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Ni 3*d*–BN π hybridization at the *h*-BN/Ni(111) interface observed with core-level spectroscopies

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The electronic structure of *h*-BN films grown on the Ni(111) surface has been studied as a function of film thickness using the synchrotron radiation based spectroscopic techniques: soft x-ray absorption, core-level photoemission and resonant Auger spectroscopy. A manifestation of the strong orbital hybridization between Ni 3*d* and *h*-BN π states has been consistently observed in all spectra, implying a rather strong interfacial interaction between *h*-BN and the substrate. In the B 1*s* and N 1*s* near-edge x-ray absorption fine structure of both bulk *h*-BN and a single monolayer adsorbed on Ni(111) we observe spectral structures, which can be interpreted as a manifestation of the interlayer conduction-band states of *h*-BN.

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I. INTRODUCTION

Interfaces of layered materials with metals are of great interest and importance both from the fundamental point of view and because of their technological relevance. The strong anisotropy of the crystal potential in these materials allows the production and study of a vast variety of atomically abrupt interfaces with essentially two-dimensional (2D) properties. Moreover, the structural and electronic characteristics of these 2D systems can be relatively easily varied in a systematic way upon insertion of different atomic or molecular species into the interface. Graphite and hexagonal boron nitride (*h*-BN) are among the most popular layered materials used for the interface engineering. Although *h*-BN is isostructural and isoelectronic to graphite, the partial ionicity of the B-N bonds pushes the highest occupied and lowest unoccupied states apart making *h*-BN an insulator with the fundamental band gap of ~5.7 eV.

Particularly, the interaction of *h*-BN with metal surfaces has gained much interest in the recent years once the possibility of producing a single-crystalline monolayer (ML) of *h*-BN on the Ni(111) surface by thermal decomposition of borazine ($B_3N_3H_6$) was reported by Nagashima and coworkers.[1] Making use of angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) and angle-resolved secondary-electron emission spectroscopy, they analyzed the electronic structure of this monolayer on Ni(111), Pd(111), and Pt(111) and came to the conclusion that (contrary to graphite) the monolayer of *h*-BN is weakly bonded to metal surfaces, without substantial mixing of the π states of the monolayer and *d* states of the substrates.[1,2] They noticed, however, that the bonding is stronger at the lattice-matched *h*-BN/Ni(111) at the other two surfaces, where the interface structure is incommensurate. Rokuta *et al.* studied phonon spectra of the same systems with high-resolution electron energy loss (HREEL) spectroscopy and suggested that the Ni 3*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).[3] The structural model for the monolayer *h*-BN on Ni(111) has been proposed as a result of low-energy electron diffraction (LEED) intensity analysis.[3,4] It has been suggested that the *h*-BN layer is rumpled (B atoms slightly below N atoms), with N atoms atop the outermost Ni atoms. This model has been confirmed in the x-ray photoelectron diffraction and scanning tunneling microscopy (STM) study by Auwärter *et al.*[5] and in the recent density-functional theory (DFT) investigation by Grad *et al.*[6] While there is a consensus on the structural properties of the *h*-BN/Ni(111) interface, the question whether the chemical bonding is strong (chemisorption due to the Ni 3*d*–BN π hybridization) or weak (physisorption) remains controversial. In the theoretical DFT study by Grad *et al.* no evidence for substantial mixing between the Ni 3*d* and BN π (and π^*) states was found, and it has been suggested that 1 ML *h*-BN remains insulating on Ni(111).[6]

In this paper we investigate electronic properties of the *h*-BN/Ni(111) interface by means of several core-level spectroscopic techniques based on the use of synchrotron radiation: soft x-ray absorption (XA), core-level photoemission (PE) and resonant Auger spectroscopy (RAS), as well as angle-integrated valence-band photoelectron spectroscopy (PES). Our goal is to understand whether the strong chemical bonding does exist in this 2D system. We also examine the question whether the *h*-BN monolayer on Ni(111) behaves as an insulator or a metal, and discuss the existence of the interlayer conduction band states predicted theoretically by Catellani *et al.*[7,8] and Blase *et al.*[9]

II. EXPERIMENT

The experiments were performed at the soft x-ray beamline D1011 of the MAX-II storage ring (MAX-lab, Lund, Sweden), equipped with a modified SX-700 plane-grating monochromator. 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). The end station is equipped with a high-resolution SES-200 electron energy analyzer, LEED optics, an ion gun for the substrate cleaning, a gas-sending system for the dosing of borazine and a multichannel plate electron yield detector. The kinetic-energy resolution was set to 75 meV for all electron spectra except for those of satellite structures following the B 1*s* and N 1*s* photoionization (Fig. 7), where it was set to 150 meV. All spectra of the B 1*s* and N 1*s* near-edge x-ray absorption fine structure (NEXAFS) are measured in the partial electron yield mode with a repulsion potential of -100 *V*. The incident beam intensity was recorded simultaneously with the XA spectra by a gold mesh monitor. All measurements were carried out under ultrahigh vacuum conditions, at a base pressure below 1×10^{-10} mbar.

