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Atomic Structure of Twin Boundaries in CdTe

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Atomic Structure of Twin Boundaries in CdTe

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ABSTRACT

Using the combination of high-resolution transmission electron microscopy, first-principles density-functional total energy calculations, and image simulations, we determined the atomic structure of lamellar twin and double-positioning twin boundaries in CdTe. We find that the structure of lamellar twin boundaries has no dangling bonds or wrong bonds; thus, it results in negligible effects on the electronic properties. The structure of double-positioning twin boundaries, however, contain both Cd and Te dangling bonds, and therefore produce energy states in the bandgap that are detrimental to the electronic properties of CdTe.

1. Introduction

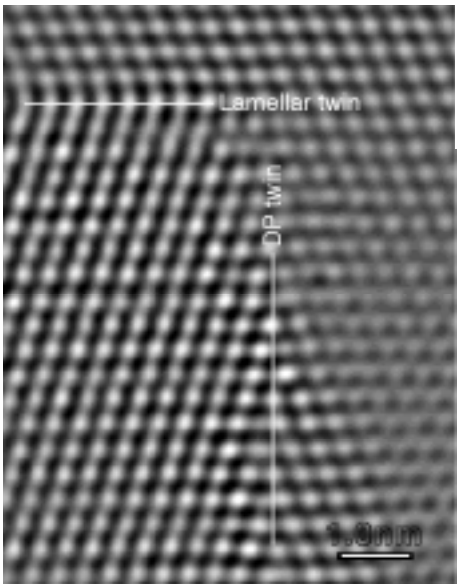

Fig. 1 HRTEM image showing a lamellar twin boundary and a double-positioning (DP) twin boundary.

It is known that as-grown CdTe thin films have very poor electrical quality [1]. In solar-cell device fabrication, one of the process steps critical to achieving high efficiency is a post-deposition heat treatment in $CdCl_2$. This result indicates that defects in the as-grown CdTe films have profound effects on the electrical and optical properties of the material. The role of the post-deposition heat treatment, however, remains ambiguous, although it is crucial for improving solar cell efficiency. It was reported that the density of extended defects, mainly planar faults, in CdTe films decreases after the treatment [2]. However, our previous work showed little difference in the structural properties. Thus, to fully understand the mechanism of the post-deposition heat treatment, it is necessary to understand the details of the extended defects. So far, the most-reported extended defects are mainly lamellar twin boundaries and double-positioning twin (DP twin) boundaries, as shown in Fig. 1. In this report, we present an atomic structural determination of both lamellar twin boundaries and DP twin boundaries using the combination of high-resolution transmission electron microscopy (HRTEM), first-principles density-functional total energy calculations, and image simulations.

2. Experimental and Methods of Calculation

TEM specimens were prepared by mechanical polishing to a thickness of ~100 μm, then dimpling the central portion of the specimens down to ~5 μm. The samples were subsequently thinned to electron transparency using a 4-kV Ar ion-beam at 14° inclination, then cleaned at a lower voltage (1.5 kV). A liquid N_2 cooling stage was used to minimize milling damage. HRTEM images were taken on a Philips CM30 microscope with a Cs=2.0 mm, operating at 300 kV. The image simulations were carried out using the EMS and MacTempas program packages [3]. The density-functional total energy calculations were done using the Vienna *ab-initio* Simulation Program (VASP) [4]. We used the local density approximation for the exchange correlation, and ultrasoft Vanderbilt-type pseudopotentials [5] as supplied by Kresse and Hafner [6]. A suitable cutoff energy for the plane-wave basis was determined to be 290 eV.

The initial structural models for lamellar twin and DP twin boundaries are obtained directly from the HRTEM images. However, there usually exist a few structure models that could fit the images. We then relax all the initial models using first-principles density-functional total energy calculations. Only the structural models that are proven to be stable are kept for HRTEM image simulations. The structural models are then determined by fitting the simulated images with the HRTEM images.

