Te inclusions, we adopted a similar process to the one above, except that a polished CdTe surface, as well as its substrate, was bound to a glass slide with optical glue and no gold deposition. However, during dissolution of the resin block for IR transmission measurement in acetone, cracks were generated in the film or some regions of the film came off from the optical slide.

RESULTS AND DISCUSSION

Growth Surface Morphology

Figure 1a is an SEM image of a CdTe layer grown on a multigrain (311) CdTe substrate. The surface morphology is similar to that observed on molecular beam epitaxy (MBE)-grown CdTe(311)/GaAs(311) by Tromson-Carli et al.[7] HRXRD proved that the resulting film on the multigrain seed was (311) oriented, providing evidence of homo-epitaxy. The CdTe(100)/Ge(100) epilayers looked smooth and shiny, though slightly curved due to a higher deposition rate at the center. However, when SEM was utilized, 'ridges' were observed, perpendicular to the (011) direction. Since (100) facets tend to appear as the epitaxial growth surface, the ridges have to be formed to accommodate the appearance of the (100) plane on the 6° mis-oriented Ge(100) substrates toward (111). Some interesting growth behaviors were observed in CdTe layers grown on GaAs(211)B and Ge/Si(100) substrates. In the latter case, large surface features appeared as hillocks or inverted tetragonal pyramids embedded in the film (Fig. 1b). These have not been observed on the surface of CdTe(100)/Ge, and it is possible that these defects were related to imperfections in the chemical vapor deposition (CVD)-grown Ge layers, which have yet to be identified. The growth morphology of CdTe(211)B/GaAs(211)B structures (Fig. 1c) exhibit growth steps, as expected, although the steps are irregular due to a higher growth rate when approaching the center of the sample. The steps are decorated with micron-scale structures and terraces. The fine structures (Fig. 1c) were not observed on the steps of CdTe(211)B/GaAs(211)B layers grown by HWE,[8] where the (111)B facets