The Ni(111) single-crystal substrate was cleaned by several cycles of Ar^+ sputtering ($U=1$ kV) and annealing ($T=800$ °C, measured by a thermocouple directly attached to the crystal) until a sharp (1×1) LEED pattern was observed and no evidence of surface contaminations could be detected by PES. The *h*-BN deposition was achieved by the thermal cracking of vaporized borazine (from Boron Biologicals, Inc.) at the substrate temperature of 800 °C. The vapor exposures were measured with a standard ion gauge located at about 20 cm away from the borazine dozer, without any correction for the vapor pressure gradient between the dozer and the gauge. Three different exposures were studied resulting in different *h*-BN thicknesses. For creating 1 ML *h*-BN about 100 L was typically used. For the *h*-BN amount corresponding to about 2 ML (estimated from the increase in the B 1*s* and N 1s intensity as compared to the case of 1 ML) the exposure of 6×10^3 L was necessary, while for the essentially thicker films (characterized by the absence of any substrate-related signals in PES) the values of 1×10^5 L or higher were applied. These numbers reflect the fact, that the first monolayer of *h*-BN grows very easily on Ni(111) while much higher exposures are necessary to accomplish further growth, which is in agreement with the original observation by Nagashima *et al.*[1] The LEED pattern from 1 ML *h*-BN was a sharp (1×1) structure with an expected redistribution of the spot intensities in comparison with the pure substrate surface. The structural quality of the single *h*-BN monolayer on Ni(111) is expected to be quite high, as reported in the STM studies of this system.[5,10] The deposition of the *h*-BN amount equivalent to the second monolayer results in a complete disappearance of the LEED spots indicating a polycrystalline growth. The *h*-BN crystallites in the second and further layers lie more or less flat on top of the first monolayer, as can be concluded from the angle dependence of the B 1*s* and N 1*s* NEXAFS, but they are probably too small and disoriented to provide any LEED pattern. Since the thickness of the "thick layer" sample was estimated to be more than 20 nm, it will be referred hereafter as "bulk." In the following we will use the terms "second monolayer" and "bulk" bearing in mind that they are essentially polycrystalline, but not completely disordered.

III. RESULTS AND DISCUSSION

A. X-ray absorption

The B 1*s* and N 1*s* NEXAFS for the *h*-BN films of different thickness grown on Ni(111) are shown in Figs. 1(a) and 1(b), respectively. All spectra are normalized to the intensity of the incident photon flux and to the absorption jumps at 210 eV (B 1*s*) and 421 eV (N 1*s*). The "raw" B 1*s*

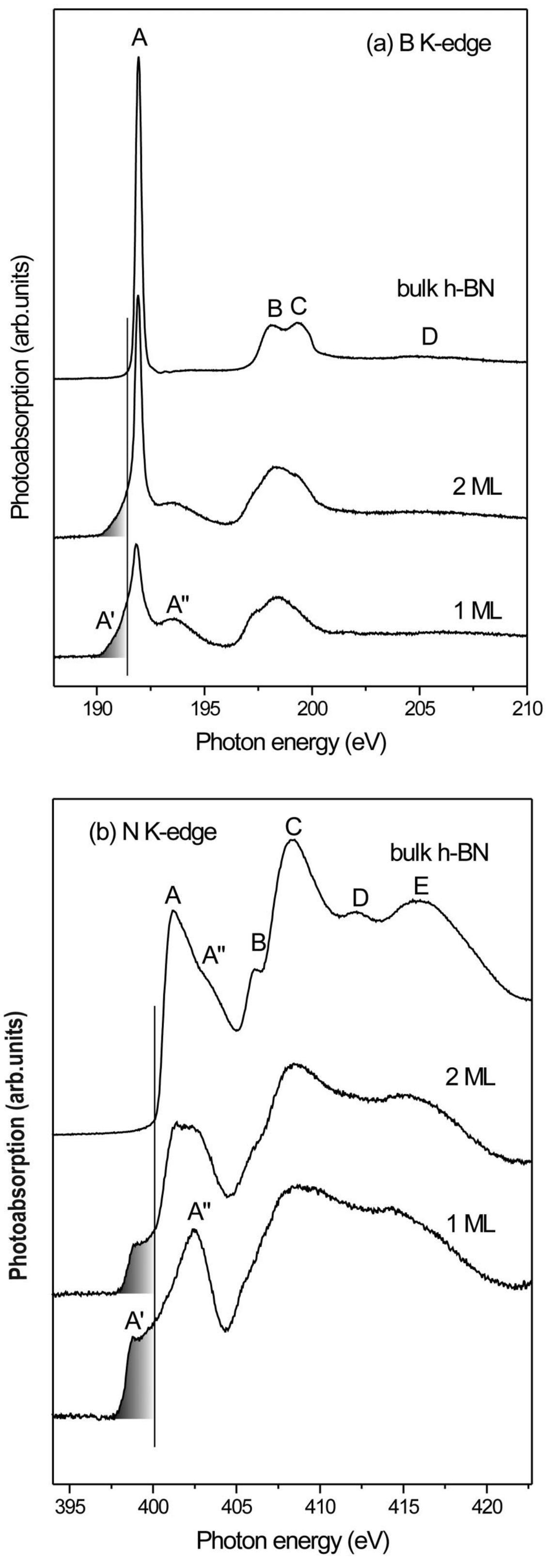

FIG. 1. B 1*s* (a) and N 1*s* (b) NEXAFS of *h*-BN films grown on Ni(111). All spectra are recorded with the angle of incidence $\Theta=50°$ in the partial electron yield mode ($U=-100$ V). Shadowed parts of the spectra correspond to the unoccupied states close to the Fermi edge accessible because of the $3d$-π hybridization.

