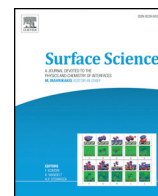




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Q2 Q1
4 **Reconciling the electronic and geometric**
3 **corrugations of the hexagonal boron nitride**
3 **and graphene nanomeshes**

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STM simulation

Moiré-structured monolayer graphene (g) and hexagonal boron nitride (h-BN) films supported on transition metals have received considerable attention recently [1–3] due to their fascinating electronic properties [4,5], and their potential to act as substrates that promote the self-assembly of molecules and metal clusters relevant to material and catalytic applications [6–8]. However, several details regarding the physical characteristics of these nanomesh structures, such as their periodicity and corrugation, remain unsettled. Here, we take h-BN/Rh(111) and g/Ru(0001) as examples, and perform self-consistent van der Waals (vdW) corrected density functional theory (DFT) calculations for both structural optimization and scanning tunneling microscopy (STM) image simulation to demonstrate a trend of divergence between the STM-measured *apparent* corrugation vs. actual *geometric* corrugation of nanomeshes formed by 2D films on transition metal surfaces. In particular, we show that relatively small apparent corrugations observed for the 2D nanomeshes in STM experiments are fully compatible with much larger geometric corrugations as predicted by DFT. This is due to a systematic electronic effect *inherent* in these corrugated 2D films. STM is now a mainstay surface characterization technique and is used, often implicitly, to evaluate the choice of density functional and the validity of structural predictions in theoretical modeling. Therefore, this trend has important implications for the understanding and prediction of the surface structure–function relationship of corrugated 2D films, such as the ability of the h-BN and graphene nanomeshes to trap macromolecules [2,9] and metal clusters [6,7], where the effect of the surface corrugation on global diffusion is important [10–14].

Recently, Patterson et al. identified a discrepancy in the experimental and theoretical values of the corrugation of the h-BN/Rh(111) nanomesh [15], which consists of alternating low-lying “pore” and high-lying “wire” regions [2] (Fig. 1). The apparent corrugation in STM at a sample voltage of +1.0 V was found to be 0.5 Å, consistent with Brihuega et al., who reported the apparent corrugation of h-BN/Rh(111) to be 0.5–1.0 Å over a sample voltage range of –5 to +1 V [7]. However, the geometric corrugation calculated using DFT with several different exchange–correlation functionals ranges from 2.2 to 2.6 Å [15]. Furthermore, because the h-BN/Rh(111) nanomesh is much more effective than, e.g. g/Ru(0001), at nucleating Au nanoclusters and preventing them from agglomerating [15,16], a corrugation that is

comparable to g/Ru(0001) (0.15–1.5 Å based on different experimental techniques [17–19]) seems puzzling.

Here, we examine the disagreement between the STM and DFT estimates of the h-BN/Rh(111) nanomesh corrugation in detail, and establish that an apparent corrugation of 0.5 Å is fully consistent with an actual geometric corrugation of >2.0 Å. In particular, we show that the chemically distinct low/high-lying regions of the h-BN nanomesh make unequal contributions to the local density of states (LDOS) near the Fermi energy (E_F), similar to what has been previously noted for the g/Ru(0001) nanomesh [20]. This leads to an apparent electronic corrugation that differs significantly from the geometric corrugation in both cases, a factor that should be considered in addition to voltage dependencies and tip effects [21] when interpreting STM measurements.

