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Characterization and Analysis of Large-Area h-BN on Sapphire

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***Abstract*—Extensive post-growth microscopic and spectroscopic characterizations are performed to leverage true potentials of high-quality hexagonal boron nitride (h-BN). Compressive residual strain between h-BN and sapphire is estimated and corroborated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Raman spectroscopy also supported the result.**

Keywords—h-BN, CVD, transmission electron microscopy, Raman

I. Introduction

H-BN is a ultrawide bandgap semiconductor (~6 eV) two-dimensional (2D) material which finds its applications in several types of devices including photodiodes, solar cells, deep-ultraviolet classical light sources, and single photon emitters [1,2]. This van-der Waals (vdW) material is free from dangling bonds and getting attention due to presence of a sharp zero phonon line (ZPL) and large Debye-Waller factor. These properties have ignited the spark for growing research to unveil the quantum behavior associated with the point defects in h-BN. Since the first demonstration of high quality h-BN grown by metalorganic chemical vapor deposition (MOCVD), this vdW material has emerged as one of the exciting platforms for making a wide range of next-generation devices. As a substrate material, sapphire is a low-electrical-conductivity choice for MOCVD-grown h-BN films, when compared to other catalytic transition metal substrates such as Ni. However, h-BN grown on sapphire creates wrinkles which leads to strain. Despite, investigations on strained h-BN have been done theoretically by few groups but a comprehensive material analysis is still missing which is important as this understanding could help to engineer the strain to control the spectral tunability of single photon emission. In this paper, we report morphological, structural, and vibrational properties of multilayer thick bulk-like strained h-BN films grown on sapphire. Scanning electron microscopy (SEM), and atomic force microscopy (AFM) were used for morphological analysis. High resolution transmission electron microscopy (HRTEM) and Raman measurements were carried out for analyzing structural and vibrational properties.

II. Experimental Results and Analysis:

Multilayer h-BN was grown by CVD in a MOCVD reactor using non-metalorganic borazine ($B_3H_6N_3$) precursor at 1500°C. During growth, the partial pressure of the precursor was held at 130 µTorr. A constant flow was maintained at 1.9 µmol/min and film thickness was varied throughout the 3 hours growth time. The growth details of h-BN have been described elsewhere [3]. We analyzed surface morphology by SEM imaging. The top-view SEM image of the as-grown h-BN films is shown in Figure 1(a). This image shows presence of the wrinkles in the films which is obvious when a 2D material is under in-plane strain. Additionally, such wrinkles can also occur if h-BN with relatively smaller in-plane lattice constant (a = 2.478Å) is grown on a substrate like sapphire.

Figure 1(b) shows the AFM images of the surface morphology of h-BN films. AFM image also confirmed the presence of wrinkles in addition with number of hillocks across the surface which creates some degree of surface roughness on

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the h-BN films. Films under biaxial stress do not relax uniformly and can create a potential gradient between relatively relaxed grains and the surrounding films. This causes a flow of the atoms along the interface of the film and substrate and finally the relaxed area grows out from the base as a hillock. Such hillock-like features were reported as debris or islands on h-BN films grown on sapphire substrates by MOCVD [4]. However, their density was found to be a function of NH_3 flux. Although we did not use NH_3 during our growth, borazine precursor can produce such particles or amino-borane oligomers due to gas-phase reactions. Formation of hillocks is mostly controlled by grain boundary diffusion, interface diffusion and lattice diffusion.

The height and lateral dimensions of the wrinkles were measured to be of ~20 nm and ~200 nm, respectively. The absence of strong interfacial interaction between films and underlying substrates eventually leads to wrinkles. However, these wrinkles may also initiate from the defects on the interface between the film and substrates. Such wrinkles could also occur due to isotropic biaxial compressive strain resulting from a thermal expansion coefficient (TEC) mismatch between the substrate and the film. This is obvious phenomena when a cooling process from high growth temperature introduces compressive strain. This creates energy in the form of wrinkles which leads to the roughness in the sample. The measured root mean square (RMS) roughness of the sample was found 3.9 nm.

