

Monolayer of h-BN chemisorbed on Cu(1 1 1) and Ni(1 1 1): The role of the transition metal 3d states

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Received 25 December 2004; accepted for publication 24 February 2005

Available online 17 March 2005

Abstract

The role of the transition metal 3d states in the adsorption of h-BN on Cu(1 1 1) and Ni(1 1 1) has been studied by NEXAFS and PE spectroscopies and by work function measurements. Based on the analysis of drastic differences in the spectra from h-BN/Cu(1 1 1) and h-BN/Ni(1 1 1), it has been concluded that the strength of chemical bonding at the interfaces under study is determined mainly by the strength of the TM 3d–h-BN π orbital hybridization. On Ni(1 1 1) h-BN is found to be strongly chemisorbed, while on Cu(1 1 1) only weak chemisorption is observed. On Ni(1 1 1) the h-BN monolayer is probably metallic. On Cu(1 1 1) the monolayer should possibly also be considered as metallic, however its metallic properties are much less pronounced, and the situation is somewhat uncertain.

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Keywords: Boron nitride; Graphite; Nickel; Copper; NEXAFS; Photoelectron spectroscopy; Work function measurements; Chemisorption

1. Introduction

Layered materials like graphite and hexagonal boron nitride (h-BN) are known to form structurally perfect interfaces with many metals upon thermal cracking of molecular precursors at the metal surface [1]. In this process the very first monolayer (ML) grows very rapidly forming an atomic mesh

over the surface, while the further growth is greatly suppressed. The resulting interfaces are of great interest and importance, because the structural and electronic characteristics of these two-dimensional systems can be relatively easily varied in a controllable way using different metallic substrates, different precursors, as well as upon insertion of different atomic or molecular species into the interface. It is possible to create and study either graphite-based or h-BN-based systems depending on the desired conductivity in the plane of interface: graphite is a classical semiconductor,

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while h-BN is an insulator with the fundamental band gap of ~ 5.7 eV, although they are isostructural and isoelectronic to each other.

For h-BN, a very interesting question is whether the monolayer remains insulating or it obtains metallic properties on metal surfaces. In the angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) and angle-resolved secondary-electron emission spectroscopy studies by Nagashima et al. it has been suggested that on Ni(111), Pd(111) and Pt(111) the monolayer of h-BN is physisorbed, although the bonding at the lattice-matched h-BN/Ni(111) interface was found to be stronger [2,3]. Therefore, the h-BN monolayer was considered to be insulating. By contrast, in a high resolution electron energy loss spectroscopy (HREEL) study of the same three systems by Rokuta et al., it has been demonstrated that the transition metal (TM) d–BN π hybridization must be responsible for the changes in the HREEL spectra in going from h-BN/Pd(111) and h-BN/Pt(111) to h-BN/Ni(111) [4]. On the other hand, in the theoretical DFT study by Grad et al. no evidence for substantial orbital mixing between the Ni 3d and BN π (and π^*) states has been reported, and it has been suggested that 1 ML h-BN remains an insulator on Ni(111) [5]. Very recently, Shimoyama et al. [6] and Preobrajenski et al. [7] have shown by near-edge X-ray absorption fine structure (NEXAFS) and photoemission/Auger (PE/AE) spectroscopies that a rather strong chemical bonding due to orbital hybridization (i.e., strong chemisorption) does exist at the h-BN/Ni(111) interface. Moreover, it has been suggested that the h-BN monolayer on Ni(111) is metallic, and it is the Ni 3d–BN π hybridization that plays the crucial role in the interaction [7]. On the other hand, partly occupied Ni 4s and unoccupied Ni 4p states may also participate in the hybridization. To our knowledge, no conclusive experiments revealing the exact nature of chemical bonding at the h-BN/Ni(111) interface has been performed so far.