The h-BN/Rh(111) and g/Ru(0001) nanomeshes are optimized using self-consistent periodic DFT calculations based on the optB86b vdW functional of Klimeš et al. [22], and the projected augmented wave method as implemented in the VASP code (version 5.3) [23, 24]. The Kohn–Sham eigenstates are expanded in a plane-wave basis up to an energy cutoff of 400 eV. The Methfessel–Paxton scheme is used to smear the electronic states with a width of 0.1 eV. h-BN/Rh(111) is modeled by placing a (13 × 13)-h-BN monolayer on a (12 × 12)-Rh(111) surface (i.e., 13-on-12) [15]. For g/Ru(0001), the unit cell is comprised of a (12 × 12) graphene monolayer on an (11 × 11)-Ru(0001) surface [25]. 25-on-23 and 11-on-10 g/Ru(0001) structures have also been proposed, but their DFT-calculated corrugations are similar [26,27]. The optimization of h-BN/Rh(111) and g/Ru(0001) both proceed from an initially flat film on one side of a three-layer thick metal slab. In each instance, the unit cell is based on the equilibrium lattice constant of the transition metal resulting in an initially strained 2D film, and the strain is partially relieved upon optimization to the corrugated minimum-energy structure. The optB86b lattice constants for Rh and Ru ($a = 3.803$ Å, and $a/c = 2.702/4.266$ Å) closely match those in experiments ($a = 3.80$ Å, and $a/c = 2.70/4.266$ Å) [28]. The atoms in the nanomesh and the topmost metal layer are relaxed until the force in each relaxed degree of freedom fall below 0.03 eV/Å. At least 10 Å of vacuum space is included between the top of the optimized nanomeshes and the neighboring metal slabs in the z direction, with electrostatic decoupling applied in the z direction [29]. Due to the large size of the unit cells, reciprocal space is sampled at the Γ point only during geometry optimization. The electronic structures of the optimized cells are subsequently evaluated on a $3 \times 3 \times 1$ Monkhorst–Pack k -point grid while keeping the structures frozen.

For the optimized h-BN/Rh(111) nanomesh, the minimum pore–Rh distance is found to be 2.14 Å. The highest nanomesh atom is an N in the wire region, and the lowest a B atom in the pore region. Their height difference (the maximum corrugation), 2.39 Å based on optB86b, is in fair agreement with the corresponding values based on LDA (2.65 Å) and GGA-PBE (2.20 Å) [15], but differs significantly from the 0.5 Å and 1.2 Å obtained by Laskowski et al. [30] and Diaz et al. [31] using the WC and revPBE + D3 functionals, respectively.

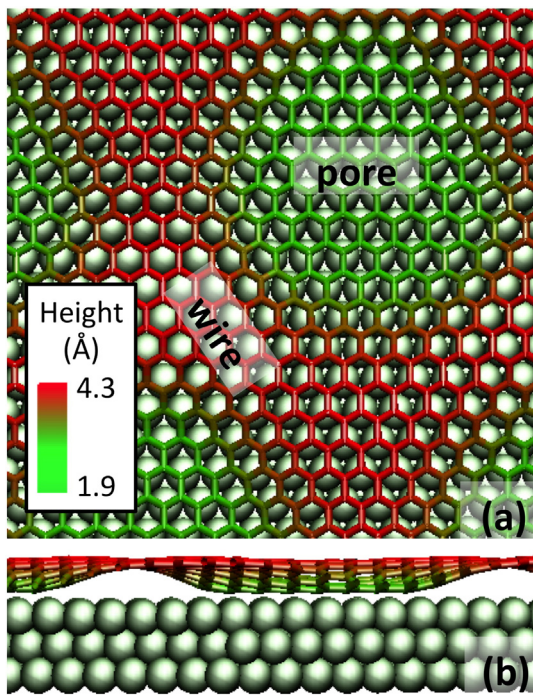


Fig. 1. (a) Top and (b) side views of the DFT-optimized structure (using the optB86b vdW functional) of the h-BN nanomesh on Rh(111). The nanomesh is colored according to its height above Rh(111) (pore region in green/lighter shades and wire region in red/darker shades). Rh atoms are shown as spheres.

Recently, Iannuzzi et al. have also reported different geometric corrugations for h-BN/Rh(111) based on the vdW-DF of Dion et al., revPBE + D3, and PBE-rVV10 (0.9, 1.1, and 2.3 Å, respectively), and concluded that PBE-rVV10, another self-consistent vdW functional, is best suited to describing the structure of the h-BN nanomesh and the adsorption properties of phthalocyanines thereon [9]. The large spread in the h-BN corrugation values given by the different functionals

highlights the need for careful validation of the theoretical results by comparison with experiment. We therefore also simulated STM images for the h-BN/Rh(111) nanomesh over a range of bias voltage for comparison with the available experimental data.

