e-J. Surf. Sci. Nanotech. Vol. 8 (2010) 62-64 Conference - ALC09 -

Graphene and Hexagonal Boron Nitride Layers: Nanostructures with 3 bond hierarchy levels*

Thomas Greber†
Physik-Institut, Universität Zürich, Winterthurerstrasse 190, CH 8057 Zürich, Switzerland
(Received 8 January 2010; Accepted 9 January 2010; Published 6 February 2010)

Single layers of carbon (graphene) and hexagonal boron nitride may be grown on transition metal surfaces. The substrates take the role of the support and allow due to their catalytic activity the growth of perfect layers by chemical vapor deposition. The layers are sp^2 hybridized honeycomb networks with strong in plane σ- and weaker out of plane π-bonds to the substrate and to the adsorbates. This hierarchy in bond strength causes anisotropic elastic properties, where the sp^2 layers are stiff in plane and soft out of plane. A corrugation of these layers imposes a *third* hierarchy level in bond energies (α-bonds), with *lateral* bonding of molecular objects with sizes between 1 and 5 nanometer. The lateral extra bond energies due to the polarizability α of the adsorbates are in the range of thermal energies kT_R at room temperature and are particularly interesting for nanotechnology. The concomitant template function will be discussed. The peculiar bond hierarchy also imposes intercalation as another property of sp^2 layer systems. Last but not least sp^2 layer systems are particularly robust, i.e. survive immersion into liquids, which is a promise for sp^2 layers being useful outside ultra high vacuum. [DOI: 10.1380/ejssnt.2010.62]

Keywords: Graphene; Boron nitride; Nano-films; Nano-scale imaging; Photoemission; Dipole rings; Alpha bonds; sp^2

I. INTRODUCTION

Ultra-thin epitaxial films of graphite –nowadays called graphene– and hexagonal boron nitride on solid surfaces have been pioneered by Oshima and Nagashima, who studied the electronic and vibronic structure of these sp^2 hybridized layer systems [1]. They noticed that the comparison of graphene and hexagonal boron nitride is helpful for the understanding of their properties, and that a successful combination of the two would realize new materials. These films have been considered to be *flat*, and only later it was found that other substrates like *Rh* and *Ru* impose a *corrugation*, i.e. a strong vertical deformation that can be described as a static distortion wave of the sp^2 layers with typically 3 nm wavelength and 0.05 to 0.15 nm peak-to-peak amplitude [2, 3]. The corrugation results from the epitaxial stress due to the lattice misfit *and* a strong site dependent lateral lock in energy of the sp^2 layer and the substrate [4]. Here the remarkable consequences of this corrugation are discussed: It generates strong lateral electric fields in nanostructures and a template functionality that allows the trapping of single molecules at room temperature in localized, nanometer-sized traps. These electric fields are traced back to "dipole rings" [5], i.e. ring like, lateral charge inhomogeneities within the supercells containing up to 1250 atoms per layer [6].

Figure 1 shows a three dimensional view of the boron nitride nanomesh (h-$BN/Rh(111)$) with one trapped Cu-phthalocyanine molecule. The traps are locations where the h-BN is in close contact to the rhodium substrate and are called "holes" of the nanomesh. The hole-hole distance is 3.2 nm and the mesh has a corrugation of about 0.1 nm. The concomitant lateral electrostatic fields give rise to weak polarization induced α-bonds where the label

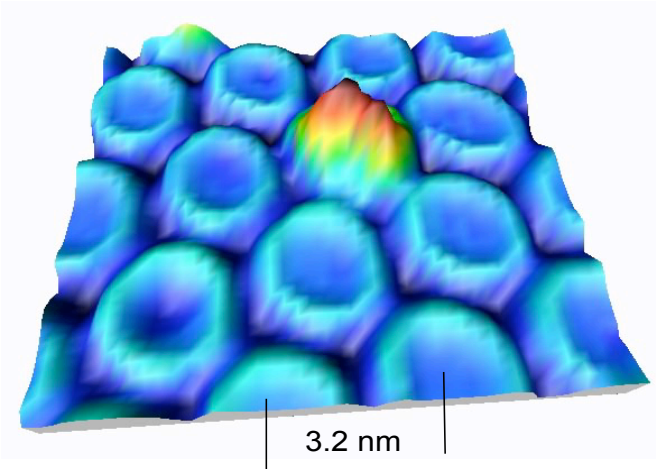

FIG. 1: Three dimensional view of the boron nitride nanomesh (h-$BN/Rh(111)$) with one Cu-phthalocyanine molecule ($C_{32}H_{16}CuN_8$) trapped in a hole. The mesh has a corrugation of about 0.1 nm and a lattice constant of 3.2 nm. Data from [5].

