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$[1\bar{1}00]/(11\bar{2}2)$ Twin Boundaries in Wurtzite ZnO and Group III-Nitrides[a]

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ZnO is a useful material for optically transparent conducting layers in displays and photovoltaic devices. So far, most ZnO thin films and bulk crystals have been found to contain a high density of extended defects, such as stacking faults, dislocations, and twin boundaries [1]. It has been reported that in bulk ZnO synthesis, $[1\bar{1}00]/(11\bar{2}2)$ twin boundaries are often present, resulting in zigzagged morphology [2]. Here, we present our studies on the atomic structure and electronic effects of the $[1\bar{1}00]/(11\bar{2}2)$ twin boundaries in wurtzite ZnO and group III-nitrides using the combination of high-resolution Z-contrast imaging, first-principles density-functional total-energy calculations, and image simulation. We find that the $[1\bar{1}00]/(11\bar{2}2)$ twin boundary has a head-to-tail polarity configuration, which avoids dangling bonds, leading to a low twin-boundary energy of 0.040 J/m^2. We further find that the head-to-tail polarity configuration can be more generally adopted for this twin boundary in other wurtzite materials, such as the group III-nitrides. However, the twin-boundary energies, 0.109 J/m^2 in AlN, 0.107 J/m^2 in GaN, and 0.051 J/m^2 in InN, are significantly higher than in ZnO. These results suggest that the $[1\bar{1}00]/(11\bar{2}2)$ twin boundary is easier to form in ZnO and InN than in AlN and GaN. Investigations of the electronic structure reveal that the twin boundary does not introduce localized energy states in the bandgap in either ZnO or the wurtzite III-nitrides.

Figure 1(a) shows a Z-contrast image of a $[1\bar{1}00]/(11\bar{2}2)$ twin boundary in ZnO along the $[1\bar{1}00]$ zone axis. The twin boundary is indicated by the white dashed line. Each bright spot in this image is the projection of a single column of Zn atoms. The distance between a Zn column and its nearest O column in the bulk in this projection is only 0.61 Å; hence, the O columns cannot be resolved, but the bright Zn columns in the Z-contrast image clearly exhibit an elongated shape due to the closely spaced O columns. The two black solid lines indicate a (0002) plane at each side of the boundary. It is seen, interestingly, that the two sides of the boundary are not mirror images, which is what one would expect from a simple twinning operation. The two planes have a relative shift along the twin boundary. This is clear by comparing the black solid line and the black dashed line on the right side of the twin boundary. The black dashed line is in the ideal twin position of the black solid line on the left side of the twin boundary.

Figure 1(b) shows the atomic structure of the $[1\bar{1}00]/(11\bar{2}2)$ twin boundary in ZnO determined by Z-contrast image simulation and twin boundary energy calculations. The structure has the head-to-tail ($\searrow|\nearrow$) configuration. Here, the arrows indicate the polarities. The black balls denote O atoms, whereas the gray balls denote Zn atoms. The structure contains no Zn-Zn or O-O wrong bonds and

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dangling bonds. The twin-boundary energy is calculated by $E_{TB} = (E-E_{bulk})/2A$, where E is the total energy of a supercell containing two boundaries, E_{bulk} is the total energy of a reference supercell with bulk structure and with an equivalent number of atoms, and A is the area of the periodic unit cell of the boundary. We found that the structures with (↘|↙) or (↙|↘) configurations have much higher boundary energies than the (↘|↗) configuration. Thus, the combination of Z-contrast imaging, image simulation, and total-energy calculations convincingly determine that the $[1\bar{1}00]/(11\bar{2}2)$ can only have the structure shown in Fig. 1(b).

The electronic structures of the structures with different configurations are investigated. We find that the head-to-tail structure shown in Fig. 1(b) does not introduce any energy level in the bandgap, because this structure does not have any dangling bonds. Thus, this twin boundary should be electrically inactive, unless high-concentration impurities segregate into the boundary. We find that the $[1\bar{1}00]/(11\bar{2}2)$ twin boundaries in wurtzite III-nitrides also adopt the head-to-tail structure. They exhibit very similar electronic properties as that of the twin boundary in ZnO.

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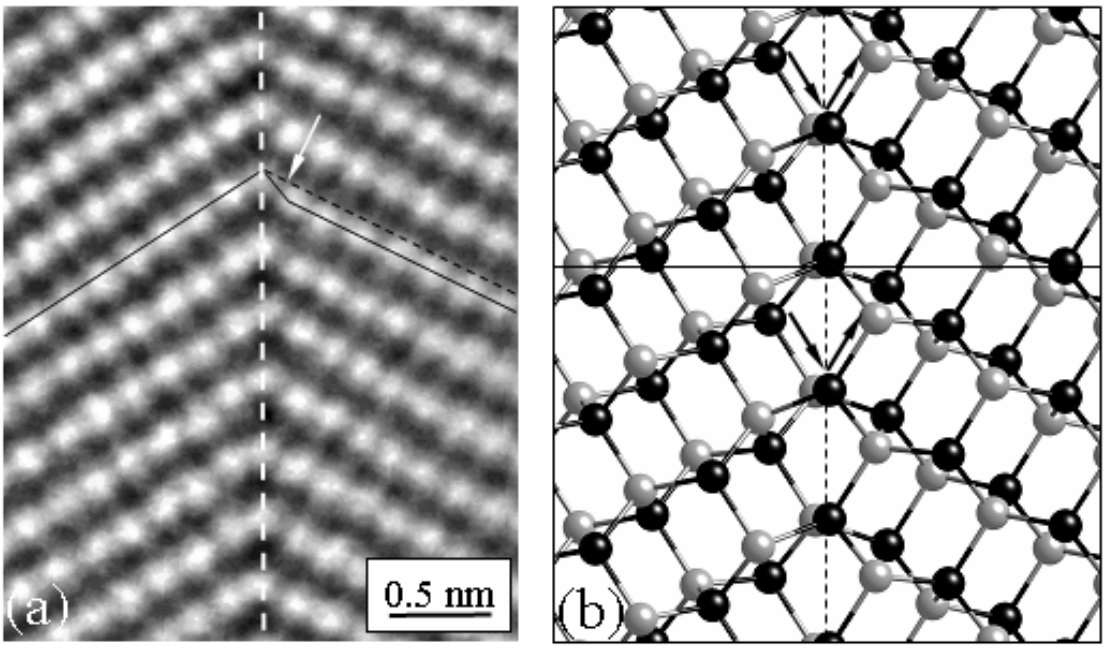

Fig. 1. (a) Z-contrast image of a $[1\bar{1}00]/(11\bar{2}2)$ twin boundary in ZnO along the $[1\bar{1}00]$ zone axis. (b) Atomic structure of the $[1\bar{1}00]/(11\bar{2}2)$ twin boundary in ZnO determined by Z-contrast image, image simulations, and twin-boundary energy calculations.

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