spectra had several weak artificial features above 200 eV due to the N 1*s* absorption in the second-order light, which were carefully subtracted and are not present in Fig. 1(a).

Before proceeding to the discussion of the substrate effect on the spectra, we should briefly describe the details of the NEXAFS in bulk *h*-BN. The conduction-band structure of bulk *h*-BN has been extensively studied by x-ray absorption.[11–18] Our spectra for bulk *h*-BN (Fig. 1) reproduce the general spectral shapes known from the literature; however they differ from some published results in minor details. The differences can be attributed to the rather high quality of our samples, grown *in situ*.

The first peak *A* in both B 1*s* and N 1*s* NEXAFS of bulk *h*-BN is due to promotion of the core electrons into the lowest unoccupied π^* states. The B 1*s* core excitation is much more localized in comparison with the N 1*s*. This difference is reflected primarily in the much smaller width of this resonance in the B 1*s* spectrum. Besides, peak *A* is shifted by 1.65 eV to lower photon energies in the B 1*s* spectrum in comparison with the N 1*s* if they are aligned on the binding energy scale using the difference of 207.67 eV in binding energies of the B 1*s* and N 1*s* photolines (not shown). This shift reflects the fact that the final-state effect is stronger for the more localized B 1*s* excitation. Bands denoted *B-E* are derived from the σ^* states of *h*-BN. Between features *A* and *B* there is a rather intense shoulder A'' in the N 1*s* spectrum. In previous works this was assigned to the second π^* resonance in *h*-BN (Ref. 14 and 17) by analogy with the second π^* resonance in molecular borazine.[19] Although we agree with this qualitative interpretation, and even find it quite instructive from the quantum-chemical point of view, the periodicity of the *h*-BN crystal calls for an essentially solid-state description of this feature. As will be discussed below, shoulder A'' can be associated with the interlayer conduction band states first predicted in the calculations by Catellani *et al.*[7,8] These states can be considered as quantum-well states of nearly free-electron-like character localized in space between the *h*-BN planes and delocalized parallel to the planes.[9]

The B 1*s* and N 1*s* NEXAFS change dramatically in going from bulk *h*-BN to the monolayer grown on Ni(111) (Fig. 1). This is especially true for the shape of peak *A*, which becomes much less intense in the B 1*s* spectrum and which can hardly be seen in the N 1*s* one. The reduction in intensity is accompanied by the appearance of broad spectral tails on both sides of peak *A*. The low-energy tail A' is particularly pronounced in both spectra; in the N 1*s* NEXAFS it even develops into a shoulder. Another significant change happens in the region between features *A* and *B*, where a broad maximum appears in the B 1*s* spectrum and where shoulder A'' develops into a broad and strong peak in N 1*s*. Finally, minor changes also become visible in the range of σ^* resonances in both spectra. In the case of 2 ML *h*-BN the spectral shapes are intermediate between those obtained for the bulk and for 1 ML on Ni(111).

In order to get a better insight into the nature of all these changes, we have plotted the B 1*s* and N 1*s* NEXAFS for 1 ML *h*-BN on the common energy scale making use of the difference in binding energies of 208.10 eV (0.43 eV larger than for the case of bulk material) between the B 1*s* and N 1*s* photolines (Fig. 2). The onsets of the low-energy features A' are seen to coincide, and it is plausible to suggest that they are of common origin in the two spectra and to denote them with a common symbol. The same is true for the features denoted A'': they appear at similar energies and gain in intensity synchronously in the B 1*s* and N 1*s* NEXAFS in going from the bulk to the adsorbed monolayer, allowing them to be treated as a manifestation of common unoccupied states. Core-hole effects can hardly affect energy positions of A' and A'' significantly, since these features are rather broad implying a delocalized character of the corresponding unoccupied states.