In order to reveal the role of different nickel states in the orbital hybridization at the h-BN/Ni(111) interface, we investigate in this paper the formation and electronic structure of another similar interface, h-BN/Cu(111), by means of

NEXAFS and PE spectroscopy, and compare the results with those for h-BN/Ni(111). Cu(111) is chosen here for the following reasons. Firstly, Cu has the same lattice structure as Ni, with the lattice parameter being only $\sim 2.5\%$ larger. Since the lattice misfit between h-BN monolayer and Ni(111) is about -0.4% (resulting in a weak rumpling of the monolayer [4,8]), one can expect that the misfit of about $+2\%$ between h-BN and Cu(111) will allow a commensurate growth of a slightly strained (expanded) flat monolayer. Secondly, the s–p electronic structure of Ni(111) and Cu(111) is similar. Thirdly, the 3d electron states are very different: in Ni the 3d states are partly occupied and located energetically at the Fermi level (E_F), while in Cu the 3d states are fully occupied and fall in the range between 2 and 5 eV below E_F . This also implies that the spatial localization of the 3d states is different: in Cu they shrink towards the core, being thereby more localized than in Ni. Thus, by replacing Ni(111) with Cu(111) we modify mainly the 3d states of the substrate without considerable changing the structural parameters and the electronic states other than 3d (s and p).

The main goal of this work is to investigate how the modification of the TM 3d states affects the hybridization at the interfaces of h-BN with TMs. Strong changes in the NEXAFS and PE spectra and in the work function behaviour in going from h-BN/Ni(111) to h-BN/Cu(111) would reflect a key role of the 3d states in the hybridization, while weak or no changes would be representative of their low significance.

2. Experiment

All spectra were measured at the D1011 beamline at MAX II storage ring in MAX-lab (Lund, Sweden), using a modified SX-700 plane grating monochromator and a high-resolution SES-200 electron energy analyzer. The photon energy resolution was set to 50 meV at the B K-edge (~ 190 eV) and to 150 meV at the N K-edge (~ 400 eV). In addition to the analyzer, the end station was equipped with LEED optics, an ion gun for the substrate cleaning, a gas-sending system and a multi-channel plate electron yield detector.

The kinetic energy resolution was set to 75 meV for all PE spectra. All NEXAFS spectra were measured in the partial electron yield mode with the repulsion potential of -100 V. The incident beam intensity was monitored by a gold mesh. All measurements were carried out under ultra-high vacuum conditions, at a base pressure below 1×10^{-10} mbar.

The Cu(111) and Ni(111) substrates were cleaned by several cycles of Ar^+ sputtering ($U = 1$ kV) and annealing ($T = 750$ °C for Cu and 800 °C for Ni, measured by a thermocouple directly attached to the crystal) until sharp (1×1) LEED patterns were observed and no evidence of surface contaminations could be detected by PE for both substrates. For the growth of h-BN we used thermal decomposition of vapourized borazine ($\text{B}_3\text{N}_3\text{H}_6$) at the substrate temperature of 750 °C for Cu(111) and 800 °C for Ni(111). The vapour exposures were measured with a standard ion gauge located about 20 cm away from the borazine dozer.

For Ni(111) it is well known that the pyrolytic reaction with borazine slows down abruptly as soon as the first ML of h-BN is formed [2]. We found that the same is basically true for the reaction with Cu(111), with the exception of a considerably higher exposure required for creating one complete monolayer of h-BN: ~ 2000 L for Cu(111) but only ~ 100 L for Ni(111). The monolayer was considered as complete if further exposures did not change the intensity ratio of adsorbate-to-substrate signals in the PE overview spectra. The LEED pattern from 1 ML h-BN was a sharp hexagonal (1×1) structure on both substrates.

It should be noted that on Cu(111) it is more difficult to grow a structurally perfect h-BN monolayer than on Ni(111), because the window of the possible substrate temperatures is narrower. If T_{surf} is higher than 800 °C the Cu(111) surface becomes optically dull (i.e., rough) because of the overheating; if it is lower than 750 °C the monolayer grows with defects. These defects manifest themselves, e.g., in the B 1s PE spectrum as two additional core-level peaks shifted from the position of the main B 1s line to lower binding energy by 1.3 eV and 2.5 eV (not shown). The peak at

1.3 eV corresponds to boron atoms coordinated by less than three nitrogen atoms, while the second peak (at 2.5 eV) results from the atomic boron dissolved in copper. In the following we report only the results obtained from the samples without such defects.