α establishes the link to the polarizability of the molecule that is often abbreviated with α. This is considered to be, after the strong sp^2 σ-bonds and the intermediate π-bonds the *third* bond hierarchy level in sp^2 hybridized single layer systems. The α-bonds are selective to the polarizability and the given geometric structure of the template imposes a size selectivity. As a consequnce the α-bonds open new functionalities for this kind of interface systems.

II. DIPOLE RINGS

Figure 2 shows the dipole ring concept that rationalizes lateral electrostatic potential variations in corrugated nanostructures. This potential and the related electrostatic fields are important for the understanding of the trapping of molecules as shown in Fig. 1. For in plane dipoles that sit on a ring the difference in electrostatic

*This paper was presented at 7th International Symposium on Atomic Level Characterizations for New Materials and Devices, The Westin Maui Resort & Spa, Hawaii, U.S.A., 6-11 December, 2009.
†Corresponding author: greber@physik.uzh.ch

 © 2010 The Surface Science Society of Japan (http://www.sssj.org/ejssnt)

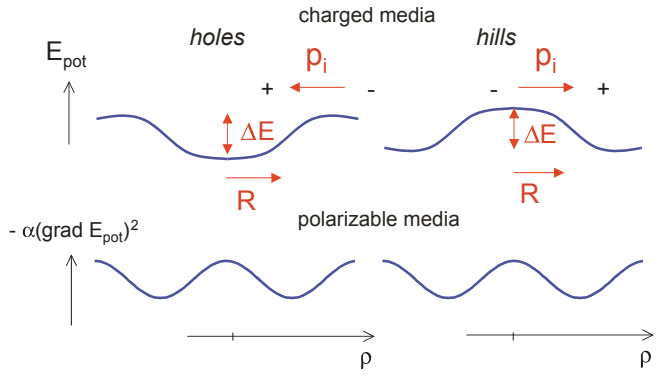

FIG. 2: Model for the electrostatic potential of dipole rings as a function of the radius ρ. The lateral electrostatic potential $E_{\rm pot}$ implies a strong bonding for charged particles. The bonding due to polarization is expected to be proportional to the polarizability α of the particles and the square of the gradient of $E_{\rm pot}$. Accordingly, polarizable media (atoms and molecules) should bind, irrespective on whether the electrostatic potential is attractive (hole) or repulsive (hill) at the rims of the corrugated nanostructures.

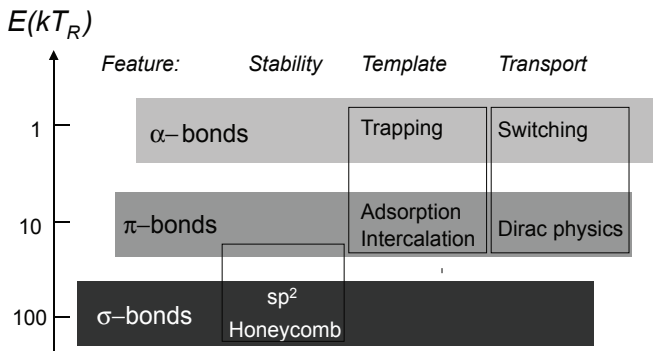

FIG. 3: The three bond hierarchy levels for bond energies in sp^2 hybridized single layer surface systems. The energy scale is referred to room temperature $kT_R = 25$ meV. The σ-bonds provide the strong sp^2 bonds between the atoms, constituting the single layers. The π-bonds involve the p_z orbitals and are responsible for the adsorption and intercalation energies, and the "Dirac-physics" with respect to electron and spin transport. The third hierarchy level is ruled by polarization induced α-bonds, which are weak, though may allow lateral trapping and switching of molecules.

potential energy difference ΔE between the center of the ring and infinity is:

$$\Delta E = \frac{e}{4\pi\epsilon_0}\frac{P}{R^2} \qquad (1)$$

where e is the elementary charge, R the radius of the ring, and $P = \sum|\mathbf{p}_i|$ the sum of the absolute values of the dipoles on the ring. The sign of P determines whether the potential is attractive of repulsive. For h-BN/Rh(111) R is 1 nm and ΔE=0.3 eV and attractive for electrons [5]. This value of ΔE is measured at the center of adsorbed Xenon with a van der Waals radius of 0.216 nm. ΔE is determined from the core level binding energy difference of Xe that is adsorbed in the holes and on the wires of the h-BN nanomesh [5]. From this P gets 10 Debye, which is equivalent to the dipoles of 5.4 water molecules with the hydrogen atoms pointing to the center of the holes. It has to be mentioned that the potential energy difference ΔE will increase in approaching the surface and thus also the bonding strength will increase. For large distances z from the surface ΔE will vanish $\propto \frac{1}{z}$. For graphene on ruthenium it was found that the corrugation of graphene causes an "inverse" landscape, where instead of "holes", "hills" with opposite gradients form [8]. The variations of the electrostatic potential imply strong lateral electric fields that may be exploited for trapping atoms, molecules, or charged particles. The square of the gradient of the electrostatic potential, or the electric field, is expected to be proportional to the polarization induced

