



Characterization of hexagonal boron nitride layers on nickel surfaces by low-energy electron microscopy



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ABSTRACT

The thickness and interfacial geometry of hexagonal boron nitride (hBN) films grown by chemical vapor deposition on polycrystalline nickel foils is studied using low-energy electron microscopy (LEEM). The reflectivity of the electrons, measured over an energy range of 0–20 eV, reveals distinct minima and maxima. The measured data is compared with simulations based on a first-principles description of the electronic structure of the material. From this comparison, the number of hBN layers and the separation between the lowest hBN layer and the nickel surface is deduced. The coupling of interlayer states of the hBN to both image-potential and Shockley-type surface states of the nickel is discussed, and the dependence of the reflectivity spectra on the surface orientation of nickel grains is examined.

1. Introduction

For many reasons, hexagonal boron nitride (hBN) is an ideal candidate for graphene-based vertical and horizontal heterostructures: hBN and graphene have a small lattice mismatch ($< 2\%$); it is atomically flat, unlike SiO_2 ; it is chemically inert; and it produces no charge traps, again, unlike SiO_2 [1,2]. Devices based on vertical heterostructures have been predicted to have unique properties [3], properties which have been realized recently in devices incorporating exfoliated hBN [4]. Such a device construction is not scalable, however, and a large portion of recent efforts in the growth of hBN have therefore centered on epitaxial growth [5–10]. Following the success achieved in the growth of graphene, most of these efforts have focused on chemical vapor deposition (CVD) of hBN on metal foils.

Optimization of this growth cannot proceed, however, without a definitive and convenient means of determining the number of monolayers (MLs) present on the surface. Many researchers have attempted to use two methods that are commonly used in graphene systems: optical microscopy, and Raman spectroscopy. Unfortunately, neither method can confidently perform such a measurement in hBN systems [11,12]. Cross-sectional TEM is certainly definitive, but it is a time consuming procedure that characterizes only very small portions of the surface.

Another instrument, the low-energy electron microscope (LEEM),

has been established to be a powerful tool in determining the number of MLs of graphene or hBN present on a substrate, in particular by study of low-energy electron reflectivity (LEER) spectra [10,13–16]. For the case of graphene in particular, it was demonstrated by Hibino and co-workers that by counting the number of *minima* in the 0–7 eV energy range of a LEER spectrum, one can confidently determine the number of graphene MLs present [13]. While a qualitative explanation of this phenomenological method was presented in that early work, a quantitative explanation has become available more recently, in the form of a first-principles simulation method for LEER spectra [17,18].

Here, we present data on single- and multi-ML hBN films grown on polycrystalline nickel foils. These studies were the result of both a desire to characterize the growth of such films for their incorporation into devices, as well as to explore the applicability of quantitative characterization of the hBN based on its LEER spectra. We find that the oscillations seen in the low-energy portion (0–7 eV) of the experimental spectra, similar to those seen in graphene, are reproduced by our first-principles method. The participation of various bands of the hBN in the reflectivity, which turns out to be different than for graphene films, is also revealed. Additionally, we find that different surfaces of the Ni yield slightly different LEER spectra, with one source of this difference believed to be Shockley-type surface states of the Ni surface affecting the reflectivity spectra at very low energies.

Compared to prior works involving LEER of two-dimensional (2D)

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layered materials, the present work achieves greater understanding of how the various bands of the 2D overlayer and the substrate contribute to the LEER spectra. Our experimental results are in good agreement with the prior LEER spectra of Hibino and co-workers for single- and few-layer graphene and hBN films [10,13]. Additionally, our work demonstrates good agreement of theoretically computed spectra with experimental results (focusing on 1 and 2 ML thick films). We find considerable differences between LEER spectra of graphene and hBN, which we demonstrate is due to the different character (symmetry) of their respective electronic bands. Certain bands contribute to the spectra of hBN, but not graphene. It turns out that these same bands for hBN are strongly influenced by inelastic effects (since they are localized on the atomic planes, as opposed to in the interlayer spaces), so a complete computation is needed to understand their contribution to the spectra. We thus understand how the LEER spectra can be used as a means of *chemical identification* between graphene and hBN, and future computations for other materials may yield similar (predictive) capability.

We note that our method of including inelastic effects is more approximate than the prior theory of Krasovskii and co-workers [19–21]. Both theories include an energy-dependent imaginary term in the potential, but for the theory of Krasovskii et al. this term is employed within a full solution to the Schrödinger equation whereas in our theory it is applied in a more phenomenological manner, *ex post facto* to an elastic-only solution of the Schrödinger equation. Our theory is thus considerably simplified, since it requires only a standard electronic-structure computation e.g. using the Vienna Ab Initio Simulation Package (VASP), followed by relatively straightforward post-processing of those results. Importantly, we find good agreement between our computed spectra and the experimental ones, thus providing some degree of confidence in the method we employ for including inelastic effects.