3. Results and discussion

3.1. X-ray absorption

The B 1s and N 1s NEXAFS spectra from 1 ML of h-BN grown on Cu(111) are shown in Fig. 1(a) and (b), respectively, as a function of the angle θ between the surface normal and the direction of photon polarization. Corresponding spectra at both absorption edges for 1 ML h-BN/Ni(111) can be found in Ref. [7] and also in Ref. [6] (only B 1s), although the authors of the latter work assign them to 2 ML h-BN. All spectra are normalized to the intensity of the incident photon flux and to the area under the curves (in order to facilitate comparison of corresponding spectral structures). The “raw” B 1s spectra had several weak artificial features above 200 eV due to the N 1s absorption in the second-order light, which were carefully subtracted and which are not displayed in the figures.

All spectral features for both B 1s and N 1s NEXAFS can be separated into two groups according to their angle dependence: features labelled A' , A , A'' and A_1 reflect transitions of a core electron into the states of π symmetry (i.e., oriented perpendicular to the plane of h-BN), while all the remaining features correspond to transitions with predominantly σ character (in-plane). Feature D is set in brackets in Fig. 1(b), because it cannot be seen there, but it is present in the spectrum of bulk h-BN, as shown in Fig. 2. Evidently, B 1s and N 1s NEXAFS reflect one and the same system of unoccupied states; therefore, spectral features are labelled with the same letters. However, if the boron and nitrogen spectra are aligned in energy (as shown in Fig. 3) the positions of the corresponding features do not coincide precisely because of the different final-state effects of the B 1s and N 1s core holes. For example, the position

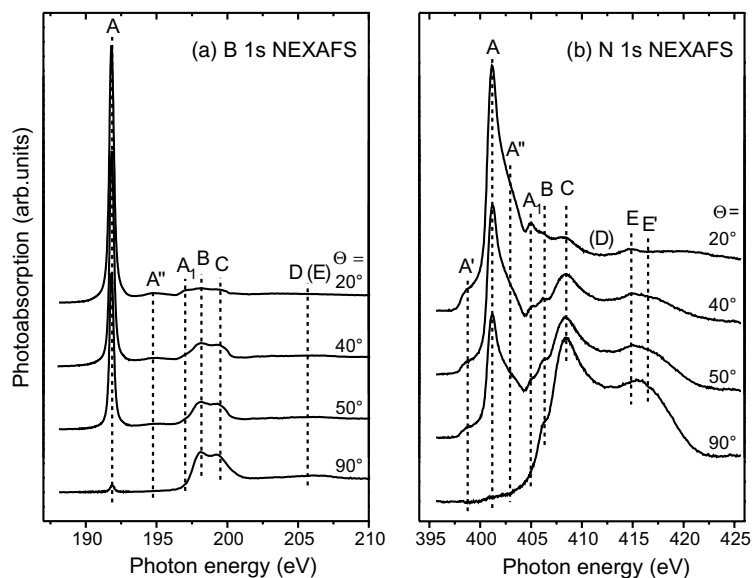


Fig. 1. B 1s (a) and N 1s (b) NEXAFS of 1 ML h-BN grown on Cu(111) as a function of the angle θ between the surface normal and the direction of photon polarization.

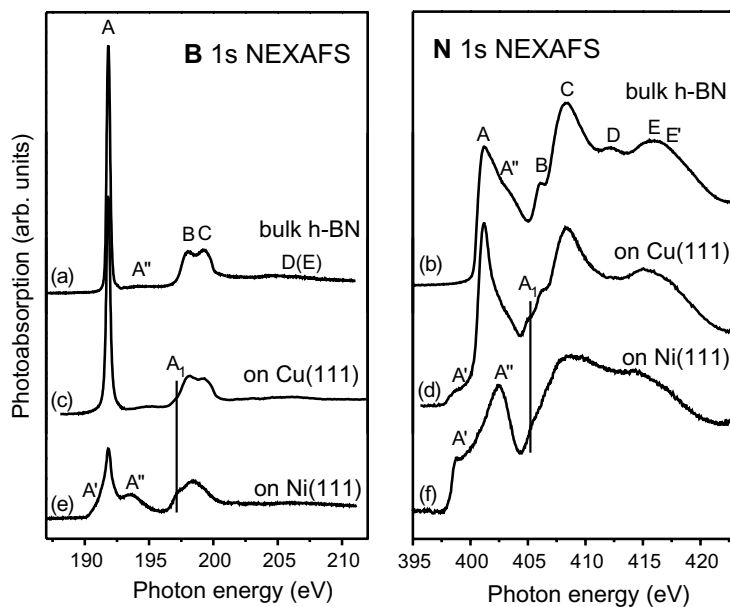


Fig. 2. B 1s and N 1s NEXAFS of bulk h-BN (thick film) and 1 ML h-BN grown on Cu(111) and Ni(111). All spectra are recorded with the angle of incidence $\theta = 50^\circ$.

of resonance A is shifted in the B 1s spectrum by 1.8 eV to lower photon energy as a consequence

of very high localization of the corresponding B $1s^{-1}\pi^*$ excitation.