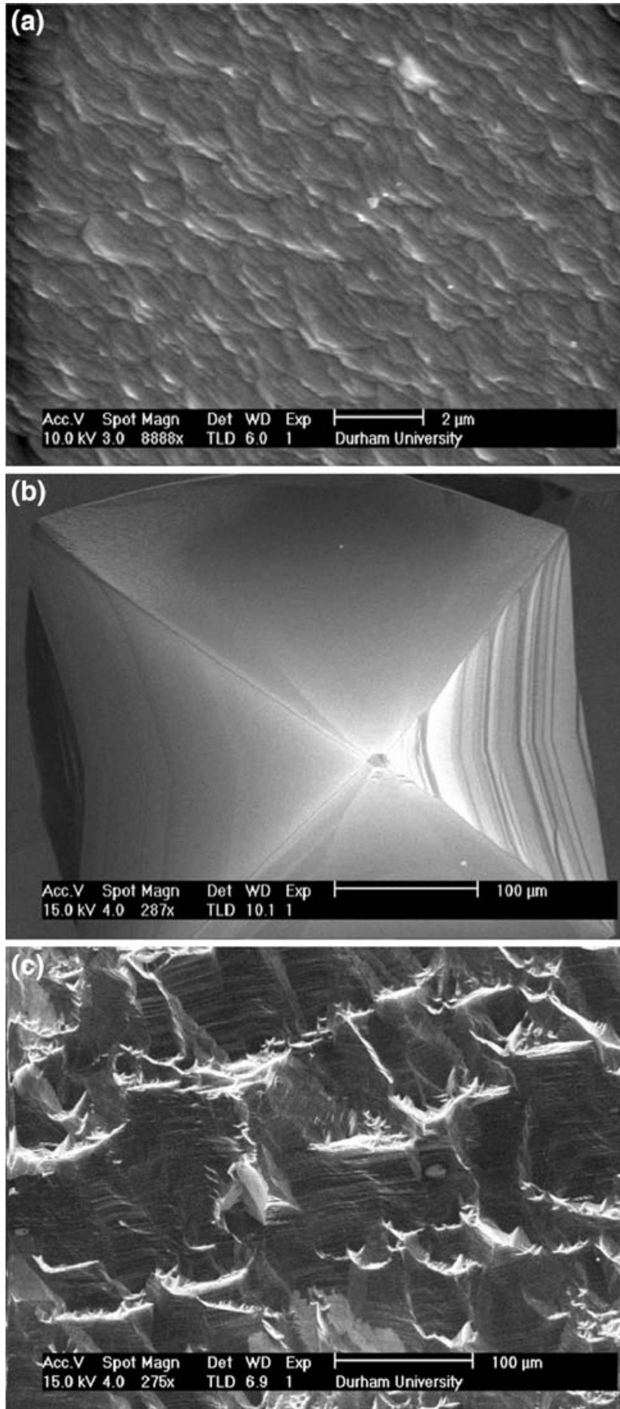

Fig. 1. (a) Homo-epitaxial growth morphology of CdTe(311). (b) Point defects in CdTe/Ge/Si(100) epilayers. (c) Hetero-epitaxial growth morphology of CdTe(211)B/GaAs(211)B.

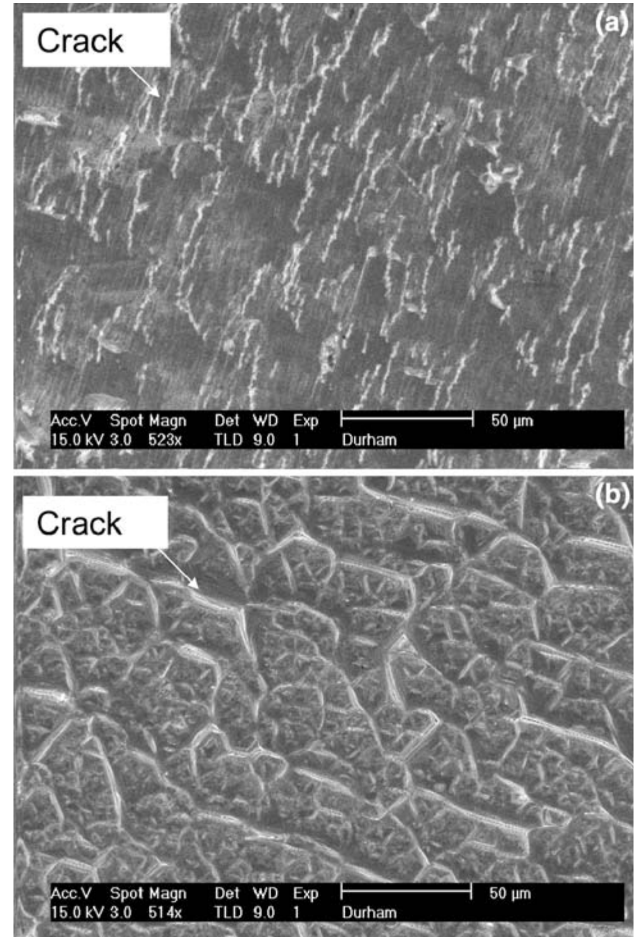

Fig. 2. 'Dual epitaxy' growth on GaAs(100). (a) (100) Growth pits; (b) (111)B growth pits. Crack lines, which were induced by the different thermal expansion, appear parallel to each other in a CdTe(100)/GaAs(100) epilayer while parallel or with an angle of ~120° in a (111)B/GaAs(100) epilayer.

were flat faces. The reason for this difference has yet to be identified.

Dual Epitaxy

The occurrence of so-called dual epitaxy on a single substrate, which has been reported in a series of studies,[9,10] may lead to thick films of poor quality. During MCSS growth using mis-oriented GaAs(100) substrates, (111)B and (100) regions (Fig. 2) (thickness: ~50 μm) were found on a single GaAs(100) substrate, in spite of the same growth and wafer processing conditions. This is not yet fully understood, but it may be related to some unknown non-uniformity in the commercial GaAs wafers. Therefore, mis-oriented GaAs(100) substrates were not selected for thick CdTe film growth. 'Dual epitaxy' may also occur on Ge(100) substrates[10] and leads to the coexistence of (100) or (331) oriented films. However, this was not generally seen in our study, although occasionally weak (331) XRD peaks, similar to the level of the background noise, were observed under conditions of large beam size and flux (typically 45 kV/40 mA) in a double axis configuration. Thus, the quality of CdTe(100)/Ge(100) does not appear to be degraded by the 'dual epitaxy' phenomenon. Furthermore, we found no evidence for the coexistence of CdTe(331) and CdTe(211)B on GaAs(211)B substrates.