2. Experimental and theoretical methods

2.1. Growth

Samples were prepared using two custom-built growth systems. The first is a UHV system with a $\sim 1 \times 10^{-10}$ Torr base pressure. This system uses gaseous ammonia and diborane precursors, and was used to prepare the first sample (Sample 1) discussed in this paper. The second system is a low-pressure CVD tube furnace which uses a solid ammonia-borane precursor, and was used to prepare the second and third samples (Samples 2 and 3). The substrates used are 99.9999% pure Ni foils, with thickness of 12.5, 25, 50, or 150 μm . We found that the UHV system allows for the growth of well-ordered hBN multilayers. Sample 1 was grown on a 150- μm -thick foil in this system and yielded a hBN film with average thickness > 2 ML. In this system, a typical growth starts with the system pumped to the base pressure ($\sim 10^{-10}$ Torr). Then the samples are exposed to a flow of H_2 (2 sccms) while heating the chamber and annealing the samples at the growth temperature (~ 1050 °C). Finally, a flow of 2 sccms of diborane and ammonia for is used for the hBN growth (15 min growth time for Sample 1). After the growth is concluded, the samples are cooled down to room temperature in the presence of H_2 .

Samples 2 and 3 were synthesized in a home built LPCVD system working with ammonia-borane and H_2 . In this case, 25 μm foils were folded into Ni enclosures [22] were used (the full details of the growth will be published shortly) [23]. Briefly, the system is pumped down to the base pressure of ~ 10 mTorr. Then a flow of 2 sccms of H_2 is added and the sample is heated to the growth temperature (1050 °C). The samples are annealed for ~ 30 min and then exposed to ammonia-borane (which is heated in a separate heater to ~ 100 °C). The growth for samples 2 and 3 were about 10 and 15 min, respectively, yielding hBN films that were thinner than that of Sample 1.

2.2. Low-energy electron microscopy

Samples were transferred through air to an Elmitec III system. In this instrument, the sample and electron emitter are kept at high voltage. After leaving the emitter, electrons are accelerated to high-energies (~ 20 keV) into the illumination column wherein the beam is focused. The beam is subsequently diverted towards the sample at normal incidence by a magnetic deflector/beam-separator. Before coming into contact with the sample, the beam may or may not be collimated by an *illumination aperture*. This aperture restricts the area of the beam to sizes between ~ 1 – 7 μm in diameter. Such a confined beam makes possible the performance of selected-area low-energy electron diffraction (μLEED).

Upon approaching the sample, the electrons are decelerated to low-energy (typically 0–20 eV) and are then either reflected (or diffracted) from the surface or are absorbed in the sample. Those electrons which are reflected or diffracted are re-accelerated to high energy, passed into the imaging column by the magnetic beam-separator, and are focused either into a real-space image or into an image of the diffraction pattern of the illuminated portion of the surface. Real-space images of the surfaces presented in this work were all done in bright-field imaging mode. Bright-field images are formed by filtering the beam with a *contrast aperture*, allowing only those electrons which are specularly reflected from the sample to pass through; electrons which obtain a non-zero momentum component parallel to the surface during scattering do not take part in image formation in this mode.

2.3. First-principles calculations

Our method for theoretically predicting LEER spectra has been previously described, including the important role of inelastic effects in such spectra [18,24]. In the absence of inelastic effects, then for a given structure of the hBN/Ni system we perform a parameter-free computation of the LEER spectra, employing post-processing of electronic states obtained from VASP using the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) for the density-functional and a plane-wave energy cutoff of 400 eV [25–28]. This procedure involves computing the states of a supercell consisting of a hBN/Ni/hBN slab with at least 20 Å of vacuum on both sides, and making a detailed analysis of the states thus obtained with those of bulk Ni of the same orientation. The results depend on the structure through the separation of the hBN and the Ni and through buckling of the hBN. To model inelastic effects, a parameter is introduced: the magnitude of the imaginary part of the potential in the solid, V_i , which determines the degree of electron absorption [19–21]. In general, V_i will have some energy dependence, so actually more than one parameter is involved. The dominant absorption mechanism at the low energies considered here occurs due to plasmons in the solid. However, the plasmon energy is typically above 15 eV [19–21], which is at the upper edge of the energies that we consider. For lower energies, the absorption mechanisms are less well understood, and they may involve surface defects or disorder [19].

In our prior work [24], considering single- or few-layer graphene or hBN on various substrates, we have argued that a linear form for V_i given by $0.4 \text{ eV} + 0.06 E$ where E is the energy relative to the vacuum level fits the experimental reflectivity data fairly well (for energies below the plasmon turn-on), and we continue to use this form for all of our analysis in the present work. Additional parameters in the inelastic analysis are an “inner potential” for the electrons in the solid, and a “turning point” (relative to the surface plane) for the incident electrons. We have demonstrated previously that our results are very insensitive to the choice of these parameters [24], and we employ values of 13 eV and 0.9 Å, respectively, for all of our analysis.

In the theoretical results shown throughout this work we will compare the computed reflectivity with the band structure of the hBN overlayer (i.e. following the useful presentation method intro-

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