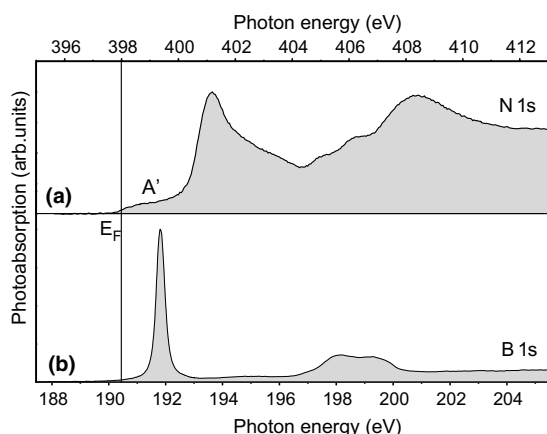


Fig. 3. N 1s (a) and B 1s (b) NEXAFS of 1 ML h-BN grown on Cu(111) aligned in energy relative to the Fermi level. Note that shoulder A' stretches down to E_F .

The angle dependence in Fig. 1 shows that the h-BN formed on Cu(111) is indeed very flat, as expected for a single h-BN monolayer. In the following we will discuss only the excitations corresponding to π states, because these states are involved in chemical bonding much stronger than σ states.

In Fig. 2 we compare NEXAFS spectra from 1 ML h-BN/Cu(111) taken at $\theta = 50^\circ$ with those from bulk h-BN and from 1 ML h-BN/Ni(111). Spectra (a), (b), (e) and (f) are from our previous work [7]. It should be emphasized that the spectra (c)–(f) correspond to exactly 1 ML h-BN, because already for a 2 ML film they look differently [7]. As can be seen in Fig. 2, both B 1s and N 1s spectra are drastically distinct for 1 ML h-BN on Cu(111) and Ni(111). Generally speaking, on Cu(111) the spectra are quite similar to the spectra from bulk h-BN, while on Ni(111) they are quite different. Indeed, the B 1s NEXAFS from h-BN/Cu(111) (c) and from bulk h-BN (a) are almost identical, with the exception of weak shoulder A_1 appearing in (c). If the N 1s NEXAFS spectra are compared (curves b and d), one can see more distinctions: not only does shoulder A_1 appear in (d), but also shoulder A'. In addition, the main resonance A becomes somewhat sharper and feature D disappears.

On the contrary, spectra from h-BN/Ni(111) differ strongly from those of bulk h-BN. In B 1s

NEXAFS from h-BN/Ni(111) (e) the shape of peak A changes and its intensity decreases greatly, a low-energy tail A' develops, feature A'' becomes very pronounced, shoulder A_1 develops, and some changes become visible also in the range of σ^* resonances B–C. In the N 1s NEXAFS of the same system (f) the distinctions from the case of bulk h-BN (b) are also quite strong, and resemble those for B 1s spectra. In this case shoulder A' even develops into a peak, while the main resonance A can hardly be seen at all.

Since the electronic structure of the 4s,p states in Cu and Ni is similar, while the 3d states are quite different, we assign the variations in the spectral behaviour between h-BN/Cu(111) and h-BN/Ni(111) mainly to the different bonding effect of the surface d states: strong for Ni and weak for Cu. It is evident from Fig. 2 that 3d states play the main role in the chemical bonding of h-BN with Ni(111), because their characteristics determine the strength of orbital hybridization with the h-BN states. We expect mainly the π states of h-BN to participate in the bonding, because the σ states lie parallel to the surface plane. Thus, we conclude that the bonding at the h-BN/Ni(111) interface occurs mainly due to the Ni 3d–h-BN π orbital hybridization.

