

## Unraveling the Structure of h-BN / TM(111) Nanomeshes with Ab Initio Calculations

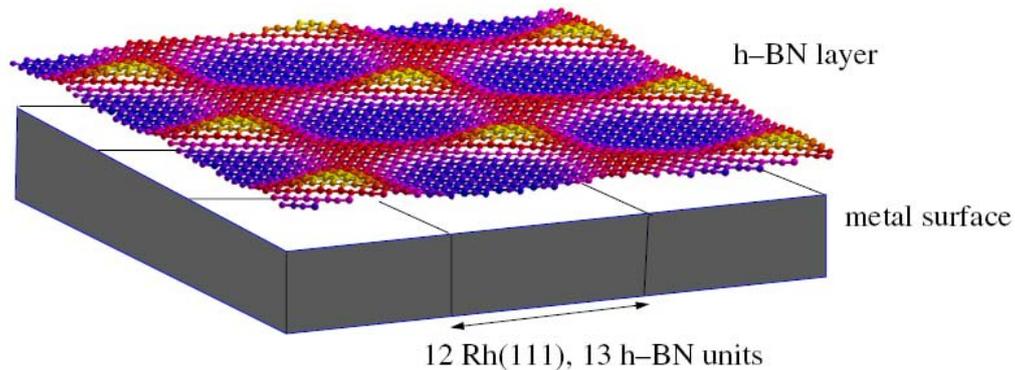
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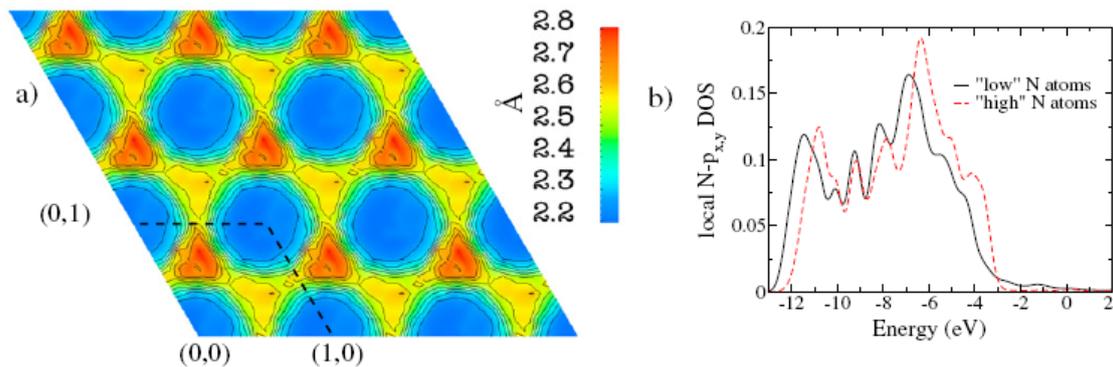
Recently, a self-assembling structure was detected when borazine is thermally decomposed on a Rh(111) surface. Later on similar structures were found on other transition metal surfaces. Hexagonal boron nitride forms a highly regular h-BN/Rh(111) “nanomesh” structure with a periodicity of about 3.2 nanometers. A hexagonal unit cell consisting of a  $12 \times 12$  Rh substrate on which  $13 \times 13$  h-BN layers form was deduced from LEED patterns and STM pictures. A periodic hole structure of about 2 nm diameter was observed within this unit cell. Based on the STM images and on UPS data, which showed a splitting of the BN- $\sigma$  bands, an atomic model was suggested, which consists of two (partially incomplete) BN layers [1].

Such a model, however, has many broken BN-bonds and is energetically very unfavourable. Therefore we have performed DFT based calculations using the APW+lo method as embodied in the WIEN2k package [2]. In order to optimize the geometry of the BN layer we used both, an ab initio derived force field model (which also gives us insight into the various interactions leading to the nanomesh structure) and a direct DFT-simulation of the full nanomesh structure with a unit cell of more than 1100 atoms/cell. We propose an alternative model of the h-BN/Rh(111) nanomesh [3,4] which consists of only one, but strongly corrugated layer of h-BN covering the whole Rh surface (Fig. 1). The final geometry is a result of a competition between the B-Rh and N-Rh attraction and repulsion, which varies strongly with the BN position relative to the underlying Rh surface, and the elastic properties of the isolated h-BN layer, which wants to keep BN flat. This leads to a highly corrugated structure with “holes” (pores), where BN is close to the metal surface because N is close to the on-top of Rh position, while on the “wires” BN is  $0.6 \text{ \AA}$  further away from the metal surface and N sits near fcc or hcp sites above Rh (Fig. 2a). The B-metal and N-metal interactions become weaker when the d-band filling is increased leading to more or less pronounced nanomesh structures on other metals like Ru or Pt.

This model has been verified by new experiments [5] and explains the splitting of the BN  $\sigma$ -band by about 1 eV as observed in UPS spectra (Fig.2b). The theoretical STM images can explain the voltage dependency of the contrast inversion of the experimental STM images [4]. The BN/Rh(111) nanomesh is also capable to trap single molecules and form self-assembled molecular structures. The origin of this ability could be traced back to dipolrings which arise at the edges of the pores [6].



**Figure 1** Schematic image of the corrugated h-BN layer on top of the Rh(111) surface. The periodicity of the layer is equal to 13 h-BN units and 12 Rh(111) units.



**Figure 2** (a) Contour map of the  $z$  coordinate of N atoms above Rh in a  $3 \times 3$  nanomesh unit cell predicted by *ab initio* calculations. (b) *Ab initio* calculated local density of states projected on N- $p_{xy}$  states ( $\sigma$  bands) calculated for the 45% highest and 45% lowest N atoms in the full nanomesh unit cell.

## References

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