Hexagonal Boron Nitride Nanomeshes

Joseph Buthker   Literature Seminar   November 4, 2008

The chemical vapor deposition (CVD) of borazine on transition metal surfaces creates a monolayer of hexagonal boron nitride (*h*-BN).[1] On most surfaces, such as Pt(111), Pd(111), and Ni(111), *h*-BN forms a flat monolayer that is insulating and stable against high temperatures and reactive gases.[2-5] On Rh(111) and Ru(0001) surfaces, however, a unique *h*-BN nanomesh with 0.05 nm deep holes is formed.[6,7] The term nanomesh originates from the model proposed by Corso et al.,[6] which consisted of two identical and incomplete *h*-BN layers with regular 2.4 nm apertures. This model was proved incorrect by additional studies, which determined that the reported nanomesh was actually a corrugated monolayer (Figure 1).[8-10] The term nanomesh, however, is still commonly used in the literature to describe the *h*-BN corrugated monolayer.
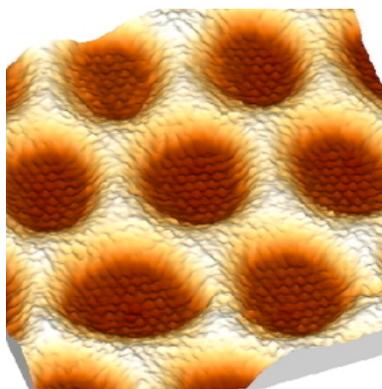
Figure 1. An atomic resolution STM image (10 x 10 nm^2) of the *h*-BN nanomesh on Rh(111).[11]

Several potential applications for the *h*-BN monolayer have been suggested. The periodicity of the nanomesh could serve as a template for self-assembly or self-organization processes by providing surface cues to guide the formation of ordered structures.[12] Such templating effects also provide opportunities for exerting fine control over the manipulation of matter on the molecular scale, allowing for continuing progress in miniturization.[13] Applications in catalysis could also be realized because the holes in the nanomesh could serve as regions to aid in the formation of nanoparticles.[14,15]

The unusual corrugation of the *h*-BN monolayer has been explained using density functional theory (DFT).[8,10] The boron antibonding band remains well above the Fermi level of the system whereas part of the nitrogen antibonding band is below the Fermi level and thus partially filled (Figure 2). The result is that the boron atoms are attracted to the Rh(111) surface, but the nitrogen atoms are repelled. The hole regions are formed where the boron attraction force is maximized and the nitrogen repulsion force is minimized—when boron and nitrogen are in the *fcc* and *top* (directly above a Rh atom) positions, respectively. Here the *h*-BN monolayer is pulled closer to the surface. The raised (wire) regions result from the *h*-BN/Rh(111) lattice mismatch that prevents every boron and nitrogen from occupying their preferred *fcc* and *top* positions. When this happens, the boron-metal attraction is weakened and the nitrogen-metal repulsion is strengthened, pushing the *h*-BN monolayer away from the surface.
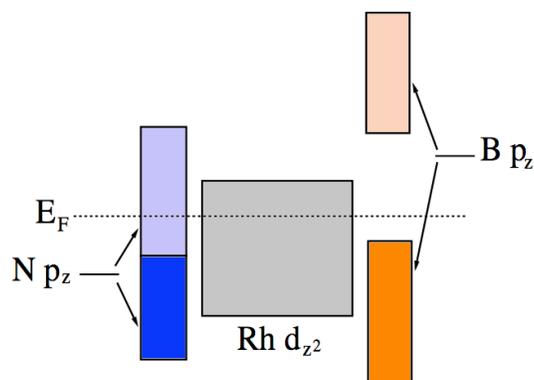
Figure 2. A schematic diagram of the density of states around the Fermi level.[10]

The corrugation of the nanomesh allows it to trap molecules in its holes. The mechanism of such trapping was investigated by photoemission spectroscopy of adsorbed Xe.[16] Three distinct regions of Xe binding energies were revealed, even though the surface has only two distinct regions, the holes and wires. One region was attributed to Xe that adsorbed to the wires. The other two were attributed to Xe adsorbed in the holes, which consist of two regions—the bottom of the holes, and the rims around the holes. The Xe at the rims was bound more strongly than the Xe at the bottom of the holes due to the strong potential gradient here, where the different work functions of the hole and wire regions meet.

Actual applications of *h*-BN nanomeshes have only begun to be investigated. Because the nanomesh is an insulator, it provides an environment in which molecules can be examined in the absence of interactions with the metal substrate. Cobalt clusters deposited on the *h*-BN nanomesh revealed a Coulomb gap, whereas their counterparts deposited directly on Rh(111) showed metallic behaivor.[11] Catalytic applications of the nanomesh include serving as an oxygen and carbon free environment for the formation of nanoparticles.[14] Gold nanoparticles can form in the holes of the nanomesh with careful control of the experimental conditions. Gold tends to diffuse through the nanomesh and form islands on the metal surface when the sample is annealed at 1050 K, or if the coverage of the deposited gold is greater than 0.3 monolayers.[14]

Comparisons between *h*-BN and graphene are of interest because they are isoelectronic and structurally similar. The hole size in corrugated graphene monolayers is similar to that in the *h*-BN nanomeshes, but with higher lateral density of the holes.[17] Unlike *h*-BN, which forms a corrugated dielectric monolayer, graphene forms a corrugated metallic monolayer.[1,18]

Experimental studies of the nanomeshes are still in the early stages and are focused on understanding their properties. Their unusual structures, however, suggest that they will have other applications yet to be realized.

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