On the other hand, this is not the only mechanism, because substrate 4s and 4p_z (defining the z-axis to be the surface normal) states may also contribute to the bonding. The effect of TM 4s,p_z–h-BN π hybridization can be clearly seen in the NEXAFS spectra from both interfaces under study (Fig. 2) as a π -type feature A_1 at ~ 197 eV in the B 1s spectrum and at ~ 405 eV in the N 1s spectrum. Indeed, unoccupied 4s,p states of Ni and Cu lie somewhat above E_F and fall into the energy range characteristic for A_1 [9]. For the case of B 1s NEXAFS from h-BN/Cu(111) this feature is the only obvious distinction from the case of bulk h-BN. Since no distinctions can be seen at lower photon energies, one can even conclude that the 4s,p_z–h-BN π hybridization may be the dominating mechanism of bonding for the h-BN/Cu(111) interface. However, it cannot be excluded that the Cu 3d states also participate in the bonding to some extent. In spite of their localized character and energy position well below E_F they may still

mix with the h-BN π^* orbitals, although much weaker than the Ni 3d states. Possibly, this mixing manifests itself in the N 1s NEXAFS spectrum as shoulder A' (Fig. 2(d)). This feature is much more pronounced in the case of h-BN/Ni(111) interface (Fig. 2(f)) as a consequence of a stronger d– π orbital hybridization.

In our previous paper we suggested that the h-BN monolayer is metallic on Ni(111) [7]. Now we should discuss the question whether the h-BN monolayer is metallic or insulating on Cu(111). Fig. 3 shows the B 1s and N 1s NEXAFS spectra for the h-BN/Cu(111) interface aligned at the position of E_F , which is obtained taking into account binding energies of the B 1s and N 1s electrons relative to E_F (190.45 eV and 398.00 eV, respectively). Evidently, we observe some non-zero density of unoccupied states directly above the Fermi edge. Therefore, the h-BN monolayer should be considered as metallic also for this interface. By analogy with the case of h-BN/Ni(111) interface, we suppose this to be a consequence of the TM 3d–h-BN π hybridization. On the whole, however, the situation with the conducting properties of the h-BN monolayer on Cu(111) is more uncertain than on Ni(111), because the TM 3d–h-BN π hybridization is much weaker.

Thus, at both interfaces under study we observe some TM 3d–h-BN π hybridization with a corresponding charge transfer from the substrate into the initially unoccupied π^* states of h-BN. In the case of h-BN/Ni(111) this hybridization is much stronger and determines the strength of the interaction, which can be called “strong chemisorption”. On the contrary, at the h-BN/Cu(111) interface the TM 3d–h-BN π hybridization is weak. The chemical bonding at this interface can be referred to as “weak chemisorption”.

Our findings are in line with the results obtained for closely related carbon-bond system. For 1 ML graphite on Ni(111) it is well established that the bonding is mainly realized by a charge transfer via mixed Ni 3d–C $2\pi/\pi^*$ states [10,11]. Also, in the recent theoretical study of benzene chemisorption on Ni(111) the authors suggested that hybridization between the Ni 3d states and the lowest unoccupied molecular orbitals (LUMO) of ben-

zene is more important for the overall bonding than the Ni 4s,p–LUMO hybridization [12].

3.2. Photoemission

The conclusions drawn in the preceding section can be cross-checked with PE spectroscopy. The B 1s and N 1s core-level PE spectra from 1 ML h-BN on Cu(111) and Ni(111) are presented in Fig. 4, and the binding energies (E_B) measured relative to E_F are summarized in Table 1. The spectra in Fig. 4 are normalized to the underlying area.

For B 1s we observe no change in the peak position in going from h-BN on Cu(111) (Fig. 4(a)) to h-BN on Ni(111) (c), but quite a strong change in the line shape. In the case of the Ni substrate one can see an asymmetric tail at the high binding energy side of the main B 1s peak, which is mainly due to a continuum of the shake-up excitations. Such a tail is a characteristic feature of core level PE lines in metals. In the case of the Cu substrate, the full width at half maximum (FWHM) is increased from 0.45 eV to 0.90 eV, while the overall shape becomes more symmetric. Generally, such variations in the spectral shape may be attributed either to a different structure of shake-up satellites (eventually with a contribution from discrete shake-up states) or to a different vibrational broadening [13], but in any case they reflect a much weaker metallic screening of the B 1s core ionized state. This difference in the screening cannot be explained by a different electron transfer via the delocalized s, p bands, because they are quite similar in Cu and Ni. Therefore, we suggest that the screening is facilitated by the TM 3d–h-BN π hybridization: the stronger it is, the more efficient is the screening.

