Epitaxial growth of hexagonal boron nitride on Ag(111)

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The epitaxial growth of hexagonal boron nitride on a Ag(111) surface by chemical vapor deposition of borazine $(HBNH)_3$ was investigated by x-ray photoelectron spectroscopy and low-energy electron diffraction. In contrast to other transition-metal surfaces of hexagonal symmetry, such as Ni(111), Rh(111), or Ru(0001), the hexagonal BN layers form domains of arbitrary orientation, indicating that there is no preferred direction with respect to the Ag(111) lattice. This result is in accordance with recent *ab initio* calculations that predict vanishing or at least very weak bonding energies for BN on (111) surfaces of noble metals.

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After the discovery of the so-called boron nitride *nanomesh*,[1] as representing a single layer of hexagonal boron nitride (*h*-BN) on a Rh(111) surface,[2,3] the epitaxial growth of such boronitrene[4] layers gained new interest, especially since boron nitride and graphene are considered as promising ingredients for the engineering of future nanoelectronic devices.[5] So far, the epitaxial growth of boronitrene layers has been investigated for many transition-metal (TM) surfaces and, depending on substrate symmetry and lattice misfits, a large variety of superstructures has been observed.[6–22] In this Brief Report, the epitaxial growth of boronitrene layers on Ag(111) is investigated in order to extend the list of experimental studies to the late TM. According to a recent *ab initio* density-functional study[23] the bonding between boronitrene layers and TM surfaces is largest for the elements in the 4*d* row but it decreases with an increasing number of *d* electrons. Compared to the strongest bonding of the BN/Ru(0001) system, the calculated bonding energies for BN/Ag(111) range from 0–20 %, depending on the applied density functional [local-density approximation (LDA), Wu-Cohen (WC), and Perdew-Burke-Ernzerhof (PBE)]. In Ref. 23, the bonding between a TM surface and a boronitrene layer correlates with the strength of the TM-d_z^2 and B p_z and N p_z interaction. Between the electropositive B and the TM only the lowest (and thus bonding B p_z) states are occupied, leading to a bonding interaction for all TM whereas antibonding states become occupied between N and TM, making the interaction in total repulsive. However, in case of strong bonding-antibonding interactions with TM states right at the Fermi energy (E_F) some of these antibonding states may be shifted above E_F, which can reduce the strong Coulomb repulsion between the TM and N. For the case of BN/Ag(111) the d_{z^2} density of states of the Ag(111) substrate is hardly affected upon the formation of the BN/Ag(111) interface, since all Ag d_z^2 states are well below E_F and thus fully occupied. Finally the weak bonding comes from a partial cancellation between strong repulsive forces for the N sublattice and weak attractive forces for the B sublattice, which appear at relatively long distances from the Ag(111) surface.

Initially, our investigation of growing boronitrene layers on Ag(111) was motivated by the lattice mismatch between the boronitrene layer and Ag(111) with in-plane lattice constants of 250 pm and 289 pm, respectively, resulting in a mismatch of about 16% for a $1\times1R0°$ orientation or 0.2% for a $\sqrt{3}\times\sqrt{3}R30°$ orientation. On the one hand, BN/Ag(111) would be an ideal system to reveal the influence of symmetry and commensurability on epitaxial growth in terms of the distribution of $1\times1R0°$ and $\sqrt{3}\times\sqrt{3}R30°$ domains, as discussed for BN/Pt(111) in Ref. 14. On the other hand, no preferred orientation can be expected from the results of the theoretical calculations, which predict vanishing (or at least very small) bonding energies.[23]

In order to proof the predictions in Ref. 23, the epitaxial growth of boronitrene layers on Ag(111) was investigated with the experimental setup described previously[14,20,21] by using the standard procedures to deposit boron nitride via chemical vapor deposition (CVD) of borazine $(HBNH)_3$, cf. Refs. 14 and 21 and references therein. If CVD of the precursor is performed with usual doses in the range of 50 L at about 10^{-7} mbar [i.e., if the setup is operated with the same parameters that resulted in well-ordered boronitrene layers on, e.g., a Rh(111) surface[21]], neither boron nor nitrogen can be detected in x-ray photoelectron spectroscopy (XPS) and the low-energy electron diffraction (LEED) pattern is the same as for the clean Ag(111) surface. This is our first experimental hint that the bonding energies for BN on Ag(111) are strongly reduced. Only after increasing the dosage by

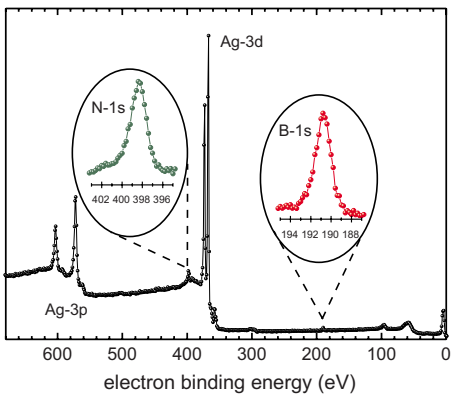

FIG. 1. (Color online) XPS data (Al-$K\alpha$, $\hbar\omega$=1486.6 eV) of BN/Ag(111) after deposition of 13500 L borazine $(HBNH)_3$ at 950 K.