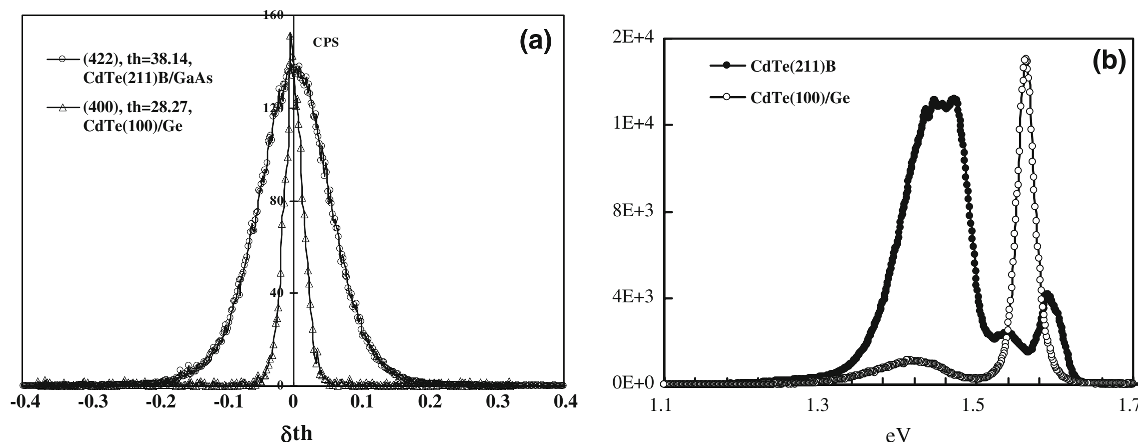

Fig. 3. (a) Rocking curves of CdTe(100)/Ge and CdTe(211)B/GaAs. (b) The PL spectra of CdTe(100)/Ge and CdTe(211)B/GaAs.

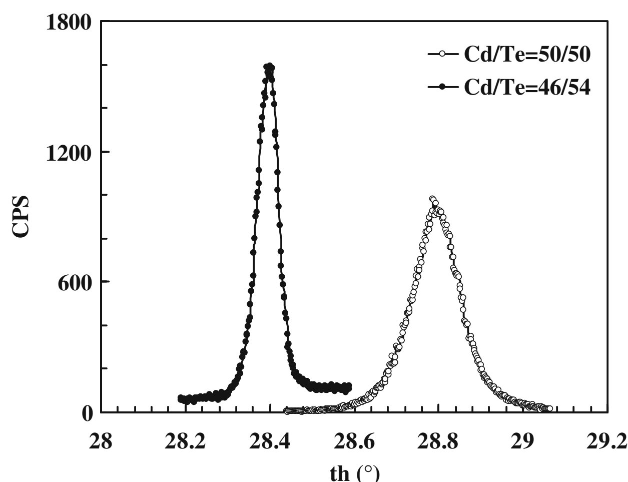

Fig. 4. Rocking curves of CdTe(100)/Ge epilayers show improved epilayer quality by the usage of Te-rich sources.

Epilayer Quality

Figure 3a shows the typical rocking curves of ~250 μm thick CdTe/Ge(100) and CdTe/GaAs(211)B films, with full width at half maximum (FWHM) values of ~100 arcsec and 300 arcsec, respectively. Because of their greater thickness (>250 μm) than those grown on GaAs(100) (~50 μm) (Fig. 2), the films did not shown any cracking during post-growth cooling, as verified by SEM imaging. Therefore, the thermal strains may exist in both the substrate and the epilayer and explain the measured values of FWHM. The photoluminescence (PL) spectra of CdTe epilayers on both Ge(100) and GaAs(211)B are shown in Fig. 3b. CdTe/Ge(100) exhibits a standard CdTe PL of high-quality CdTe materials, without any defect peaks such as 'A-center.' However, CdTe(211)B/GaAs shows a peak at 1.4 eV, the nature of which has yet to be investigated.