3. Atomic Structure of Lamellar Twin Boundaries

Figure 2(a) is an enlarged HRTEM image showing the details of a lamellar twin boundary lying on a (111) plane, as indicated by a white line. The image is viewed along the $[1\bar{1}0]$ zone axis. Through-focus and through-thickness image simulations showed that the value of defocus is about 60 nm, and the specimen thickness is about 10 nm for the image. It is clearly evident that the two crystals adjacent to the boundary show a 180° rotation in the [111] direction, indicating that this boundary is likely to be a lamellar twin boundary. The inset in Fig. 2(a) is the simulated image of the lamellar twin boundary structure model shown in Fig. 2(b) at a defocus of -60 nm for a thickness of 10 nm. First-principles density-functional total energy calculations reveal that there is no expansion or compression perpendicular to the twin boundary included in the structure. The good fit

demonstrates that the boundary shown in Fig. 2(a) is indeed a lamellar twin boundary. The lamellar twin boundary contains no dangling bonds or wrong bonds. Thus, it does not produce defect states in the bandgap. It is expected that lamellar twin boundaries should not have significant detrimental effects on the electronic property of CdTe thin films. Because the Cd-Te bonds are preserved through the boundary, a lamellar twin boundary usually has very low formation energy. Thus, lamellar twin boundaries are often observed in CdTe thin films.

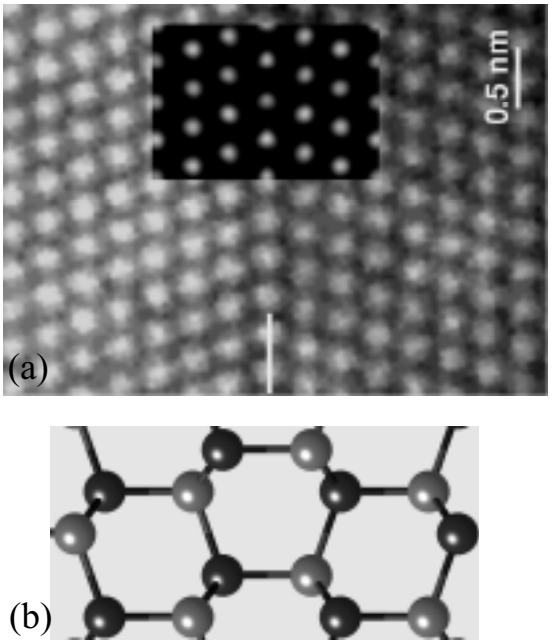

Fig. 2 (a) HRTEM image of a lamellar twin boundary; (b) Structure model for the lamellar twin boundary.

4. Structure of Double-Positioning Twin Boundaries

Figure 3(a) is an enlarged HRTEM image showing the details of a double positioning twin boundary lying on a $(11\bar{2})$ plane, as indicated by a white line. The image is viewed along the $[1\bar{1}0]$ zone axis. The DP twin is formed by a 180º rotation about the [111] normal direction. It is clearly evident that the two crystals adjacent to the boundary show a 180° rotation in the [111] direction. From the HRTEM image, the relationship between the two sides of the boundary can be determined. However, the atomic structure of the boundary remains unclear. Four possible structures are obtained from the image. These four structures are relaxed by first-principles density-functional total energy calculations. Only one of these structures is found to be stable. Its optimized structure is shown in Fig. 3(c). Figure 3(b) is the simulated image of the DP twin boundary structure model shown in Fig. 3(c) at a defocus of -65 nm for a thickness of 50 nm. The simulated image fits very well with the HRTEM image. Thus, the combination of first-principles density-functional total energy calculations and HRTEM image simulation demonstrates that the atomic structure shown in Fig. 3(c) is a convincing model for the DP twin boundaries. It is seen that DP twin boundaries contain both Cd and Te dangling bonds. These dangling bonds result in defect states in the bandgap of CdTe that could trap both electrons and holes. Thus, DP twin boundaries are detrimental to the electronic properties of CdTe. However, because of the existence of dangling bonds, the DP twin boundaries have much higher formation energies than the lamellar twin boundaries. The density of DP twin boundaries is expected to be much lower than those of the lamellar twin boundaries.

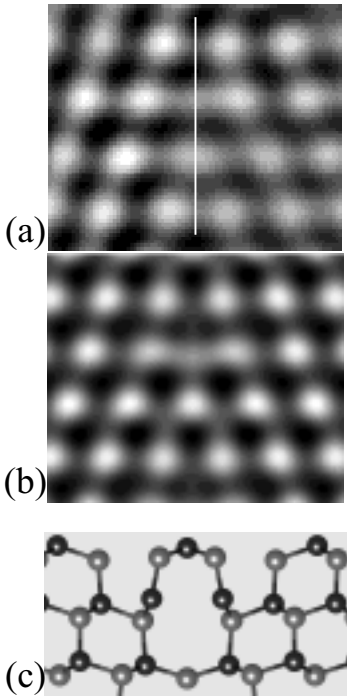

Fig. 3 (a) HRTEM image of a DP twin boundary; (b) Simulated image using the structural model in (c); (c) Structural model relaxed by first-principles density-functional total energy calculation.

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