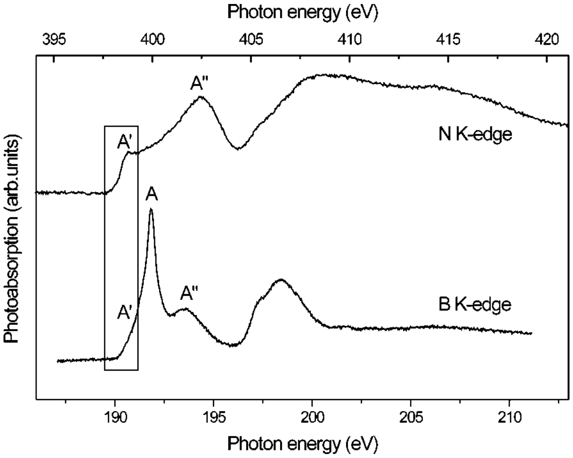

FIG. 2. B 1*s* and N 1*s* NEXAFS for 1 ML *h*-BN grown on Ni(111) (from Fig. 1) aligned in energy with ΔE_B(N 1*s*−B 1*s*) =208.10 eV. The rectangle illustrates the fact that the lowest unoccupied states probed by B 1*s* and N 1*s* absorption (features A') coincide in energy relative to the Fermi level.

Turning back to Fig. 1, one can see that the NEXAFS onset lies at substantially lower photon energies in the case of the monolayer adsorbed on Ni(111) in comparison with the spectra of bulk *h*-BN. The reduction in energy is as large as about 1.5 eV for B 1*s* and about 2.0 eV for N 1*s*. Thus, unoccupied states of the *h*-BN monolayer adsorbed on Ni(111) can exist in the fundamental gap of *h*-BN down to 2 eV below its conduction-band minimum. This finding proposes the existence of a strong orbital mixing between the Ni 3*d* states at the Fermi level (E_F) and unoccupied π^* states of *h*-BN (3*d*-π hybridization). Moreover, taking into account a dramatic reduction in intensity of peak *A* in going from bulk *h*-BN to the adsorbed monolayer, one has to suggest a great reduction in the lifetime of the corresponding π^* core excitation. The excitation can decay faster only if the electron promoted into the π^* state can travel into the substrate via the hybridized states located energetically below E_F. Thus, the observed dramatic decrease in the lifetime of the π^* core excitation indicates the existence of the *h*-BN derived states at E_F. In other words, the monolayer of *h*-BN on Ni(111) may be metallic. On the other hand, all our observations are made in the presence of a core hole. Although it has been suggested above that the hybridized states are delocalized and must therefore only weakly be affected by the core hole, we cannot exclude that in the ground state the π^* bands, modified by the 3*d*-π interaction, still lie above E_F and the covalent bonding is realized only via the 3*d*-π bands at several eV below E_F.

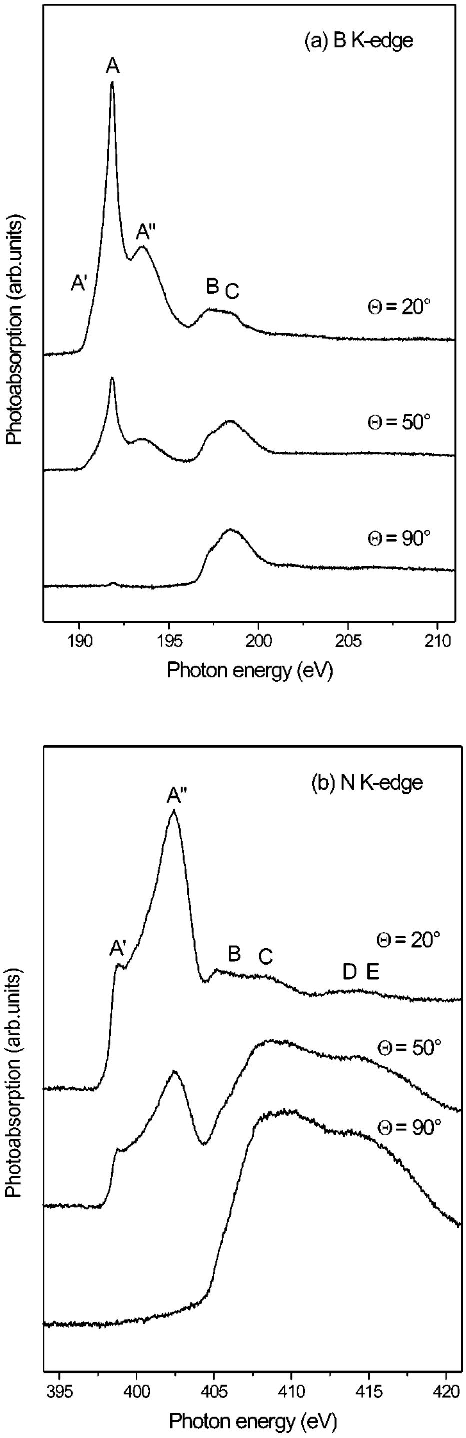

FIG. 3. B 1*s* (a) and N 1*s* (b) NEXAFS of 1 ML *h*-BN grown on Ni(111) as a function of the angle Θ between the surface normal and the direction of photon polarization.