It has been shown by Bhat and Wang[11] that a higher substrate temperature can promote the initial bonding between Te and Ge atoms so that the population of so-called anti-phase domain defects may be reduced. In this work, a single Ge substrate was placed between two CdTe sources of different

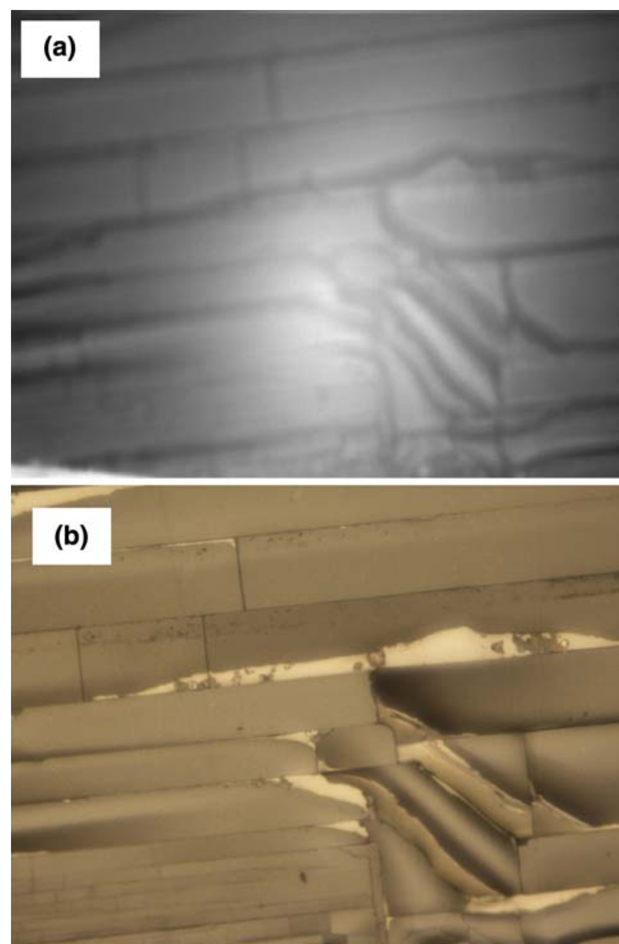

Fig. 5. (a) IR transmission image of the CdTe epilayer (0.712 × 0.543 mm^2) after the Ge substrate had been removed. (b) Surface image of a CdTe(100) epilayer. The cracks appearing in the film were caused by the reaction between the optical glue and the acetone used in dissolving the resin block.

