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Direct Determination of the Local Polarity in Wurzite Crystals

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Direct Determination of the Local Polarity in Wurzite Crystals

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In hexagonal crystals with wurtzite structure, physical and chemical properties are different not only along the major c and a axes, but they are also different parallel and anti-parallel to the c-axis. This unique property of wurtzite (A-B) compounds is the result of non-symmetric stacking of the atomic layers along the [0001] direction (Fig. 1, A). Polarity, therefore, was introduced to describe the sequence of the A and B layers along c-axis. In the age of nano-science, these compounds are becoming useful for many applications ranging from CdSe quantum dots and rods to GaN-AlN quantum wells and nano-wires. And in most cases, like in wurtzite III-V nitrides, the existence of directional polarization is the driving force behind their applications. Therefore, the ability to measure polarity at the atomic scale would open new prospects for understanding new phenomena present in these nanosctructures, such as: selective growth of PbSe with a rock-salt structure on the tips of wurtzite colloidal nanorods *(1)* and classifying of the grain boundaries between zincblend CdTe core and wurtzite CdTe/CdSe branches in nanocrystals *(2)*.

For a long time, determination of the polarity in materials at the atomic scale was not possible. Early methods were based on differences in surface properties of bulk crystals along [0001] and [000-1] directions (chemical reactivities, surface reconstructions etc.) or in cases where cross-sectional examinations were needed, polarity was obtained from analysis of diffraction data obtained in the conventional transmission electron microscope (TEM) *(3-4)*. Unfortunately, these techniques cannot reveal local, atomic level polarity in nanoscale structures, because they lack the required spatial resolution. Recent developments in aberration corrected scanning TEMs (STEMs), where now an electron probe smaller that 1 Å can be achieved *(5-6)*, have opened new possibilities for determination of local polarity.

Fig. 1, B shows an annular dark field (ADF) image of a small area of wurtzite AlN in the [-2110] projection. This image was recorded using a VG HB-501 dedicated STEM equipped with a Nion aberration corrector and operating at 120kV acceleration potential. Operation at this low energy is important to minimize irradiation damage from direct impact. This instrument has a practical probe size lower limit of about 0.7 Å, and has demonstrated a 0.75 Å probe in systematic tests *(5)*. Use of the ADF detector, which forms the image by collecting incident probe electrons scattered from atoms in the specimen into a 65 to 210 mrad solid conical angle, provides direct imaging of the projected atomic columns, with minor dependence on focusing conditions or specimen thickness *(7-8)*. The challenge here is to ensure visibility of low atomic number (Z) atoms, like nitrogen, located in close proximity to strongly scattering, high-Z atoms. In the [-2110] orientation of AlN the smallest spacing between neighboring Al and N columns is 1.1 Å, which is significantly bigger than in the [01-10] orientation where it is only 0.6 Å. As a result we are able not only to determine local polarity in AlN but also, for the first time, directly image a single column of nitrogen atoms. In Fig. 1 C, the visibility of nitrogen is enhanced even further by the removal of the Al column signal from the total signal of the Al-N pair; two line profiles were taken from of the ADF image of a single Al-N pair, first along the line connecting Al and N columns and second, perpendicular to first, across the Al column only. Then, the intensity of the Al signal was subtracted from the combined intensity.

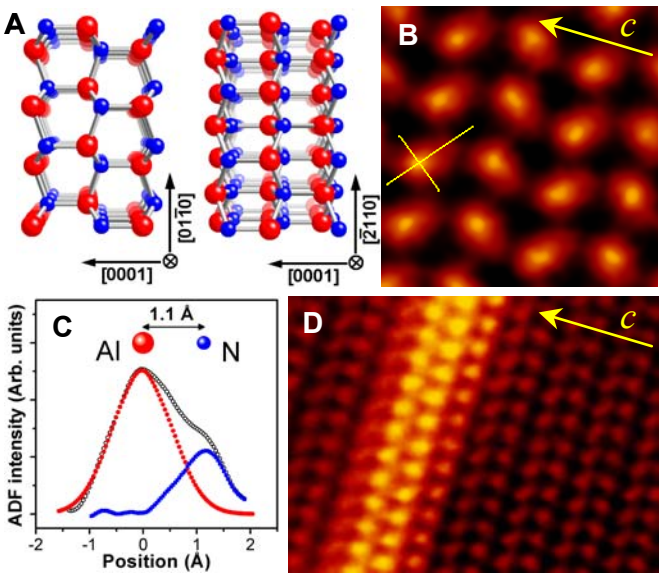

Fig. 1. (**A**) Models of the binary compound in wurtzite crystal structure in the two major orientations perpendicular to c-axis: left – [-2110] and right - [01-10] orientation. These models have B-face polarity, because of their ABABAB… sequencing of the atomic layers along [0001] direction, where A is the blue and B is the red atom. (**B**) ADF-STEM image of AlN in the [-2110] projection. To reduce instrumental noise this image was filtered with a 0.65 $Å^{-1}$ low-pass Gaussian filter. (**C**) The nitrogen column was fully revealed when signal from the Al column (red dots) was subtracted from the total signal of the Al-N pair (open circles). The two intensities were obtained by line scans whose positions are indicated in (**B**) by yellow lines. (**D**) High-resolution ADF image of the GaN QW grown in the AlN matrix. Local polarity can be easily traced across the structure.

To show how the polarity can be traced at the atomic level we recorded a high-resolution ADF image of the GaN quantum well inside AlN (Fig. 1, D). Weaker visibility of the nitrogen columns inside the well is due to a strong background signal created by heavy gallium atoms.

References and Notes

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8. Materials and methods are available in supporting material on Science Online.

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