Characterization of Hexagonal Boron Nitride Thin Films Grown by Molecular Beam Epitaxy

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Principal Investigator: Dr. Debdeep Jena

User: Ryan Page

Affiliation(s): Department of Materials Science and Engineering, School of Electrical and Computer Engineering; Cornell University

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Contact: djena@cornell.edu, rlp238@cornell.edu

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Abstract:

Hexagonal boron nitride (hBN) is a layered material with a wide variety of promising applications, from being used as a substrate and dielectric in Van der Waals heterostructures, to hosting bright, room temperature single photon emitters. Here we report molecular beam epitaxy (MBE) growth and characterization of hBN thin films on sapphire substrates. Films up to 20 nm thick were grown at substrate temperatures up to 1750°C to study the interplay between substrate temperature and source material flux on the morphology and crystallinity of the films. It was observed that films grown at high temperatures (greater than 1650°C) and low boron fluxes (3E-9 torr beam equivalent pressure) resulted in the smoothest and highest quality films. Films were characterized extensively in the Cornell NanoScale Science and Technology Facility using the Veeco Icon atomic force microscope.

Summary of Research:

Hexagonal boron nitride (hBN) is an atomically thin crystalline material, isostructural to graphene, consisting of sheets of boron and nitrogen atoms arranged into a two-dimensional hexagonal net. While the in-plane bonds between each boron and nitrogen atoms in each sheet are very strong, the sheets themselves are bound to one another only by weak Van der Waals forces. Hexagonal boron nitride, along with other so-called two-dimensional materials such as graphene and the family of transition metal dichalcogenides (TMDs) have been the subject of intense research interest in recent years due to the prospect of devices and heterostructures based on stacked monolayers of different 2D materials [1]. The realization of such devices and applications will depend critically on hBN for use as a substrate and dielectric layer. Additionally, hBN has applications in deep ultraviolet photonics and lighting, exhibiting strong emission in the UV-C spectrum [2]. Finally, point defects in hBN layers have recently been discovered as bright, room temperature single photon emitters, opening up this material to applications in quantum cryptography and precision sensing [3].

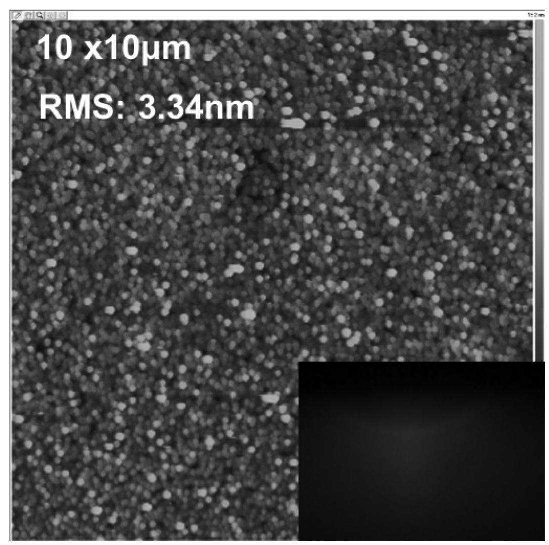

Figure 1: Atomic force microscope image of lower substrate temperature (1600°C) hBN film shows rough, polycrystalline morphology. Inset: diffuse, ringed RHEED pattern.

Despite all of these applications, the synthesis of hBN, particularly epitaxial layers, has proven to be a challenge. In this work, we focus on the growth and characterization of hBN thin films grown by molecular beam epitaxy (MBE) on sapphire substrates. The films are grown at ultra-high substrate temperatures (1600 to 1800°C) in order to overcome kinetic barriers of the crystal growth. The quality and morphology of the films were studied extensively with the Veeco Icon

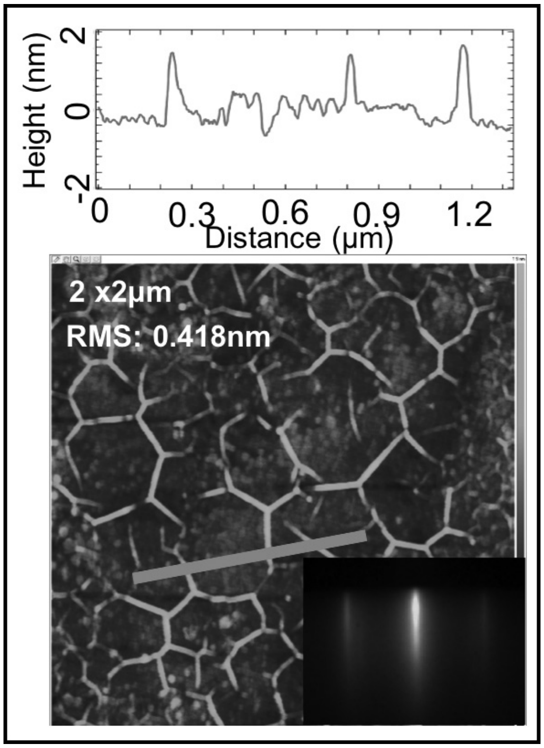

Figure 2: Atomic force microscope image of higher substrate temperature (1650°C) hBN shows smooth surface with network of ripple-like folds, line height profile of inset line shown above. Inset: bright, streaked RHEED pattern.

