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Assessing Hexagonal Boron Nitride Crystal Quality by Defect Sensitive Etching

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Hexagonal boron nitride (hBN), the graphite-like polymorph, has been employed for more than 55 years as powders, ceramics, amorphous films, and deposited fine-grain polycrystalline pyrolytic forms (pBN) in applications that take advantage of its high thermal stability, chemical inertness, high thermal conductivity, low x-ray absorption, high electrical resistivity, and lubricating properties [1-4]. Recently, new applications have been envisioned for hBN that take advantage of its unique structural, optical and electronic properties. These include nanophotonics [5] exploiting its highly anisotropic optical properties, two dimensional atomically-thin transistors that employ hBN's ultra-smooth surfaces, high resistivity, and lattice matching with graphene [6, 7], deep ultraviolet emission, made possible by hBN's large energy band gap (5.8 eV) and high exciton binding energy [8, 9], and solid-state neutron detectors, which rely on the strong interaction of thermal neutrons with the boron-10 isotope [10, 11]. These applications require hBN of high structural perfection; defects such as dislocations create charge traps, scattering centers, and recombination sites that degrade its optical and charge transport properties (mobility and minority carrier lifetimes) [9, 12-14].

Here we develop defect sensitive etching (DSE) to quantify the density of non-basal plane dislocations in hBN single crystals. Single crystals were precipitated from a molten nickel-chromium flux saturated with hBN at 1500 °C under 1 bar of flowing N_2, followed by slow cooling (2-4 °C/hour). Etching the crystals in a molten eutectic mixture of NaOH and KOH between 450 °C and 525 °C for 1 minute produced hexagonal pits on (0001) planes. The morphology and topography of these pits were characterized using optical microscopy, SEM and AFM. All etch pits were oriented in the same direction within individual grains. Three types of hexagonal etch pits formed: pits with inclined side walls, flat-bottom pits, and pits combining these features. From an Arrhenius plot of the log of the etch rate versus the inverse temperature, an activation energy of 60 kJ/mol was estimated. Screw and mixed-type threading dislocations were also identified in the crystal bulk using diffraction-contrast transmission electron microscopy (TEM). This work demonstrates that DSE is an effective method for estimating the density of non-basal plane dislocations in hBN [15].

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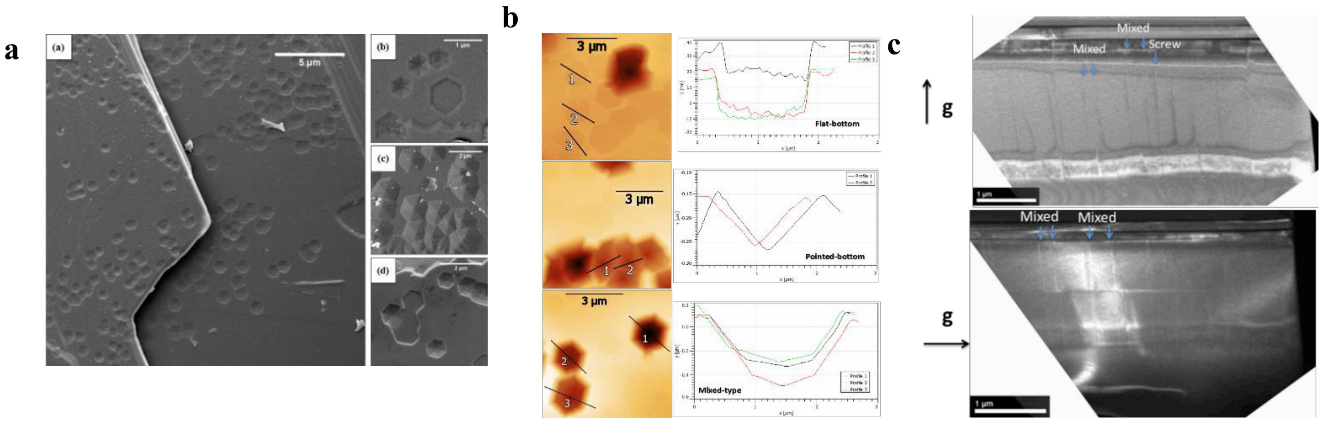

Figure 1. (a) SEM images showing pit shape and distribution on the flakes with different magnifications. **(b)** AFM images and associated height profiles (from top to bottom) of flat-bottom, pointed bottom and mixed-type etch pits observed on hBN flake. **(c)** Diffraction-contrast TEM images of hBN flake cross sections taken with screw dislocation imaging conditions (top) and edge imaging conditions (bottom). Defects only observed in the top image are screw dislocations, while those only observed in the bottom are edge type. Dislocations present in both are mixed-type, as they have components of both screw and edge dislocations.