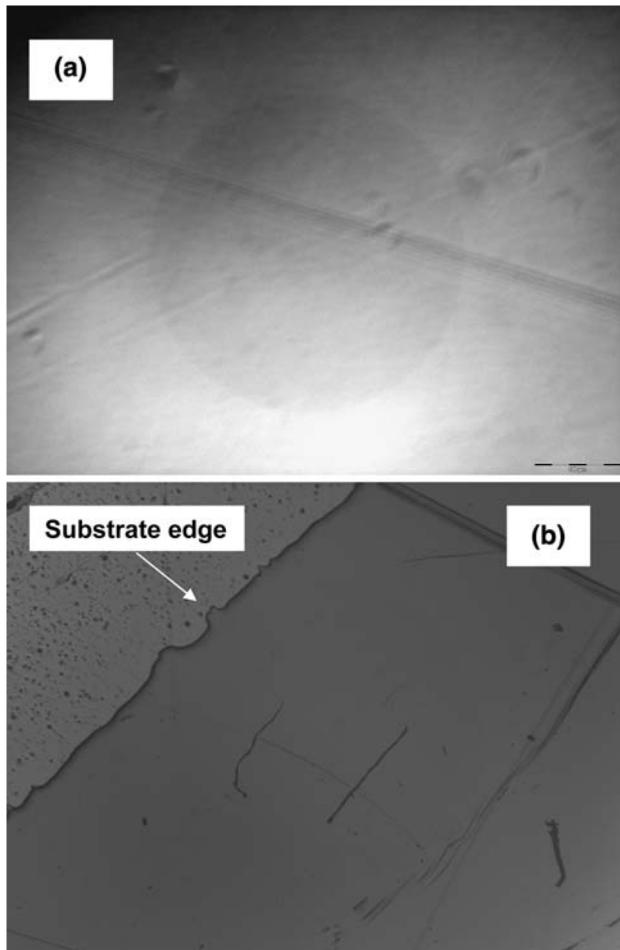

Fig. 6. (a) IR transmission image (0.712 × 0.548 mm^2) of the part of the CdTe epilayer without the GaAs substrate. (b) Surface image of a CdTe(211)B/GaAs(211)B epilayer after the GaAs substrate has been partially removed.

Cd/Te ratios during the growth. Thus, any difference in the quality of the epilayers was assumed to be caused solely by the ratio of Cd/Te in the source materials. The region grown with a Te-rich source (Cd:Te = 46:54) had a smaller FWHM (150 arcsec) than that grown with a stoichiometric CdTe source (~500 arcsec), as shown in Fig. 4. This confirms the notion that a Te-rich environment also promotes the bonding of Te onto the Ge surface for improved film quality. The difference in peak positions is more likely due to the curvature that was formed in the cooling process because of the different thermal expansion coefficients of CdTe and Ge.

Reduction in Number of Te Inclusions

Te inclusions or precipitates of a few microns to tens of microns in size often appear in commercially available CdTe or CdZnTe crystals and have been a consistent issue, as they reduce the critical parameter $\mu\tau$.[12] Figure 5a is the IR transmission image of a CdTe film (~100 μm) after the Ge substrate had been removed, in comparison with its surface reflection image (Fig. 5b). Figure 6a is the IR transmission image of a CdTe film whose substrate had been partially polished to form a wedge, while Fig. 6b is the surface reflection image. In both cases, no Te inclusions or Te-decorated grain boundaries were observed by this IR transmission method. This may have been due to the dynamic mass transport that prevented Te atoms from accumulating locally on the growth surface.

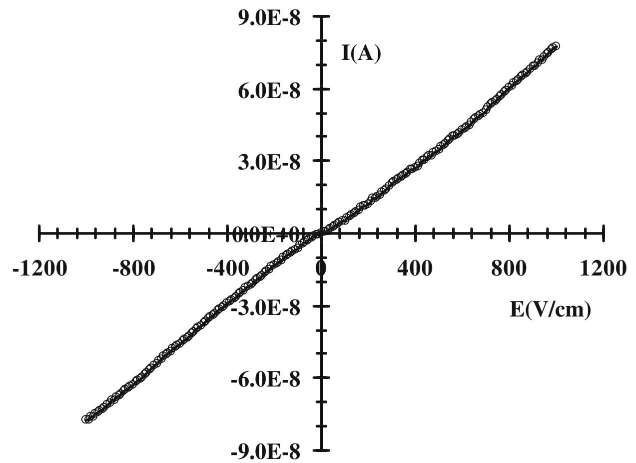

Fig. 7. *I–V* characteristics of a ~100 μm thick CdTe layer showing the resistivity at the order of 10^{10} Ω cm. The top electrode area was ~1 cm^2.

Electrical Property

Figure 7 is the *I–V* curve of a CdTe thick film (~100 μm), and its resistivity is on the order of 10^{10} Ω cm, which is ideal for x-ray or γ-ray detection. Furthermore, the thick film has shown a response to particles from ^{241}Am—further experiments are being conducted.

CONCLUSIONS

In conclusion, we have adapted the cost-effective CSS method to a reliable epitaxial deposition method for the growth of high-quality, highly-resistive, CdTe epilayers a few hundred microns thick. Particularly, thick films appeared to exhibit a low density of Te precipitates or precipitate-decorated grain boundaries, suggesting that thick CdTe epilayers are potentially a class of radiation detection materials with a unique character.

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