Atomic Resolution Imaging of Grain Boundary Defects in Monolayer Chemical Vapor Deposition Hexagonal Boron Nitride

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Supporting Information

Chemical Vapor Deposition of Hexagonal Boron Nitride (h-BN) Films. Hexagonal boron nitride was grown on 25 μm thick nickel foil (99.99%, Alfa Aesar) using a low pressure chemical vapor deposition (LPCVD) process. Nickel acts as a catalytic substrate for monolayer and few-layer h-BN growth. To maintain a low vapor pressure of the precursor, liquid borazine (Gelest Inc) was cooled in a slush of acetonitrile and chloroform to a temperature of approximately -55°C and introduced at a partial pressure of <5 mTorr.

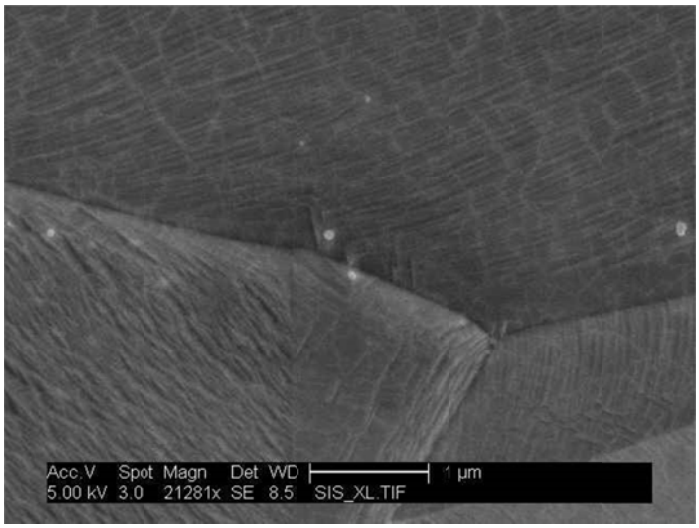

Figure S1. Scanning electron micrograph of few-layer h-BN on polycrystalline nickel foil.

Before growth the nickel foil was treated with an ozone-cleaner gas for 10 minutes at 100°C to remove any carbonaceous contaminants. Additionally, the nickel foil was annealed immediately before growth at 900°C for 30 minutes with 30 sccm of hydrogen gas and 20 sccm of argon to smooth the surface and remove any remaining surface impurities. Hexagonal boron nitride growth occurred at 900°C over 15 minutes with 30 sccm of hydrogen gas, 20 sccm of argon gas and <2 sccm of borazine for a total pressure of 315 mTorr. The use of a liquid nitrogen trap helped prevent contamination from the vacuum pump. Figure S1 is a typical scanning electron microscope image taken on an FEI XL3000 of the nickel foil after h-BN growth. Figure S2 shows the Raman signal from CVD h-BN on nickel with major peak at 1370 cm^{-1}. Raman data was obtained on a Reinshaw inVia microscope using a 514 nm laser.