For N 1s (Fig. 4(b) and (d)) the situation is different: no considerable change can be seen in the line shape, but E_B is strongly increased (by 0.65 eV) in going from h-BN/Cu(111) to h-BN/Ni(111). The presence of a significant N 1s shift immediately shows that the electronic structure is different for the h-BN layers on the two substrates. In the present case we can presumably interpret the shift in terms of a difference in electron charge density on the nitrogen site. The shift indicates that the electron density on the nitrogen sites is

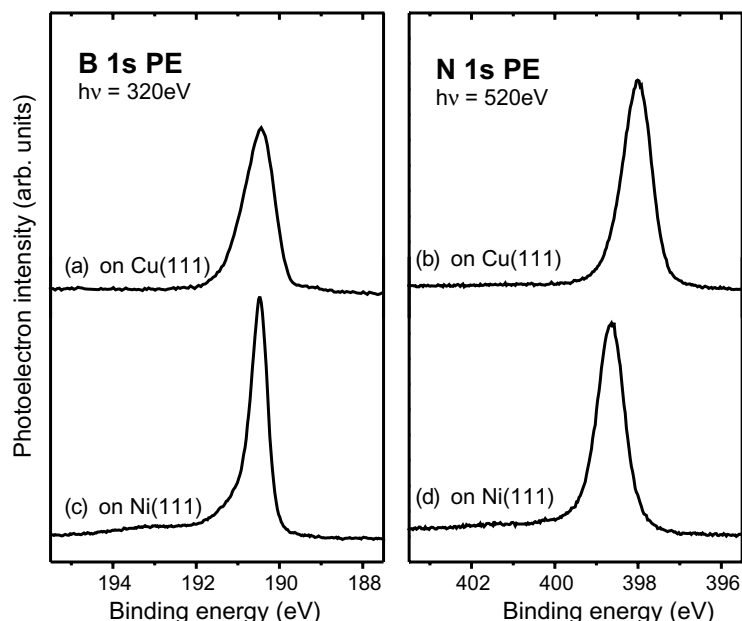


Fig. 4. B 1s and N 1s photoelectron lines in the systems h-BN/Cu(111) and h-BN/Ni(111) excited with $h\nu = 320$ eV (B 1s) and 520 eV (N 1s). Binding energies are measured relative to the Fermi level; their positions are summarized in Table 1.

Table 1

Measured binding energies (eV) of the B 1s and N 1s electrons in 1 ML h-BN adsorbed on Cu(111) and Ni(111) measured relative to the Fermi edge

	On Cu(111)	On Ni(111)	ΔE_B
E_B [B 1s]	190.45	190.45	0.00
E_B [N 1s]	398.00	398.65	−0.65

lower if h-BN is chemisorbed on Ni(111). We propose that the electron density in the highest occupied molecular orbitals (HOMO) of h-BN is rather localized on h-BN in case of interaction with Cu(111) and delocalized if chemisorption happens on Ni(111). This finding confirms that the strength of the h-BN chemisorption is mainly determined by the TM 3d–h-BN π orbital mixing. Since not only the LUMO (π^*) of h-BN but also its HOMO (π) must be considerably influenced by this mixing, one should see an effect of the TM 3d–h-BN π hybridization on the position of h-BN π band in the valence band (VB) PE spectra.

Fig. 5 shows VB PE spectra from clean Cu(111) (a), 1 ML h-BN on Cu(111) (b) and a part of the spectrum from 1 ML h-BN on Ni(111) (c) (the

complete spectra for clean Ni(111) and 1 ML h-BN on Ni(111) were reported in Ref. [7]). All spectra were recorded with a photon energy of 100 eV, in normal emission, and at an angle $\theta = 50^\circ$ between the surface normal and the vector of photon polarization. The main variation in the VB PE spectra in going from clean Cu(111) to h-BN/Cu(111) is the reduction of the Cu 3d intensity at E_B of ~ 2.5 eV. This reduction is evidently due to the disappearance of the 3d surface states resulting from the h-BN chemisorption. Another evident change in the spectrum is the appearance of shoulder α in (b), which is a characteristic feature of the h-BN density of states (DOS) with a mixed π – σ character. The same DOS feature of h-BN appears also in the VB PE spectrum from 1 ML h-BN on Ni(111) (c). It is difficult to determine energy positions of α exactly, because of its rather broad shape and low intensity on the background of the TM 3d DOS, but even at a conservative estimate the onset of α is shifted to higher E_B in the case of h-BN/Ni(111) by at least 1.5 eV. A similar shift (~ 1 eV) of the h-BN π band to higher E_B has been observed in h-BN/Ni(111) as compared to h-BN/Pd(111) and h-BN/Pt(111) in the ARUPS

