

Adsorption-induced gap states of *h*-BN on metal surfaces

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The formation of hexagonal boron nitride (*h*-BN) monolayers on Ni(111), Rh(111), and Pt(111) has been studied by a combination of x-ray emission, angle-resolved valence band photoemission, and x-ray absorption in search for interface-induced gap states of *h*-BN. A significant density of both occupied and unoccupied gap states with N *2p* and B *2p* characters is observed for *h*-BN/Ni(111), somewhat less for *h*-BN/Rh(111) and still less for *h*-BN/Pt(111). X-ray emission shows that the *h*-BN monolayer is chemisorbed strongly on Ni(111) and very weakly on Pt(111). We associate the gap states of *h*-BN adsorbed on the transition metal surfaces with the orbital mixing and electron sharing at the interface because their density increases with the growing strength of chemisorption.

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I. INTRODUCTION

The performance of all solid heterojunctions critically depends on the properties of the contacts between the constituent materials. At interfaces between metals and semiconductors (insulators), these properties are determined by the electronic states formed at the contact area, generally referred to as interface states.^{1,2} The concept of interface states is broad because their origin can be quite different, including alloying, defects, etc. At well-defined and defect-free interfaces with negligible chemical interaction, they were traditionally associated with the metal-induced gap states, originating from the virtual gap states of the complex band structure of the semiconductor, “turned on” by the tails to the metal wave functions.³ These states are an intrinsic property of the semiconductor, nearly independent of the metal. If the interfacial chemical bonding is considerable, the band structure of the semiconductor is modified in the interface region, and new interface states may appear due to orbital mixing and electron sharing. However, it is difficult to reveal the net “chemical” effect (i.e., the influence of covalent or ionic bonding) on the density of gap states experimentally because reactive metal/insulator systems are typically prone to interdiffusion and cannot be considered as well defined. Therefore, it is a challenging task to study the effect of chemical reactivity on the density of gap states without disrupting the actual interface.

An ideal candidate for studying the effects of chemical bonding on the formation of gap states at metal/insulator interfaces is hexagonal boron nitride (*h*-BN) adsorbed on transition metal (TM) surfaces, for the following good reasons. First, the layered nature of *h*-BN prevents any interdiffusion and other imperfections. Second, it is easy to grow exactly one *h*-BN monolayer by thermal decomposition of molecular borazine.⁴⁻⁷ Third, the strength of the chemical interaction can be varied over a wide range by choosing suitable TM substrates.^{8,9} Thus, a combination of *h*-BN with TMs represents a set of well-defined metal/insulator inter-

faces with an adjustable strength of chemical interaction.

On the other hand, the very fact that *h*-BN gap states do exist in *h*-BN/TM heterojunctions is rather controversial. On the theoretical side, there exist three recent density functional theory studies of the *h*-BN/Ni(111) interface,¹⁰⁻¹² but the results are inconclusive. Grad *et al.*¹⁰ and Che and Cheng¹¹ used a generalized gradient approximation (GGA) for the exchange and correlation potential, and found *h*-BN to be physisorbed (weakly bound) on Ni(111) and insulating. This result supported the original conclusion made by Nagashima *et al.* in their angle-resolved photoemission spectroscopy (ARPES) study.⁵ Huda and Kleinman demonstrated that only a physisorbed state can be obtained with GGA, but using a local density approximation (LDA) results in a chemisorbed state,¹² in agreement with some more recent experiments.^{13,14} In the same theoretical study, Ni bands at the Fermi level (E_F) were found to be slightly hybridized with the *h*-BN bands, and in this sense *h*-BN was suggested to be “barely metallic.”¹²