Let us now consider the origin of feature A'' in the NEXAFS of 1 ML *h*-BN on Ni(111). Figure 3 shows a dependence of the B 1*s* and N 1*s* spectra on the angle Θ between the surface normal and direction of the photon beam polarization. With increasing Θ, features A'-A-A'' lose their intensity as compared to the structures at higher-photon energies, and (almost) vanish completely at $\Theta = 90°$. This is clear evidence that the electron density in the states corresponding to features A'-A-A'' is located out of the *h*-BN plane, while the states reflected by structures *B*-*E* are typical σ^* bands. As mentioned above, the feature corresponding to A'' in the N 1*s* NEXAFS of bulk *h*-BN was previously assigned to the second π^* resonance of the B_3N_3 ring.[14,17] Indeed, our angle dependence is consistent with this explanation. In order to reveal distinctions in the charge-density distribution corresponding to states *A* and A'' we sputtered the *h*-BN monolayer adsorbed on Ni(111) with Ar^+ ions for 1 min. This treatment resulted in removal of about every second boron and nitrogen atom, as estimated with PES. The B 1*s* NEXAFS of the partly sputtered and as-prepared samples are compared in Fig. 4. As can be seen, feature *A* survives this heavy treatment of the *h*-BN monolayer, while A'' does not. In the N 1*s* spectra (not shown) structure A'' did not disappear after the bombardment but it was reduced in intensity. Evidently, the bombardment results in destroying the long-range bonding in the monolayer, however the short-range bonding may survive. Therefore we conclude that the states giving rise to peak *A* are localized laterally (delocalized, however, perpendicular to the surface due to the $3d$-π hybridization), whereas the states responsible for peak A'' are delocalized laterally.

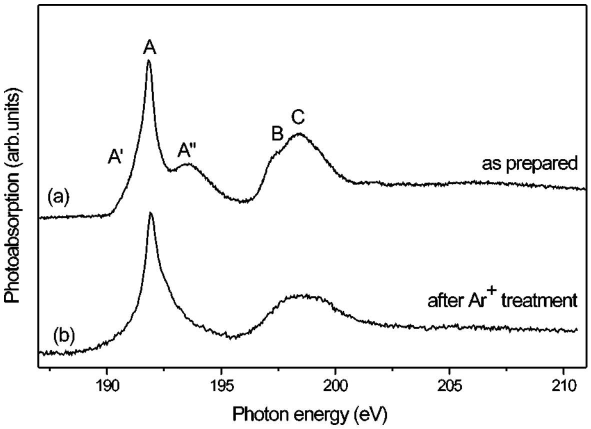

FIG. 4. B 1*s* NEXAFS of 1 ML *h*-BN grown on Ni(111) (a) and the same spectrum after Ar^+ sputtering resulting in the removal of every second atom in the BN monolayer. (b) Both spectra are recorded with the angle of incidence $\Theta = 50°$ in the partial electron yield mode ($U = -100$ V).

The most plausible explanation for the nature of band A'' can be given in terms of the interlayer conduction-band states. In both bulk material, and the hypothetical isolated 1 ML *h*-BN, the band of these states has been calculated to be strongly dispersing across the Brillouin zone, particularly around its minimum at Γ.[7–9] This is consistent with our conclusion that the states corresponding to band A'' are strongly delocalized. Moreover, the charge density in the interlayer conduction-band states is situated not in the plane of the *h*-BN sheets but in the space between the sheets. Therefore, the angle dependence of NEXAFS for these states must be similar to the dependence presented in Fig. 3. As mentioned by Blase *et al.*,[9] it is difficult to describe the structure of the interlayer states in terms of atomic orbitals of individual atoms because of the delocalized character of these states. However, based on the NEXAFS data of Fig. 1 we can sug-

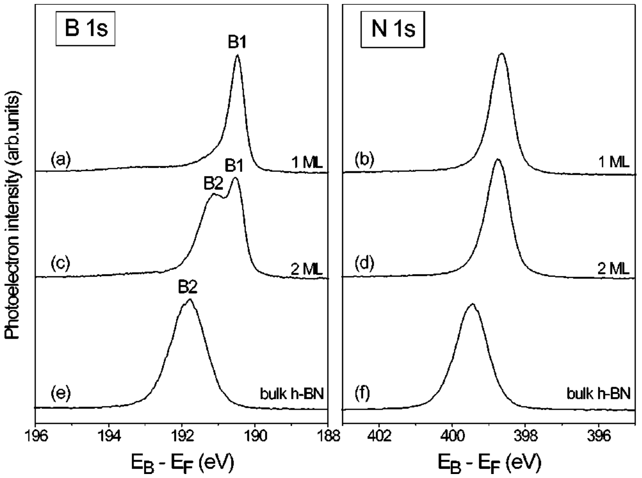

FIG. 5. B 1*s* (a, c, e) and N 1*s* (b, d, f) photoelectron lines in the system *h*-BN/Ni(111) excited with $h\nu=320$ ev and 520 eV, respectively. B1 and B2 stand for the boron chemical species in the first monolayer (B1) and all other layers (B2). Binding energies are measured relative to the Fermi level.

gest that in the bulk *h*-BN there must be a high N 2*p* contribution to the interlayer states and almost no B 2*p* contribution. In contrast, the B 2*p* contribution becomes considerable in the case of a monolayer interacting with Ni(111). This is definitely one more manifestation of the interface 3*d*-π hybridization, however the exact mechanism of the corresponding charge redistribution is unclear.