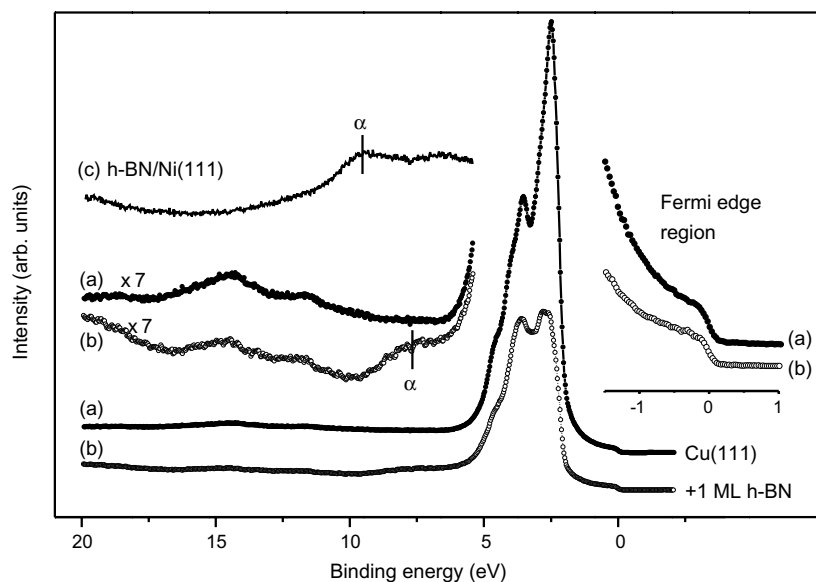


Fig. 5. Valence-band PE spectra excited with $h\nu = 100$ eV and $\Theta = 50^\circ$ between surface normal and photon polarization direction and recorded in normal emission from Cu(111) (a), 1 ML h-BN on Cu(111) (b) and 1 ML h-BN on Ni(111) (c). Inset: Fermi edge region for (a) and (b).

study by Nagashima et al. [2]. This shift clearly indicates the influence of the Ni 3d states on the h-BN valence band despite the rather high energy difference (at least 3 eV) between the Ni 3d and h-BN HOMO. In h-BN/Cu(111) the Cu 3d states are energetically closer to the h-BN valence band states, but they interact more weakly as a consequence of the more localized character of the Cu 3d states as compared to Ni 3d. No new features can be observed after the formation of 1 ML h-BN on Cu(111) in PE at the Fermi edge (Fig. 5,

inset) because of the weakness of the Cu 3d–h-BN π orbital mixing. For h-BN/Ni(111) this energy region is strongly dominated by Ni 3d states, and no definite conclusion can be drawn.

In Fig. 6 we illustrate our NEXAFS and PE results with a schematic representation of the TM 3d–h-BN π interaction at both interfaces under study. This scheme does not take into account the mixing with the TM 4s, p states. Generally speaking, Ni 3d states mainly determine the bonding with h-BN, while Cu 3d states participate in

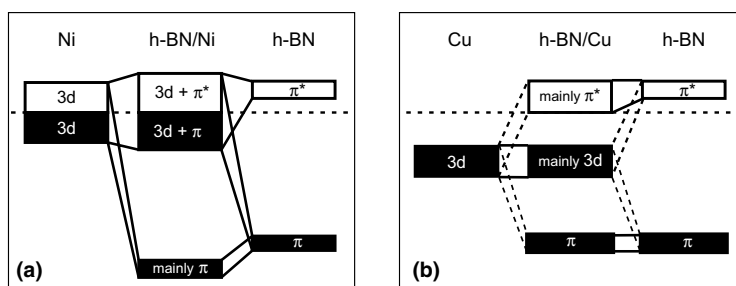


Fig. 6. Schematic illustration of the TM 3d–h-BN π hybridization at the h-BN/Ni(111) (a) and h-BN/Cu(111) (b) interfaces, as can be deduced from the experimental data. Black (white) colour corresponds to occupied (unoccupied) states. Dotted line denotes the position of E_F ; strong (weak) orbital mixing is shown with solid (dashed) connecting lines.

the orbital hybridization rather weakly. In Fig. 6 strong d- π hybridization is visualized by solid lines, weak—by dashed lines. The dotted line shows the position of E_F .

