Direct Determination of Local Lattice Polarity in Crystals

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Materials with the wurtzite structure, such as CdSe quantum dots and rods, GaN-AlN quantum wells, and nanowires, play an increasingly important role in nanoscale science. For some, like the III-V nitrides, the existence of directional polarization is the driving force behind technical applications. Hexagonal crystals with the wurtzite (AB) structure exhibit physical and chemical properties that are different when they are parallel and antiparallel to the *c* axis. This difference is a result of particular stacking of A and B atomic layers, i.e. lattice polarity, along the [0001] direction (Fig. 1A). For a long time, atomic-level determination of the local lattice polarity was not possible. Early methods were based on differences in the surface properties of bulk crystals. Later, microscopic analysis relied on diffraction data recorded by conventional transmission electron microscopy (TEM) (*1*) or on a statistical analysis of scanning TEM (STEM) images (*2*).

Unfortunately, these techniques cannot reveal local, atomic-level polarity in nanoscale structures, because they lack the required lateral spatial resolution or are limited to thick samples, where extensive analysis of dynamical diffraction is needed. Demonstration of polarity at the atomic level would allow for understanding and control of phenomena occurring in nanoscale objects, such as selective growth of PbSe with a rock-salt structure on the tips of wurtzite colloidal nanorods (*3*) and the bonding of zincblende CdTe cores with wurtzite CdTe/CdSe branches in nanocrystals (*4*). Recent developments in TEM analysis techniques (*5*) and aberration correction in the TEM (*6*) and in the STEM (*7*), where an electron probe smaller that 1 Å has been achieved (*8*, *9*), potentially allow for atomic-level determination of local polarity. TEM analysis has been successful in improving the effective resolution from 1.7 Å (experimental) to ~0.8 to 0.9 Å with computational analysis using many experimental images (*5*). We show here that annular dark field (ADF) imaging in an aberration-corrected STEM can provide direct quantitative discrimination during observation in real time without extensive analysis.

Figure 1B shows an ADF image of a small area of wurtzite AlN in the [$\bar{2}$110] projection, recorded using a VG HB-501 dedicated STEM equipped with an aberration corrector at an energy of 120 keV. Operation at this low energy is important to minimize irradiation damage from direct electron impact. This instrument has demonstrated a 0.75 Å probe in systematic tests (*8*). ADF imaging in crystals uses large-angle elastic scattering to locate individual atoms and projected atomic columns, with good sensitivity to atomic number *Z* but with minor dependence on focusing conditions or specimen thickness. The challenge in this case is to image low-*Z* atoms, such as N, located in close proximity to very strongly scattering high-*Z* atoms. In the [$\bar{2}$110] orientation, the smallest projected spacing between Al and N columns is 1.1 Å, requiring a very small electron probe for discrimination. In Fig. 1B, the N columns are seen as elongations of the column images alternately pointing diagonally up and down. This image represents the local polarity in AlN but also, for the first time, the identification of the single column of N atoms near the Al. In Fig. 1C, the visibility of N is enhanced by removal of the Al column signal. Because the column signal should be azimuthally symmetric, we measured the Al profile in the direction perpendicular to the line joining it with N (Fig. 1B, yellow line), and then subtracted to obtain the N profile.

Fig. 1D shows an example of the use of this technique for a strained AlN/GaN/AlN quantum well, where we can easily pick out the polarity of the AlN substrate and cap. In the quantum well, the much stronger Ga scattering makes direct polarity determination there difficult, but establishing the lattice position and polarity in the AlN matrix allows comparisons of the positions of Ga columns with image calculations (Fig. 1D, inset) to obtain the polarity in the quantum well. This particular structure is unfaulted and carries the substrate polarity through the well to the capping material.

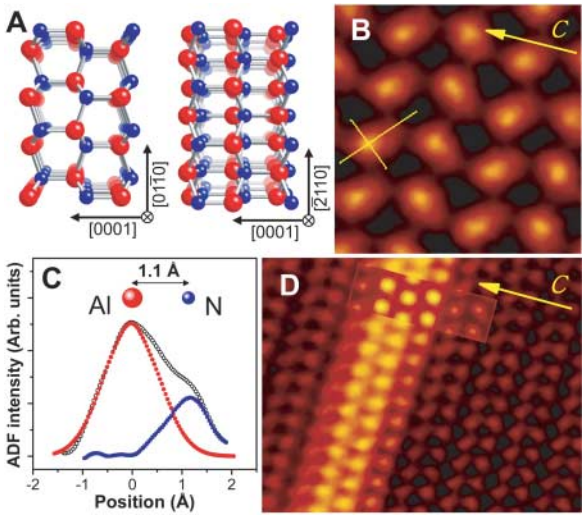

Fig. 1. (**A**) The wurtzite crystal in the two major projections perpendicular to the *c* axis. The left image shows the [$\bar{2}$110] projection and the right image shows [01$\bar{1}$0]. These models have B-face polarity, because of ABABAB… stacking along the [0001] direction, where A is the blue and B is the red atom. (**B**) ADF-STEM image of AlN in the [$\bar{2}$110] projection. To reduce instrumental noise, this image was filtered with a 0.65 Å^{-1} low-pass Gaussian filter. (**C**) The N column is revealed when the Al column profile is removed from the total. These intensities were obtained from line scans whose positions are indicated in (B) by yellow lines. (**D**) ADF image of a GaN quantum well inside the AlN. The inset shows a calculation for a three-layer well to verify the polarity from the Ga positions.

References and Notes

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Supporting Online Material

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Materials and Methods
Figs. S1 to S3
References

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