B. Photoelectron and Auger electron spectroscopy

The conclusion made in the preceding section about the importance of the 3*d*-π hybridization at the *h*-BN/Ni(111) interface can be crosschecked with several innershell techniques exploring occupied states. Figure 5 shows the B 1*s* and N 1*s* core-level spectra at this interface measured with $h\nu=320$ eV and 520 eV, respectively, for specific *h*-BN thicknesses. Binding energies (E_B) are measured relative to the Fermi edge. In the case of 1 ML *h*-BN the B 1*s* and N 1*s* spectra have only one component each, with $E_B = 190.47$ eV and 398.65 eV, respectively. It should be noted that one more (relatively weak) component can appear in the N 1*s* PE spectrum at lower E_B if the borazine exposure is below the saturation value (about 100 L), which can be attributed to the layer imperfections. It is evident from Figs. 5(a) and 5(b) that the photolines under discussion are strongly asymmetric. We fitted these spectra numerically with the Doniach-Sunjic line shape[20] and found out that the asymmetry parameter α is as large as 0.13 for B 1*s* and 0.06 for N 1*s*. The value of α for B 1*s* is typical for the core-level photolines in metals but can never be expected in insulators. Apparently, the “metallic” shape of the core-level PE spectra is due to the response of the electrons from the substrate to the photohole (screening effect). For this to happen, π* states of *h*-BN must be not only hybridized with Ni 3*d*, but also pulled below E_F (at least on the site with the core hole). The ground-state charge transfer from boron to nitrogen may account for the difference in α values for B 1*s* and N 1*s*.

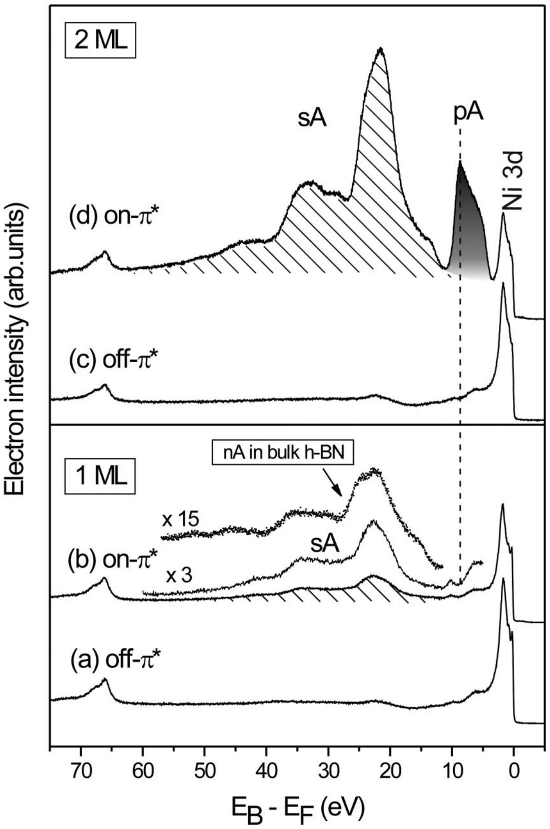

FIG. 6. Photoelectron/Auger spectra of the valence-band region in the system *h*-BN/Ni(111) excited before the B $1s^{-1}(\pi^*)$ resonance (a, c, $h\nu=189.0$ eV) and at the resonance (b, d, $h\nu=191.9$ eV) for the cases of 1 ML (a, b) and *2* ML (c, d) *h*-BN. Participator Auger signal is shadowed and denoted pA; spectator Auger signals are hatched and denoted sA. Normal B KVV Auger spectrum in bulk *h*-BN (excited with $h\nu=250$ eV) is aligned with (b) on the kinetic energy scale.

As the second monolayer *h*-BN grows on top of the first monolayer, one more component (denoted B2) arises in the B 1*s* PE spectrum shifted by 0.68 eV to higher E_B from the original line (denoted B1), as can be seen in Fig. 5(c). This new component has a symmetric shape ($\alpha=0$) typical for insulators and semiconductors, and is essentially broader than B1. In the N 1*s* PE spectrum no new lines can be revealed, but the asymmetry is reduced to $\alpha=0.04$. With the further increase in the *h*-BN thickness the observed trends continue, resulting finally in the single and nearly symmetric B 1*s* and N 1*s* lines of the bulk material with $E_B = 191.82$ eV and 399.47 eV, respectively, not disturbed visibly by any charging effects. Thus, the electronic properties of the first *h*-BN monolayer on Ni(111) are very different from those of the second and subsequent monolayers.