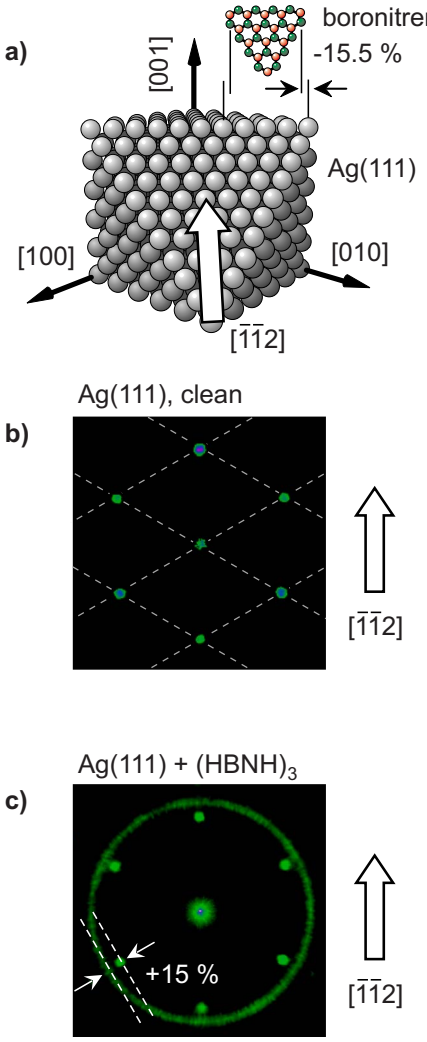

FIG. 2. (Color online) (a) Crystal lattice of Ag(111) surface and a boronitrene layer and LEED patterns (E_0=60 eV) for (b) clean Ag(111) surface, (c) BN/Ag(111) after deposition of 13500 L borazine $(HBNH)_3$ at 950 K.

about 2–3 orders of magnitude (about 13500 L), the formation of a boronitrene layer can be observed and in XPS, the B 1*s* and N 1*s* intensities (Fig. 1) display a B:N ~ 1:1.1 ratio that is close to the nominal 1:1 stoichiometry of BN. Additionally, the formation of a boronitrene layer is also displayed by the B 1*s* and N 1*s* binding energies at 190.8 eV and 398.3 eV, respectively (cf. 190.6 and 398.2 eV in Ref. 20). From the attenuation of the Ag 3*d* intensity, a coverage in the range of 0.7–1.0 monolayer is estimated. The present result is in accordance with the observations by Preobrajenski *et al.*[24] for the growth of BN on Cu(111), as representing another weak-bonding system. Compared to a Ni(111) surface, the dosage of borazine had to be increased by one order of magnitude to get one monolayer of BN on Cu(111).

With respect to the surface structure, the formation of a boronitrene layer on Ag(111) differs strongly from other hexagonal transition-metal surfaces. For strong-bonding substrates, such as, e.g., Rh(111),[1,21] the boronitrene layer exhibits a uniform orientation with its unit cell being aligned parallel to the surface lattice of the substrate. Depending on

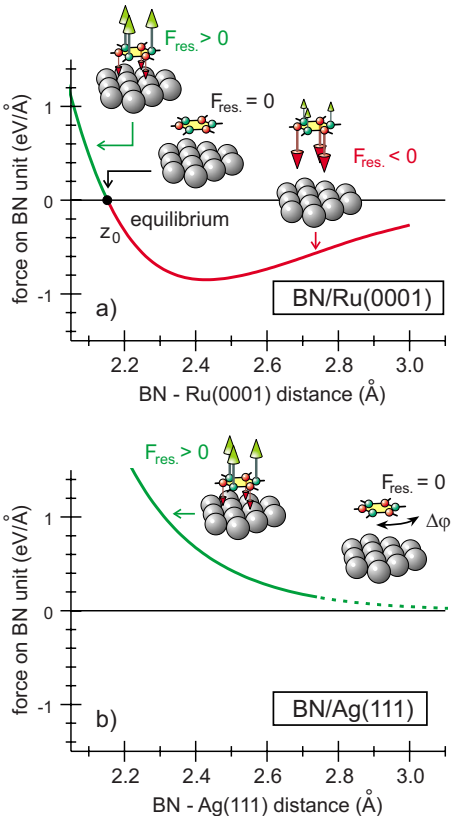

FIG. 3. (Color online) (a) Net force $F_{res}=|\underline{F}_{TM\text{-}N}+\underline{F}_{TM\text{-}B}|$ on a BN unit on Ru(0001), according to Fig. 9 in Ref. 23. For BN-TM distances $z<z_0$ (equilibrium distance, black dot), the repulsion of the N sublattice is larger than the attraction of the B sublattice (green part). For distances $z>z_0$, the situation is reversed (red part). (b) Net force on a BN unit on Ag(111), according to Fig. 2 in Ref. 23. The repulsion of the N sublattice at typical covalent bond distances is always larger than the attraction of the B sublattice. Although the covalent net force on the BN unit is repulsive, bonding finally occurs due to the presence of weak van der Waals forces that dominate at larger distances.

