Application Note

Fusion™

Atomic Scale Imaging of 2-D Materials

Introduction

True two-dimensional (2-D) materials have a thickness of just one atom. Since the first group of researchers isolated a single sheet of graphite, called graphene, interest in 2-D materials has increased significantly. While graphene in particular has seen intense interest, there are several other materials that can be synthesized directly or exfoliated into 2-D sheets from bulk samples. Hexagonal boron nitride is one such material. It has a similar honeycomb structure and is isoelectronic with graphene. However, graphene and hexagonal boron nitride (h-BN) differ in that h-BN has a band gap of over 5 eV. This band gap makes it a desirable material for many applications including optics, electrical devices, and durable coatings. When layered with graphene, h-BN can enhance the electrical performance of graphene in devices like field effect transistors. Before h-BN can see widespread adoption in these applications, the nanostructure, including the character and behavior of defects and edge states, must be understood. Researchers in Alex Zettl's lab at UC Berkeley and at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory (NCEM, LBNL) have for the first time characterized the atomic scale structure of CVD grown h-BN *in situ* in the TEM using the Protochips system. The group reported on the dynamic defect structures characterized along grain boundaries including pentagon/heptagon defects and holes induced by electron beam damage.

Experiment

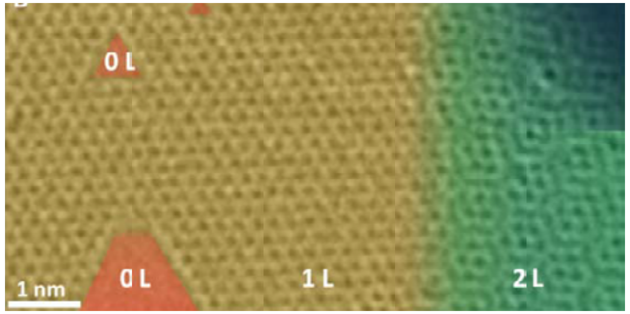

Figure 1: TEM image at 450 °C showing holes, 0 L, singe layer, 1 L, and a double layer, 2 L, of h-BN

Sheets of h-BN were grown via low-pressure chemical vapor deposition (LPCVD) on the surface of copper films. The polycrystalline structure of the copper growth substrate induces grain boundaries and defects in the h-BN layer, and these defects must be characterized to understand the behavior of the material. In order to isolate a layer of h-BN for TEM analysis the copper film was dissolved using iron chloride, and the layer was transferred to an E-chip™. Figure 1 shows a TEM image of h-BN transferred to the E-chip. Single and two-layer sheets were observed as indicated in the image. After inserting the sample into the TEM, the temperature was ramped to 800 °C to remove any contamination and residue remaining on the h-BN sheet. However, due to thermal instabilities in the material at higher temperatures, a temperature of 450 °C was used during the experiments. It was observed that imaging at 450 °C, as opposed to room temperature, provided better stability at high-resolution, because the elevated temperature prevented the build up of hydrocarbon contamination on the h-BN film. The TEAM 0.5 TEM at NCEM was used for all imaging. The microscope is an FEI Titan Cubed with spherical aberration correctors for both the image and probe forming optics and a monochromator. The aberration correctors and monochromator provide the high-resolution needed to resolve the lattice structure of h-BN. The TEM was operated in bright field mode at 80 kV to minimize beam damage. The resolution under these conditions was approximately

Reference: Nasim Alem, University of California, Berkeley. J. Am. Chem. Soc., 2013, 135, 6758–6761

1 Å. The system's high thermal stability was key in preserving the resolution required for analyzing the defect structure of h-BN at high temperatures.

Discussion

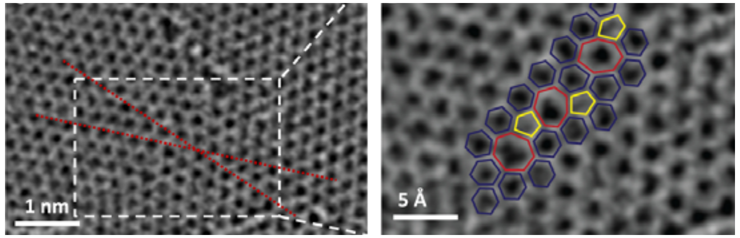

Figure 2: TEM images taken at 450 °C showing a grain boundary in a layer of h-BN. Left panels shows two grains meet at an angle of 21°. Right panel shows a close up of the grain boundary and the defect structure, including 5/7 defects as indicated by the yellow pentagons and red heptagons.

A polycrystalline copper film was used as the substrate during LPCVD growth of the h-BN. Small islands of h-BN nucleate on different grains on the Cu substrate, and grow until they contact other islands of material, which creates grain boundaries and defects in the sheet. Pentagon-heptagon (5/7) defects were observed along grain boundaries, as shown in Figure 2, as opposed to the 6 membered rings that form pristine h-BN. The 5/7 defects were unexpected, because boron-boron (B-B) and nitrogen-nitrogen (N-N) bonds result from these defects, which induce local dipole moments. The B-B and N-N bonds found in 5/7 defects are not energetically favorable in pristine h-BN, but in some instances they are favored along grain boundaries as predicted by theoretical calculations. Other defects observed were 4/8 defects, which form along ripples in the sheet. This defect structure has been predicted in BN nanotubes, and is more energetically likely to form in a curved section of the lattice than 5/7 defects.

Although imaging with an acceleration voltage of 80 kV helped minimized beam damage, the h-BN lattice structure was unstable as a result of knock-on damage. Monovacancies can occur due to boron being preferentially ejected from the lattice by the beam. These monovacancies can grow into larger triangle shaped holes, which may represent possible structures that can form in h-BN under normal conditions. Grain boundaries on the other hand were more stable under the beam, and amenable to imaging for relatively longer periods.

Applications

Research in 2-D materials has grown dramatically over the past few years, and is poised for exponential growth in the near term. The properties of these materials, such as electrical, mechanical, optical and chemical will enable the development of new devices across many applications. For h-BN in particular, engineering defects, if precisely controlled in the material may permit tunable properties for specific applications. To analyze these materials *in situ* at the atomic scale in the TEM, a stable, low drift sample holder system is required. The Fusion heating and electrical biasing platform allows atomic resolution imaging and analysis of materials, and is able to fully harness the resolution capabilities of state-of-the-art instruments such at the TEAM 0.5

Contact us to discuss the full range of capabilities of the Fusion platform with the thermal E-chip sample supports for your applications. We can be reached at (919) 377-0800 or contact@protochips.com.

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