One more illustration of the essentially metallic properties of the first monolayer can be provided by RAS. Resonant Auger spectra of the valence-band region excited at the energy of the B $1s^{-1}(\pi^*)$ absorption resonance (191.9 eV) are compared in Fig. 6 with spectra excited just before the resonance (189.0 eV) for the cases of 1 and 2 ML *h*-BN. The resonant Auger spectrum for the 2 ML film (d) is quite similar to the corresponding spectrum in the bulk material (not shown) and can be separated roughly into two spectral regions below the region of Ni 3*d* states at E_F. Between 3 and 10 eV it is dominated by participator Auger processes (pA, shadowed part), while below 10 eV both participator and spectator Auger contribute to the spectral shape with the domination of the spectator processes (sA, hatched part). A quite high participator Auger intensity in this spectrum is a consequence of high degree of localization of the B $1s(\pi^*)$ excitation in *h*-BN. A similar effect has been observed in RAS of B_2O_3 at the position of the B $1s^{-1}(\pi^*)$ absorption resonance.[21] This similarity is understandable because in both compounds boron atoms are surrounded by more electronegative atoms (N or O) in the plane triangle geometry with the same short-range symmetry D_{3h}.

In going from 2 ML to 1 ML the strong participator Auger signal completely disappears, and the overall shape of the spectator Auger signal changes considerably as well. These findings testify that the lifetime of the B $1s^{-1}\pi^*$ excitation is dramatically shortened if absorption happens in the first *h*-BN monolayer. In other words, an electron promoted from the B 1*s* level to the π^* state is immediately transferred to the substrate. As a result, the resonant Auger decay observed in the case of 1 ML [Fig. 6(b)] can be considered just as normal Auger (however, some remainders of resonant behavior cannot be excluded). Indeed, the corresponding RA spectrum is not very different from the normal B KVV Auger spectrum in bulk *h*-BN, which is shown in Fig. 6 for comparison. Again, this can happen only if the BN π^* states are hybridized with the Ni 3*d* states and pulled below E_F. Thus, we have shown that the charge transfer can happen between the *h*-BN monolayer and Ni(111) substrate in both directions: in the core photoionization process the electron density is moved from the substrate to the adsorbate, screening the core hole, whereas in the core excitation process the electron promoted into the π^* state of *h*-BN moves in the opposite direction.

Finally, the consistency of our results and conclusions can be checked analyzing the structure of the losses accompanying core photoionization. Figure 7 shows satellite structure of the N 1*s* photoline excited with $h\nu = 520$ eV for different *h*-BN thicknesses. The spectra are normalized to the main line intensity. For clarity we corrected the differences in the slope of different spectra by additional normalization with second-order polynomials fitted to the corresponding slopes. The first satellite structure between 5 and 12 eV (denoted S1) is the most intense in the spectrum of bulk *h*-BN. This structure reflects the shake-up excitations resulting in electron transitions from the upper valence band of *h*-BN to the lower conduction band. The very existence of S1 indicates the presence of energy gap in the bulk material, and the width of the gap is reflected roughly by the energy onset of this feature (about 5 eV). This loss structure can be seen so clearly because the lowest unoccupied band (π^* states) is strongly localized. In fact, the convolution of this band with the upper valence band (resulting in S1) reflects, more or less, the shape and energy position of the valence band itself. It should be noted that the absence of S1 would not automatically mean the absence of the band gap; rather it would imply the absence of localized states above E_F. In the case of 2 ML *h*-BN S1 still has a considerable intensity, so that the adsorbed film is definitely insulating. In contrast, feature S1 disappears in the case of 1 ML *h*-BN on Ni(111) implying that the π^* states are now completely delocalized as a consequence of the Ni 3*d*–BN π hybridization. The results for the satellite structure in the B 1s photoionization are similar.

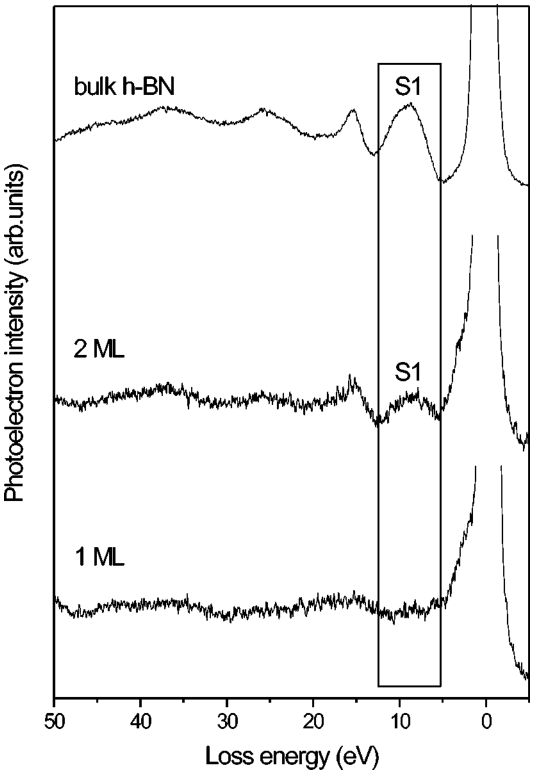

FIG. 7. Loss structures accompanying the N 1*s* excitation in *h*-BN films grown on Ni(111). Photon energy is 520 eV for all spectra. The rectangle outlines the first shake-up feature denoted S1.