In this paper, we report on experimental evidence for the existence of adsorption-induced gap states of *h*-BN grown on Ni(111), Rh(111), and Pt(111), and discuss the origin of these states. The reactivity of the studied interfaces ranges from very weak (*h*-BN/Pt) to rather strong (*h*-BN/Ni),^{4,6,8,13} allowing us to estimate the influence of chemisorption strength on the density of gap states. We apply element- and symmetry-selective techniques, B(N) *1s* x-ray absorption and emission spectroscopies (XAS and XES), to study both unoccupied and occupied *h*-BN gap states, respectively. Contrary to direct and inverse photoelectron spectroscopies, B(N) *1s* XAS and XES allow us to identify specific B(N) *2p* contributions to the valence and conduction bands of the entire heterojunction. Of primary importance are the x-ray emission spectra presented here, while the XAS data have been reported before^{9,14} and are discussed here for the sake of completeness. In addition, we report ARPES data for all three interfaces and compare them with the spectra for the corresponding clean substrates. Although the direct observa-

tion of the gap states in photoemission is obscured by the substrate emission, it is demonstrated that the ARPES data are in accord with the XES results.

II. EXPERIMENT

The XES and XAS experiments were performed at beamline I511-3 at MAX-lab (Lund, Sweden). The resolution of the XAS and XES spectra at the B 1s edge was set to 50 and 350 meV, respectively, and that at the N 1s edge to 150 and 650 meV, respectively. *h*-BN monolayers were grown on the TM substrates in a separate UHV chamber by thermal decomposition of vaporized borazine and characterized by low-energy electron diffraction (LEED), photoemission spectroscopy (PES), and XAS, as described elsewhere.^{9,14} After growth, the samples were transferred within a few minutes in air to the beamline and annealed at 300 °C in UHV to remove physisorbed gases. The samples proved to be quite resistive against oxidation, as no change in the B 1s and N 1s XAS spectra could be detected after a short exposure to air. The XE spectra were recorded using an XES-350 spectrometer (from Gammadata-Scienta), with the optical axis set perpendicular to the beamline axis in the plane of polarization of the incident radiation in order to avoid registering the Thomson scattering. Typical accumulation times for the monolayer samples were about 10 h/XE spectrum; no beam-induced damage was observed within this time. The XES spectra are normalized to the area under the curve to obtain emission intensities caused by the same number of core vacancies.

The ARPES experiments were performed at beamline D1011 at MAX-lab. The samples were grown as described above and characterized by LEED and PES. We used an SES-200 spectrometer (from Gammadata-Scienta), with the kinetic energy resolution set to 150 meV for the ARPES measurements. The resolution at the chosen photon energy ($h\nu=100$ eV) was set to 50 meV. The base pressure during the measurements did not exceed 2×10^{-10} mbar.

III. RESULTS AND DISCUSSION

Figure 1 shows N 1s XES spectra for the three interfaces studied (b)–(d) compared to the spectrum of *h*-BN powder (a). The photon-in energy was 408 eV, which is just sufficient to create a core-ionized state, but insufficient for unwanted satellite excitations. The angle Θ between the polarization vector of incident radiation and surface normal was set to 45° for the monolayer samples in order to make the contributions from π and σ states of *h*-BN comparable and to facilitate comparison with the powder sample. The N 1s XES from the powder sample reproduces (with better resolution) the familiar spectrum from bulk *h*-BN, first recorded with photon excitation by Tegeler *et al.*¹⁵ These authors studied polycrystalline *h*-BN samples with preferential orientation (texture) by angular-dependent XE and demonstrated that the sharp peak at $h\nu=394.5$ eV results from the N 2p(π) density of states (DOS), while other structures are due to the N 2p(σ) DOS.

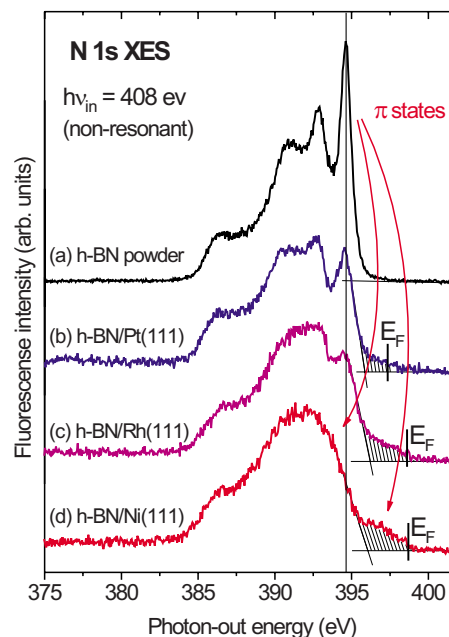


FIG. 1. (Color online) N 1s x-ray emission spectra from *h*-BN monolayers adsorbed on Pt(111), Rh(111), and Ni(111) compared with the spectrum from bulk (powder) *h*-BN. Arrows illustrate a rearrangement of the N 2p(π) DOS upon adsorption on Ni(111). Hatched regions indicate *h*-BN gap states.