3.3. Work function measurements

In Table 2 the results of our work function (ϕ) measurements are tabulated. All values are obtained by measuring the position of the secondary electron intensity onset shifted by a stable battery (~ 30 V) to higher kinetic energies. The work function changes ($\Delta\phi$) are determined with the accuracy better than ± 0.05 eV. For clean Ni(111) and h-BN/Ni(111) the obtained values of ϕ are quite close to the numbers reported by Nagashima et al. [2]: 5.3 eV and 3.6 eV, respectively.

As one can see in Table 2, the values of $\Delta\phi$ caused by h-BN are very different on Ni(111) and Cu(111), however, they are negative on both substrates. This immediately shows that there is a significant difference in the bonding of the h-BN overlayer to the two substrates under study. It might look surprising that ϕ is reduced, since there is a mixing of initially occupied substrate 3d states with initially unoccupied π^* states of h-BN resulting in a charge transfer from the substrate to the monolayer. We propose the following explanation for the observed reduction in ϕ . As shown in the preceding section, the electrons in the occupied π states of h-BN participate in the chemical interaction between h-BN and Ni(111). As a consequence, the ground-state π electron density shifts towards the substrate. Since the electron density is much higher in π than in π^* , the charge density shift from π towards the substrate outweighs the counter-flow from the substrate 3d into unoccupied π^* . The resulting electric dipole layer accelerates outgoing electrons and causes a reduction of

the work function. The large difference in the work function change caused by h-BN on Cu(111) and Ni(111) shows that it is mainly the strength of the TM 3d-h-BN π hybridization that determines the value of $\Delta\phi$.

It should be noted that the great difference in $\Delta\phi$ induced by h-BN on Cu(111) and Ni(111) can be hardly explained without taking the d- π hybridization into account. Since electronegativity values are almost the same for Cu and Ni, the magnitude of electric dipole moment at the surface cannot vary strongly within a simple electrostatic picture.

4. Conclusions

We have performed a comparative study of chemical bonding at the h-BN/Cu(111) and h-BN/Ni(111) interfaces by NEXAFS and PE spectroscopies and by work function measurements. Since the main idea of these experiments was to elucidate the specific role of the TM 3d states in the interaction between a single h-BN monolayer and TM surfaces, closely related substrates were chosen, which differ mainly in their 3d electronic structure.

It has been shown that a single monolayer of h-BN can be grown on Cu(111) by thermal decomposition of vapourized borazine. Vapour exposures required for creating one complete monolayer of h-BN on Cu(111) are larger by an order of magnitude than for its growing on Ni(111).

Based on the comparative analysis of all the spectroscopic data presented in this study, we conclude that there is a large difference in chemical bonding of h-BN with Ni(111) and Cu(111). On Ni(111) the strength of interaction is determined by a substantial Ni 3d-h-BN π orbital hybridization, and the monolayer of h-BN is strongly chemisorbed. On Cu(111) the Cu 3d-h-BN π hybridization is much weaker and the h-BN monolayer is chemisorbed only weakly. On Ni(111) the h-BN monolayer should be considered metallic as a consequence of the strong TM 3d-h-BN π hybridization. On Cu(111) its metallic properties manifest themselves much more weakly, and the

Table 2
Measured work functions (eV) of clean and h-BN covered Cu(111) and Ni(111) surfaces

Substrate	ϕ		$\Delta\phi$
	Clean surface	With 1 ML h-BN	
Cu(111)	4.97	4.73	-0.24
Ni(111)	5.23	3.62	-1.61

situation is less clear. On the whole, our results reveal crucial role of the TM 3d states in the bonding between h-BN and TM surfaces.

Acknowledgment

This work was financed by the Swedish Foundation for Strategic Research and the Swedish Research Council. A. S. V. gratefully acknowledges the support by Uppsala University and MAX-lab.

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