On the whole, our results testify that the orbital mixing between the unoccupied π^* states of *h*-BN and 3*d* states of Ni is quite strong at the *h*-BN/Ni(111) interface. The question whether this system is insulating or metallic in the ground state is however open. In the presence of a core hole it definitely demonstrates metallic properties. Since π^* states mixed with Ni 3*d* states are found to be strongly delocalized perpendicularly to the surface, it seems to be unlikely that core-hole effects are significant for such states. Therefore we tend to think that the system is metallic also in the ground state. One could argue that the valence-band photoemission can provide conclusive evidence either pro or contra the metallic nature of the system under study, because this technique deals with valence-band holes, which are much more delocalized than the core holes and should induce much weaker core-hole effects. Nagashima *et al.*[1] reported that they did not observe any metallic band related to *h*-BN close to E_F in their ARUPS study of the *h*-BN/Ni(111) interface. In Fig. 8 we show angle-integrated valence-band PE spectra of the clean Ni(111) surface (a), the same surface with a monolayer *h*-BN on top (b), and bulk *h*-BN (c) measured in the present work with $h\nu = 100$ eV at normal electron emission. Focusing on the region of first 3 eV below E_F, one can

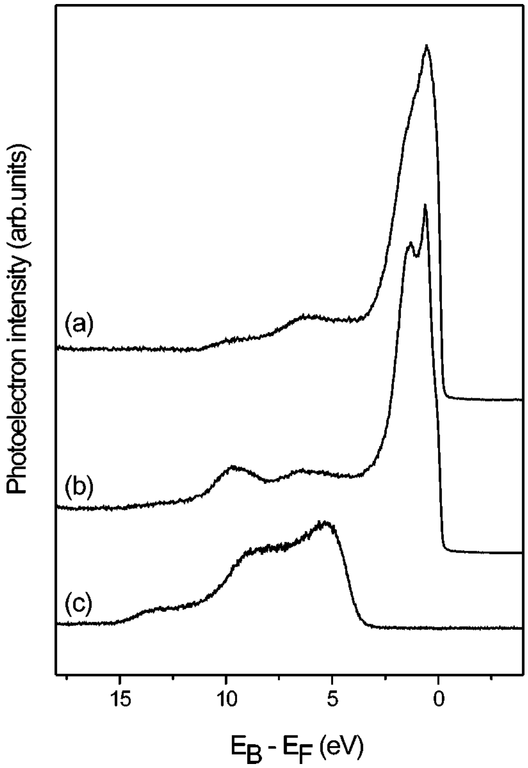

FIG. 8. Photoelectron valence-band spectra excited with $h\nu = 100$ eV and recorded in normal emission from (a) Ni(111), (b) 1 ML h-BN/Ni(111) and (c) thick film (bulk h-BN).

see significant changes in going from the clean nickel surface to the surface covered with 1 ML h-BN, which could be interpreted as an evidence of some contribution of the BN π^* states, confirming our suggestion of a metallic character of the h-BN monolayer on Ni(111). Unfortunately, this interpretation is not the only one possible. The observed changes in the spectra close to E_F can also be associated with a trivial effect of removing the surface-related part of the total Ni $3d$ intensity caused by adsorption. In other words, the effect can be the same for any adsorbate, not specifically h-BN. Thus, valence-band PE does not allow us to decide unambiguously whether the h-BN/Ni(111) interface is metallic or not in the ground state.

IV. CONCLUSIONS

Several innershell techniques (soft XAS, core-level PES, RAS) have been applied in order to investigate the details of electronic structure at the h-BN/Ni(111) interface for different h-BN thickness with the emphasis on the single monolayer coverage. Strong orbital hybridization between Ni $3d$ and h-BN π states has been consistently observed with all techniques used. In particular, it is reflected in the following:

(1) a strong change of the B $1s$ and N $1s$ NEXAFS in going from bulk h-BN to a single monolayer adsorbed on Ni(111) including the appearance of a broad band of unoccupied states in the band gap of h-BN;

(2) a strongly asymmetric shape of the B $1s$ ($\alpha = 0.13$) and N $1s$ ($\alpha = 0.06$) PE lines in the case of a single monolayer as a consequence of metallic screening of the core holes by the electrons transferred from the substrate;

(3) an absence of the resonant Auger decay in the case of a single h-BN monolayer on Ni(111) because of the fast transfer of the electron promoted into π^* states to the substrate;

(4) an absence of the shake-up features characteristic for bulk h-BN as a consequence of strong delocalization of the π^* states (perpendicular to the surface) in a single monolayer on Ni(111).

This result is in contradiction with the recent DFT calculation by Grad *et al.*,[6] where no substantial Ni $3d$–BN π hybridization has been found. The discrepancy cannot be attributed solely to the presence of a core hole in our experiments, because such a hole can, at most, shift measured energy values from the ground-state values, but cannot be a source of hybridization.

In the B $1s$ and N $1s$ NEXAFS of both bulk h-BN and a single monolayer adsorbed on Ni(111) we observe spectral structures, which can be interpreted as a manifestation of the interlayer conduction band states of h-BN predicted theoretically by Catellani *et al.*[7,8]

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