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Annular Dark-Field Imaging of Atomic Substitution Single-Layer Materials

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Aberration correction has lead to remarkable improvements in STEM imaging and analysis in the last few years. Being able to reach atomic resolution at operating energies that avoid knock-on displacement damage in light atom materials has been a particularly important development. It is now possible to image and identify single light atoms in samples that before would have either been damaged if imaged at higher energies or have given little indication of their precise atomic structure if imaged at lower energies. We present here the experimental observation of single-layer hexagonal boron nitride (BN) in freestanding membranes up to a few nanometers in size. The BN sample was prepared by liquid phase exfoliation of bulk hexagonal BN powders in N-Methyl-2-Pyrrolidone which gave monolayer BN dispersions with high yield [1]. We have used medium-angle annular dark field (MAADF) imaging to resolve single light atoms in BN and to identify their chemical types. The MAADF technique is quantitative and readily interpretable, and the cross-sections for different light atoms are very different. The imaging was performed at 60 kV in a Nion UltraSTEM, a dedicated, UHV, fifth-order aberration-corrected scanning transmission electron microscope using a cold field emission electron source. At the 50 pA probe current we typically used, the theoretical resolution of the instrument was 1.1 Å [2], sufficient to resolve the nearest neighbor separation in hexagonal BN of 1.45 Å.

Figure 1a shows an unprocessed high-magnification, MAADF image of single layer BN. The boron and nitrogen atoms are clearly distinguished by their intensity. This pattern of bright and less intense features (as in top circle) is repeated throughout the image of the single layer BN, with several exceptions. One such exception, marked by the bottom circle, shows 6 atoms which are less intense than the nitrogen atoms and more intense than the boron ones. They are carbon atoms incorporated into the BN lattice: a single ring of graphene surrounded by BN. Quantitative interpretation of the recorded image intensities requires that we account for smearing caused by the “tails” of the electron probe. We corrected for the smearing by a linear deconvolution procedure designed to remove the tail contribution from the nearest neighbors, and to avoid multiplying the image noise unnecessarily [3]. The deconvolved image is shown in Fig. 1b. Figure 1c shows intensity line profiles through the locations marked on Figure 1b. Profile A-A’ goes through the regular BN lattice. Each individual boron and nitrogen atom is clearly identifiable by its intensity. Profiles B-B’ and C-C’ go through atomic sites whose intensities are significantly different from the intensities measured for the boron and nitrogen atoms. They are due to single carbon and oxygen atom impurities incorporated in the BN lattice. Figure 1d shows the atomic structure that corresponds to the impurity atoms identified in the layer. These studies have begun to reveal a wide variety of materials science phenomena in single-layer materials, and have suggested a possible way of producing devices that control the electrical properties of the materials with atomic-level precision.

References

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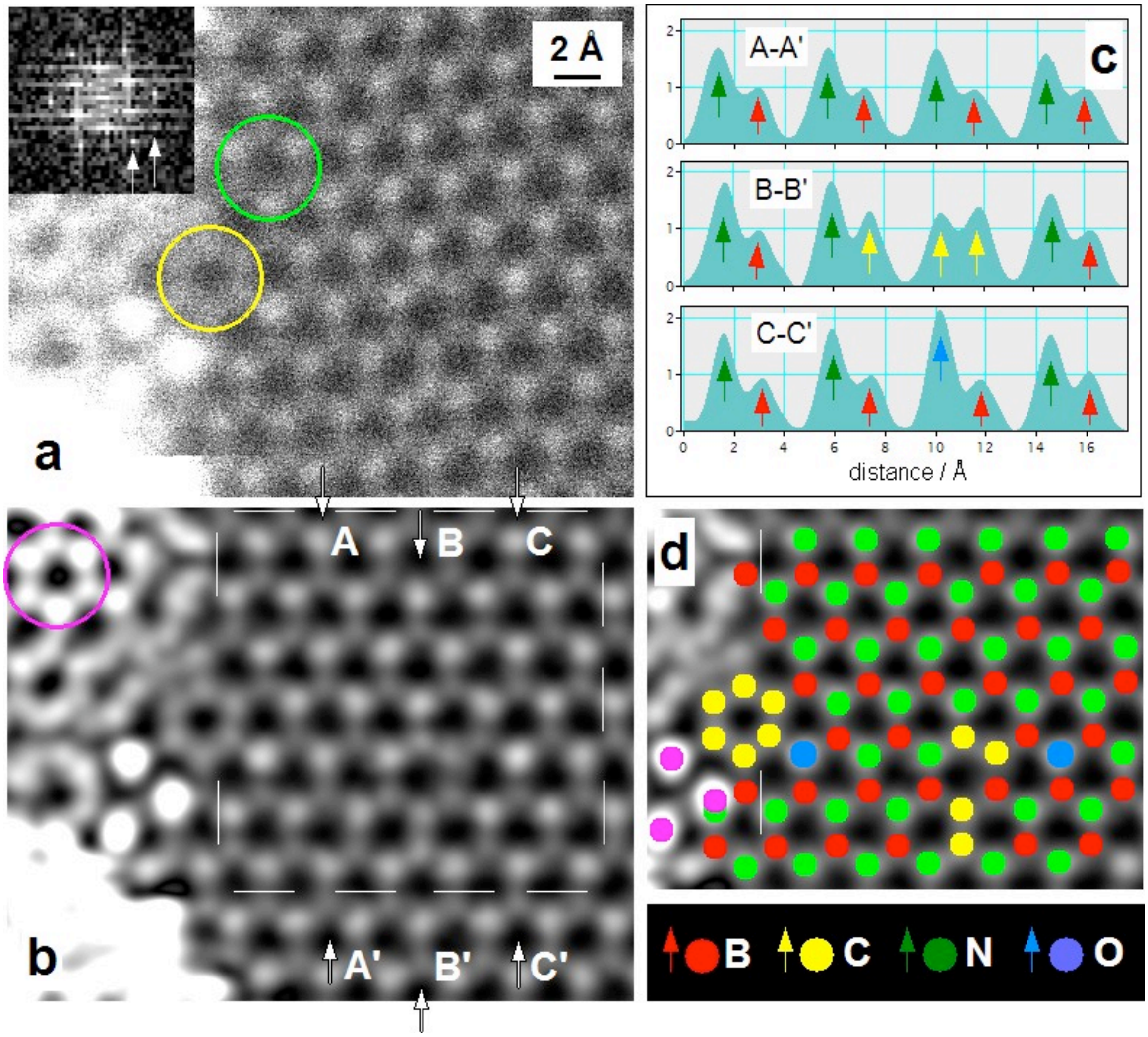

FIG. 1. Medium-angle annular dark-field STEM image of single-layer boron nitride. a) as recorded, b) Fourier-filtered with a gradual cut-off above 1 Å^{-1}, rotated and corrected for distortion, and deconvolved to remove the probe tail contributions, c) line profiles through the marked locations in (b), d) model of the observed structure.