the lattice misfit, the formation of a large superstructure with $m\times m$ periods of the boronitrene layer on $n\times n$ periods of TM(111) is observed in reciprocal space by LEED as well as in real space by scanning tunneling microscopy.[1,2,21,22] In the LEED patterns, the principal spots of the substrate are then surrounded by a sixfold array of nonintegral spots that are spaced in $1/n$ fractions (in units of the reciprocal substrate lattice). For the weaker-bonding Pt(111) surface two types of domains have been observed.[14] For one type of the domains, the BN lattice is aligned parallel to the Pt(111) surface lattice with a large lattice mismatch while for the other type of domains the orientation of the BN lattice is perpendicular at reduced lattice mismatch.

For Ag(111), the situation is different. In Fig. 2, the LEED pattern of the clean Ag(111) surface [Fig. 2(b)] is compared to the LEED pattern after the deposition of 13500 L borazine [Fig. 2(c)] at about 950 K. In Fig. 2(c), the LEED pattern exhibits a ringlike structure, that is separated by about 15% from the first-order Ag(111) spots. According to the lattice misfit of the boronitrene layer and Ag(111) of about 15.5%, the ring can be assigned to the formation of boroni-

trene domains with arbitrary azimuthal orientation. Since the intensity of the ring is distributed nearly homogeneously, there is no preferred direction for the orientation of the boronitrene domains.[25]

The ringlike structure for BN/Ag(111) resembles the LEED structures observed for graphene on Pt(111). For the latter system, the LEED data display a segmented ring due to the formation of domains with different azimuthal orientations.[26] However, for graphene/Pt(111) the LEED data display an anisotropy of the segmented ring indicating that there are still preferred directions for the orientation of the graphene domains.

These results [that are similar when the borazine precursor is replaced by trichloroborazine, $(HNBCl)_3$ (Ref. 27)] can be explained by the theoretical predictions discussed in Ref. 23. The bonding of BN on a hexagonal TM surface depends on the interplay of attractive forces on the B atoms and repulsive forces on the N atoms. This interplay of forces is strongly affected by the local atomic configuration and the most stable configuration is given by N sitting on top of a TM atom while B is at an fcc hollow site, i.e., $(N,B)=(top,fcc)$. In the case where covalent bonding occurs (e.g., on Ni, Rh, or Ru), there is an equilibrium distance z_0 between the TM substrate and BN, at which the overall force on each BN unit vanishes. For $z<z_0$ the repulsive force on the N sublattice is larger than the attractive force on the B sublattice (and vice versa for $z>z_0$), as displayed in Fig. 3(a) for BN/Ru(0001).

For noble metals, such as Ag(111), a quantitative theoretical description of the BN-metal interaction is difficult as the covalent bonds are very weak or even absent, and van der Waals bonding is not well described by conventional density functional theory. This is evident from Table I of Ref. 23, where large differences in binding energies and equilibrium distances obtained with LDA (which overestimates covalent bonding), WC, or PBE functionals (the latter gives no bonding for BN-Ag or other layered materials such as graphite[28]) can be seen. In any case, the repulsive forces on the N sublattice at covalent bond distances are predicted to be always larger than the attractive forces on the B sublattice, even for the most stable $(N,B)=(top,fcc)$ configuration [cf. Fig. 1c in Ref. 23], as depicted in Fig. 3(b). Therefore, the boronitrene lattice is repelled from the Ag(111) surface to large distances (even in LDA >2.55 Å) where the forces on B and N compensate each other to zero and weak van der Waals bonding can occur. This scenario takes place locally even for the most "stable" $(N,B)=(top,fcc)$ configuration, but of course the BN-substrate interaction also vanishes for any other local configuration and the net force is always repulsive until the van der Waals bonding dominates. As a consequence of the repulsion of the boronitrene lattice for any orientation of BN with respect to the underlying metal surface, a preferred orientation of the boronitrene layer can no longer be expected. Therefore, domains can be rotated by an arbitrary azimuthal angle $\Delta\varphi$ out of the isosymmetric orientation, cf. Fig. 3(b).

This model is in full accordance with the observation of very low sticking coefficients [i.e., a boronitrene layer forms on Ag(111) only with strongly increased deposition doses] as well as the observation of a ringlike boronitrene scattering in LEED, confirming the insignificance of local atomic configurations at large BN-TM distances.

The theoretical predictions in Ref. 23 had proven to be true for the formation of boronitrene layers on TM surfaces such as Rh(111).[1–3] In this study we have demonstrated that there is experimental evidence that these predictions are also valid in the case of noble metals, for which no or a very weak bonding is expected.

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