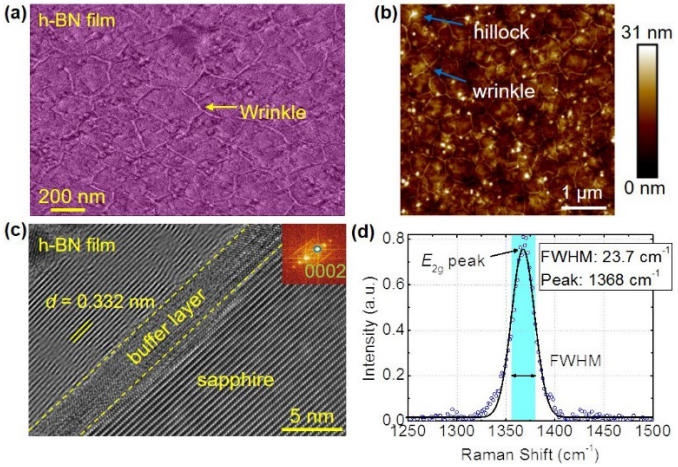

Figure 1. Images of h-BN film obtained by (a) SEM and (b) AFM, showing wrinkles and hillocks, across the surface. (c) High-resolution cross-sectional TEM image of as-grown h-BN films on sapphire, FFT pattern of the h-BN cross-section (inset), indicating high-crystallinity; and (d) E_{2G} vibrational mode of h-BN measured by Raman.

We further studied the atomic structure and stacking order of the as-grown h-BN multilayer films by cross-sectional HRTEM. Due to the lattice mismatch, we observed a reconstructed buffer layer between h-BN and sapphire, as shown in Figure 1(c). The BN interlayer spacing was measured by the Gatan Microscopy software and the value was found to be ~0.332 nm. This measurement suggests no disordered stacking sequences of crystal planes as the measured value is very close to the bulk h-BN with a spacing of ~0.33 nm. Moreover, this result further ruled out the presence of any other phases such as turbostratic-BN (t-BN) in the material. We also measured 2D fast Fourier transform (FFT) pattern of the h-BN region which is shown in the inset of the Figure 1(c). The indication of good-quality h-BN was further ascertained by the existence of the diffused spots which indicates the epitaxial relationship between the film and underlying substrate.

To get more insight of the crystal quality, we used spectroscopic tool to probe the vibrational modes in the materials. Raman spectra of the as-grown sample is shown in Figure 1(d). The peak observed at 1368 cm^{-1} corresponds to the E_{2g} vibrational mode of h-BN and supports the presence of hexagonal polymorphism. This peak is analogous to the G peak in graphene [5]. At higher phonon frequencies this peak shifts compared to the experimentally measured values (~1366 cm^{-1}). Presence of compressive and tensile strain are responsible for red and blue shifts in Raman peak, respectively. Any splitting of the peak which supports presence of biaxial strain was not observed. This is further supported by the presence of the wrinkles which is a consequence of compressive strain. The full width at half maximum (FWHM) of the Raman peak was fit to Lorentz functions and was estimated to be 23.7 cm^{-1} as shown here.

X-ray photoelectron spectroscopy (XPS) measurements were also performed on as-grown h-BN sample. Presence of core level spectra like B 1s, N 1s, O 1s and C 1s were confirmed which supported the B-N bonding in h-BN at 190.8 eV. The weak O 1s and C 1s peaks are found at 532.9 and 285 eV, respectively. The details of the XPS results will be presented in the conference.

III. Summary

In conclusion, we have performed thorough and systematic characterizations of h-BN thin films by SEM, AFM, HRTEM, Raman and XPS measurements. Our characterization results reported here will serve as the stepping-stone toward realizing h-BN based non-classical devices for quantum computation and communication.

References

[1] Q. Cai, D. Scullion, W. Gan, A. Falin, S. Zhang, and K. Watanabe*, et al.*, "High thermal conductivity of high-quality monolayer boron nitride and its thermal expansion," *Sci. Adv.,* vol. 5, no. 6, p. eaav0129, 2019.

[2] S. Ali and K. S. Thygesen, "V_NC_B defect as source of single photon emission from hexagonal boron nitride," *2D Mater.,* vol. 7, no. 3, p. 031007, 2020.

[3] A. Rice, A. Allerman, M. Crawford, T. Beechem, T. Ohta, C. Spataru, J. Figiel, and M. Smith, "Effects of deposition temperature and ammonia flow on metal-organic chemical vapor deposition of hexagonal boron nitride," *J. Cryst. Growth.,* vol. 485, pp. 90-95, 2018.

[4] X. Yang, S. Nitta, K. Nagamatsu, S. Y. Bae, H.-J. Lee, Y. Liu, M. Pristovsek, Y. Honda and H. Amano, "Growth of hexagonal boron nitride on sapphire substrate by pulsed-mode metalorganic vapor phase epitaxy," *J. Cryst. Growth.,* vol. 482, pp. 1-8, 2018.

[5] H. T. T. Nguyen, "Graphene layer of hybrid graphene/hexagonal boron nitride model upon heating," *Carbon Lett.,* vol. 29, pp. 521-528, 2019.