$$E_{\rm pol} = \frac{1}{2}\mathbf{E}_{\|}\cdot\mathbf{p}_{\rm ind} = \frac{1}{2}\alpha\cdot\mathbf{E}_{\|}^2 \qquad (2)$$

where $\mathbf{E}_{\|}$ is the lateral electric field, $\mathbf{p}_{\rm ind}$ the induced dipole, and α the polarizability of the molecule. Equation 2 is a first order approximation and neglects the weakening of the field of the dipole ring due to the induced dipole in the molecule. An inclusion of this effect does however not alter the statement that polarizable media have the maximum polarization energy gain at the largest potential gradients, i.e. at the rims of the nanostructures. In Fig. 2 it can be seen that $E_{\rm pol}$ is largest at the rims of the nanostructures, and thus rationalizes the bonding of Cu-phthalocyanine molecules to the rims of the nanomesh holes [5].

III. THE 3 BOND HIERARCHY LEVELS

sp^2 hybridized single layers of graphene and hexagonal boron nitride appear to be particularly useful "modern" [7] interface systems for a variety of nanotechnological applications. Figure 3 shows the 3 bond hierarchy levels and the related features on a logarithmic scale of energies expressed in units of kT_R, where T_R=300 K is the room temperature.

The *first* level, i.e. the σ-bonds, provides stability and high robustness due to the covalent honeycomb bonding network. The σ-bond energies are in the order of 10 eV.

The *second* level is governed by π-bonds that derive from the p_z orbitals of N, B and C, respectively. It is important to note that the π-bonds are much weaker than the σ-bonds. With regard to the feature "template-function" the π electrons are responsible for the bonding to the substrate and to adsorbing molecules. Also they allow for phenomena like intercalation, i.e. the embedding of atoms or molecules below an sp^2 hybridized layer, where the in-plane σ-bonds are not broken, while π-bonds may be formed and broken near room temperature. Furthermore, the π electrons determine the transport properties of sp^2 layers. For a honeycomb with two identical elements, in identical surroundings, this implies a "gapless semiconductor" for freestanding graphene, where "Dirac physics" is at work. Dirac physics means that the electrons at the Fermi level may be described as massless or quasi-relativistic particles, where for graphene a velocity of $\approx c/300$ is measured. For BN the symmetry breaking in the honeycomb unit cell causes a large gap of about 5 eV in the π band structure and the p_z electrons are

concentrated in pairs on the nitrogen sites.

The *third* level is named according to the label α for the polarizability, α-bonds. They constitute the weakest hierarchy level, where the bonding is guiding the molecules in a self-assembly process. They are responsible for a size and polarization dependent trapping [5]. Also they are expected to become players in molecular switching processes that may change the charge state or resistivity of a molecule [10].

[1] C. Oshima and A. Nagashima, J. Phys. Cond. Mat. **9**, 1 (1997).

[2] M. Corso, W. Auwärter, M. Muntwiler, A. Tamai, T. Greber, and J. Osterwalder, Science **303**, 217 (2004).

[3] S. Marchini, S. Günther, and J. Wintterlin, Phys. Rev. B **76**, 075429 (2007).

[4] R. Laskowski, P. Blaha, Th. Gallauner, and K.-H. Schwarz, Phys. Rev. Lett. **98**, 106802 (2007).

[5] H. Dil, J. Lobo-Checa, R. Laskowski, P. Blaha, S. Berner, J. Osterwalder, and T. Greber, Science **319**, 1824 (2008).

[6] D. Martoccia, P. R. Willmott, T. Brugger, M. Björck, S. Günther, C. M. Schlepütz, A. Cervellino, S. A. Pauli, B. D. Patterson, S. Marchini, J. Wintterlin, W. Moritz, and T. Greber, Phys. Rev. Lett. **101**, 126102 (2008).

[7] A. Goriachko and H. Over, Z. Phys. Chemie-Int. J. Res. Phys. Chem. Chem. Phys. **223**, 157 (2009).

[8] T. Brugger. S. Günther, B. Wang, J. H. Dil, M.-L. Bocquet, J. Osterwalder, J. Wintterlin, and T. Greber, Phys. Rev. B **79**, 045407 (2009).

[9] R. Widmer, S. Berner, O. Gröning, T. Brugger, J. Osterwalder, and T. Greber, Electrochemistry Communications **9**, 2484 (2007).

[10] M. Muntwiler, W. Auwärter, A. P. Seitsonen, J. Osterwalder, and T. Greber, Phys. Rev. B **71**, 121402 (2005).