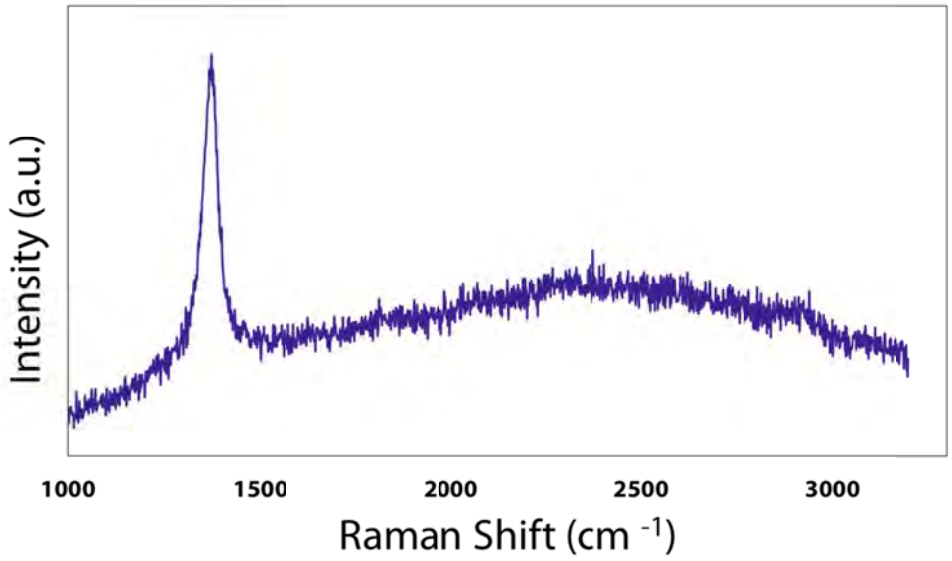

Figure S2. Raman spectra of h-BN on nickel foil with characteristic boron nitride peak at 1370 cm^{-1}.

Films were transferred using a PMMA support to a heating and biasing stage (Protochip Inc.) with 10 μm imaging windows and electron beam evaporated gold contacts, shown in Figure S3, then annealed at 300°C in hydrogen overnight.

Transmission Electron Microscopy (TEM) and *in situ* Heating. Atomic resolution TEM imaging was achieved using the TEAM 0.5 microscope operating at 80 kV with a monochomated beam and spherical aberration correction, yielding a spatial resolution of less than 1 Å. This resolution allows for atomic mapping of BN or graphene, but was not able to distinguish between these atoms in this experiment. Spherical aberration corrections were third order C3= -8.326 μm ± 2.617 μm, and fith order C5= 5.436 mm ± 1.489 mm, which yielded bright atom contrast if compensated with a small overfocus during TEM imaging.

An Aduro TEM holder (Protochips, Inc.) allowed for controlled sample heating under imaging conditions. The sample was slowly heated to 800°C, which removed any remaining amorphous residues and contaminants from the transfer process. Due to thermally induced

vibrations and mechanical oscillations which compromised resolution, imaging was performed at a lower temperature. After allowing for thermal equilibration, 450°C was found to be a suitable imaging temperature with minimal vibrations and sufficient sample stability. Interestingly, this temperature was found to be superior to room temperature for imaging boron nitride due to increased mechanical stability and lower surface contamination.

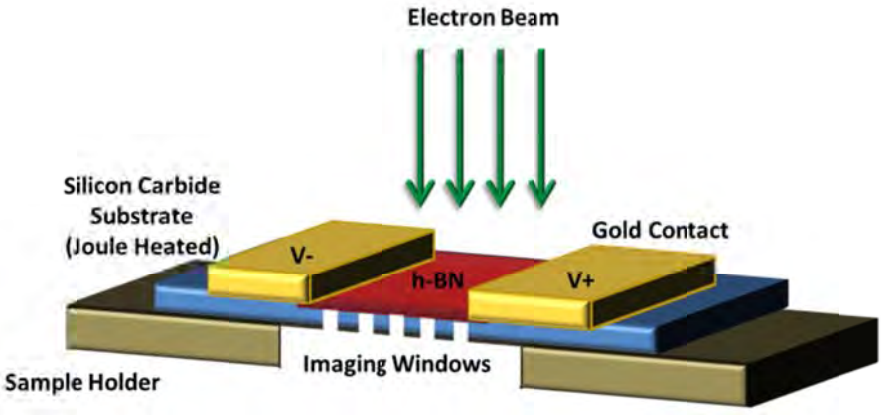

Figure S3. Aduro TEM holder capable of *in situ* heating experiments up to 1000°C. Hexagonal boron nitride film is mounted with gold contacts onto a silicon carbide substrate with 10 μm imaging windows.

Image Analysis.