STM images are simulated via the Tersoff–Hamann [32] formalism at an isodensity contour of $2.0 \times 10^{-3} e^-/\text{Å}^3$. At this contour value, the simulated apparent corrugation for h-BN/Rh(111) is 0.6 Å at a sample voltage of +1.0 V and 1.1 Å at –1.0 V, in close agreement with the experimental values of 0.5 Å at +1.0 V [15] and 0.88 Å at –1.0 V [9]. Furthermore, both the predicted apparent corrugation and its voltage dependence agree well with the experimental results of Brihuega et al. [7] in the range of –1.0 to +2.0 V. Thus, the significant geometric corrugation in h-BN/Rh(111) predicted by DFT is compatible with the shallow corrugations seen in STM. In STM measurements, the precise geometry (and hence electronic structure) of the tip is generally unknown, and may differ from tip to tip. The Tersoff–Hamann formalism, unlike more sophisticated approaches (e.g. the Bardeen method), does not account for effects due to the STM tip, but has the interpretive advantage that the resulting STM images reflect the electronic structure of the surface alone. The inclusion of the tip in STM simulation would likely further reduce the apparent surface corrugation and is beyond the scope of the present work.

Following Tersoff–Hamann [32], the tunneling current is proportional to the LDOS at the position of the tip. Hence, in the constant current mode, the tip is envisioned as moving along an isodensity contour derived from a partial charge density arising from the states in a given energy range on one side of E_F chosen to mimic the bias voltage (e.g. +1.0 V sample voltage corresponds to states in the $E_F \sim E_F + 1.0$ eV range). In the ± 2.0 eV range about the E_F , the h-BN nanomesh contribution to the LDOS originates mainly from its p_z states, with the N p_z projected DOS (PDOS) far outweighing the B p_z PDOS. The p_x and p_y states of the B and N atoms lie too low in energy (starting at about –5 eV relative to E_F) to be pertinent to the current discussion of STM imaging. Importantly, the respective contributions of the low/high-lying atoms to the LDOS are not equal. The p_z states of the low-lying atoms dominate in the vicinity of E_F (Fig. 3(a)), indicating that the BN states in the vicinity of E_F are localized in the pore regions of the

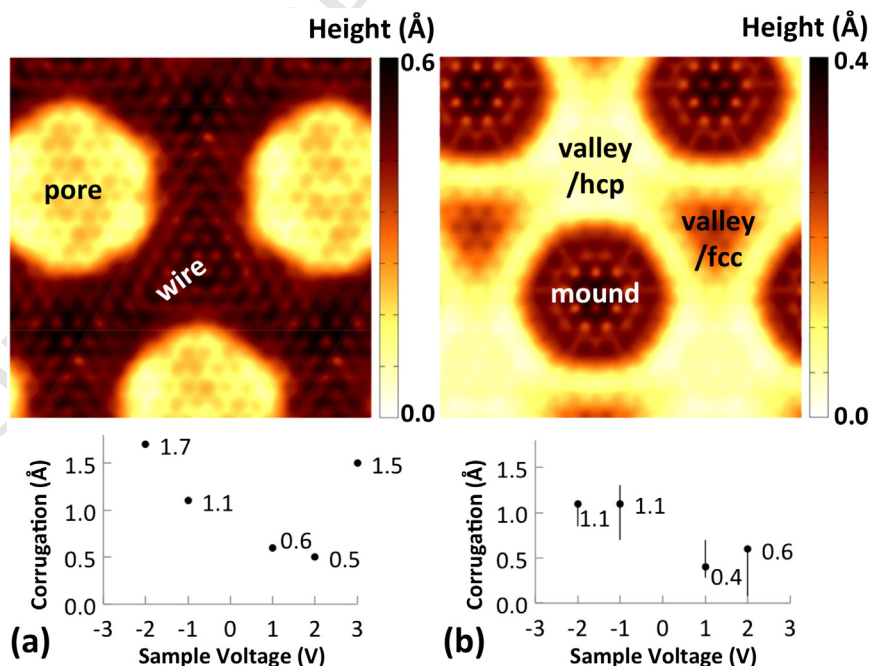


Fig. 2. Simulated STM images at a sample voltage of +1.0 V (top panel), and maximum apparent corrugations at various sample voltages (bottom panel, measured between highest atom in wire/mound region and lowest atom in pore/valley region), for (a) h-BN/Rh(111) and (b) g/Ru(0001). Different regions of the two nanomeshes are labeled. The height scale is relative to the lowest tip position in each simulation. The +3 V point for h-BN/Rh(111) is due to inverted contrast (see text). Braces around the apparent corrugations of g/Ru(0001) reflect the range of experimentally determined values from Ref. [26].

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