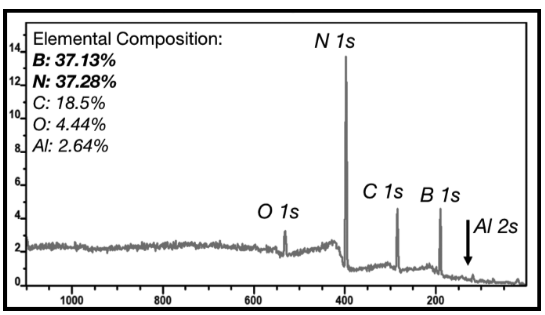

Figure 3: X-ray photoelectron spectroscopy of hexagonal boron nitride grown on sapphire confirms the chemical composition of the film is 1:1 boron to nitrogen.

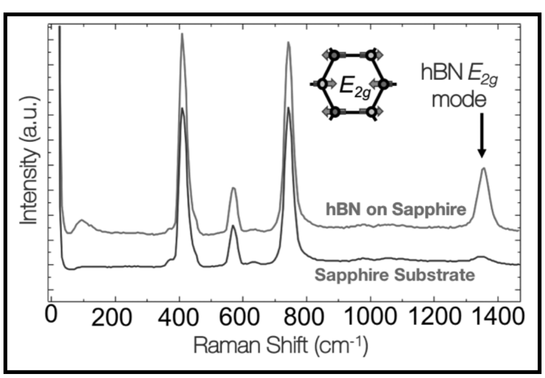

Figure 4: Raman spectrum of hBN film grown on sapphire exhibits clear hBN E_{2g} peak near 1365 1/cm. Spectrum of sapphire substrate shown for comparison.

atomic force microscope (AFM). The films were also characterized by Raman spectroscopy, ultraviolet absorption spectroscopy, spectroscopic ellipsometry, and x-ray photoelectron spectroscopy to elucidate their structural, optical, and chemical properties. To study the effect of MBE growth conditions (e.g. boron and nitrogen fluxes and substrate temperature) on the morphology and quality of the films, films throughout the growth parameter space were grown. We observed a variety of different surface morphologies, wherein several trends are noted: at lower temperatures (less than 1600°C) the hBN films consistently exhibited visible rings in the *in situ* reflection high energy electron diffraction (RHEED) patterns, indicating a polycrystalline growth mode. Subsequently, these films had very rough surface morphologies as seen in the AFM. At higher temperatures (1600 to 1750°C), clear streaks were seen in the RHEED pattern, suggesting a higher quality film growth, while we observed in the AFM images smooth films with a dense network of ripple-like features. These ripples have been reported in hBN flakes grown by chemical vapor deposition, where they are attributed to the thermal expansion mismatch between the hBN and the substrate causing the hBN to wrinkle and fold up on itself [4]. At each temperature range, there was an incident boron flux, provided by a high temperature boron effusion cell, past which the films would also become rough and polycrystalline. At all temperatures, this threshold flux was very low (approx. $3E^{-9}$ torr beam equivalent pressure), but it increased with temperature. All growths are done in excess nitrogen conditions using a radio frequency plasma nitrogen source.

X-ray photoelectron spectroscopy of these films confirmed a 1:1 boron to nitrogen ratio with no evidence of carbon contamination. The films also exhibit a sharp absorption peak centered near 6 eV, the band gap of hBN. In the Raman spectra, the hBN E_{2g} peak is observed near 1365 1/cm, confirming the phase of the grown films. Notably, hBN was also grown with isotopically purified nitrogen-15; the E_{2g} peak exhibited an approximately 15 1/cm redshift corresponding to the heavier atoms. The demonstrated isotopic control in the films allows for future studies into the electron-phonon interactions of hBN.

In conclusion, hexagonal boron nitride thin films were grown by molecular beam epitaxy and characterized by a variety of techniques to probe the structural, chemical, and optical properties of the layers. It was found that ultra-high growth temperatures and low boron fluxes produce the highest quality films. This work represents a step toward the integration of high quality hBN into a wide range of devices and applications.

References:

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