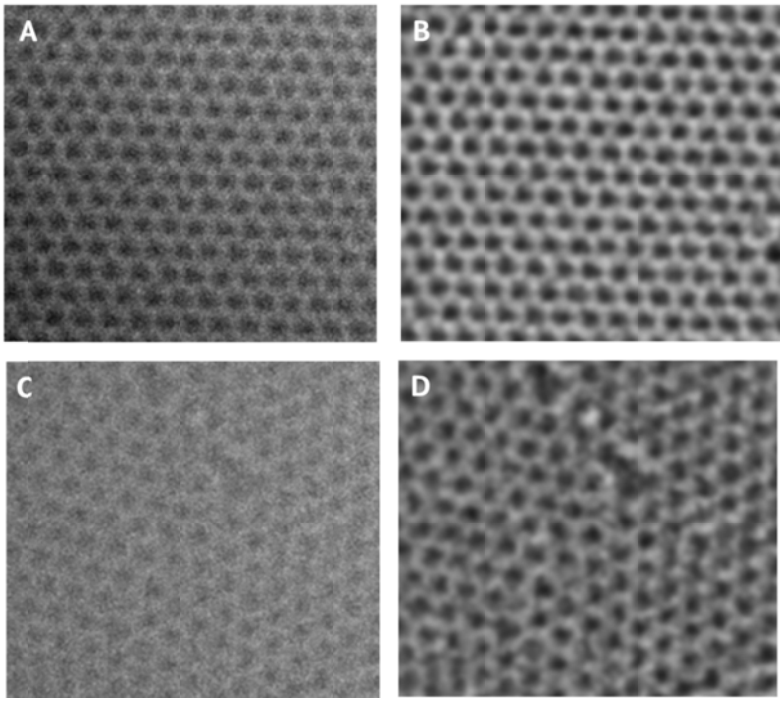

Figure S4. Raw and processed HRTEM images of h-BN from Figure 1. (A) Raw TEM image of h-BN lattice from Figure 1A. (B) TEM region shown in A after applying an FFT bandpass filter with four pixel tolerance. (C) Raw image of h-BN grain boundary from Figure 1C. (D) The same region after applying a bandpass filter to the FFT.

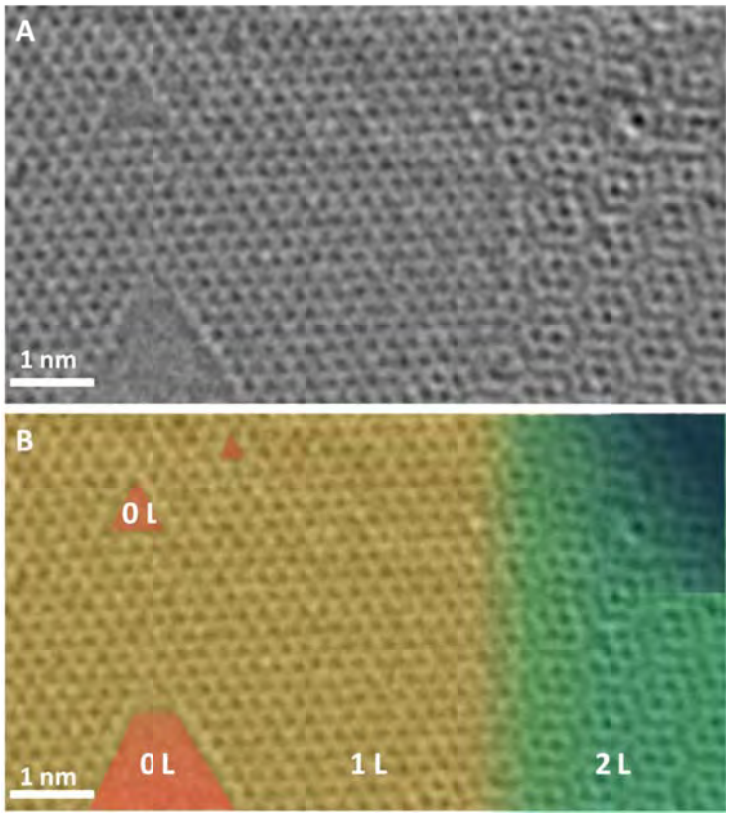

Figure S5. HRTEM images of mono and bi-layer h-BN, (A). The same region with false color highlighting different layer numbers, (B). Red depicts vacancies (zero layers), yellow monolayer region, green bilayer and blue for few-layer.