It is evident from Fig. 1 that the evolution of the N 1s XES upon *h*-BN adsorption on different TM substrates is remarkable. At all three interfaces, one can see the appearance of interface states extending to E_F , although their spectral intensity is different: The fraction of the gap states is about 2% of the entire N 2p DOS on Pt, 4% on Rh, and 5% on Ni, as estimated from Fig. 1. Note that the positions of E_F are determined from the N 1s photoemission for *h*-BN/Ni (398.65 eV) and *h*-BN/Rh (398.58 eV), while for *h*-BN/Pt it is determined from the x-ray absorption onset (about 397.3 eV).^{9,14} (Fermi levels of *h*-BN and Pt substrate do not align because of the physisorptive nature of this interface.⁶ Therefore, the position of the N 1s photoemission line relative to E_F of the substrate does not help to find E_F of the monolayer.) Due to the element- and symmetry-selective nature of the emission process, we associate the spectral intensity in the vicinity of E_F with the *h*-BN gap states of N 2p character.

Apart from the gap states, the overall spectral shape for *h*-BN/Pt(111) [Fig. 1(b)] is quite similar to that of the reference *h*-BN powder (a) and nearly identical to the spectrum of oriented bulk *h*-BN taken at the same angle.¹⁵ This is not surprising because *h*-BN is known to be weakly bound to Pt(111),^{6,9} without significant electron sharing. The density of the gap states is also very low. Therefore, these states may stem from the very weak but still present chemical bonding. Above E_F , these states are matched by a weak continuum of unoccupied states, as shown by XAS in our previous work.⁹

The most drastic changes in the N 1s XE spectrum can be seen in going from *h*-BN powder to the *h*-BN monolayer on Ni(111) [Fig. 1(d)]. Indeed, the sharp peak due to the π -DOS at $h\nu=394.5$ eV is transformed into a shoulder at about

393.5 eV, while other states appear, filling the entire gap between the valence band maximum and E_F . This is clear evidence of the strong orbital mixing of the N $2p(\pi)$ states of *h*-BN with the Ni d bands, which supports our original conclusion that the nature of the *h*-BN/Ni(111) interface must be attributed to chemisorption.¹⁴ The shift of the *h*-BN π -DOS by ~ 1 eV to a higher binding energy is in accord with the ARPES data.⁶ The fact that the gap states of *h*-BN on Ni(111) were not reported in the previous photoemission studies^{5,6} is understandable because the occupied gap states represent a weak and monotonous continuum hidden under the structured substrate signal (mainly Ni $3d$). Only the use of element-selective XAS and XES allows us to see the gap states clearly. In fact, there is no contradiction between XES and ARPES data, as will be shown below: The effect observed in ARPES is simply more subtle. Evidently, the gap states of *h*-BN on Ni(111) are chemisorption induced because the appearance of these states is accompanied by a dramatic change of the overall spectral shape. The much stronger chemisorption results in a considerably higher density of gap states than on Pt(111).

Finally, the spectral shape of the N $1s$ XES from *h*-BN on Rh(111) [Fig. 1(c)] is intermediate between that of *h*-BN/Pt and *h*-BN/Ni. This is a result of a corrugated *h*-BN nanomesh formed on Rh(111).¹⁶ The elevated parts (wires) of the nanomesh are weakly bound, while the lower parts (pores) are chemisorbed.^{9,17} The resulting XE spectrum is a superposition of two spectra produced by the pores and wires of the nanomesh. The contribution of the nanomesh wires to the density of *h*-BN gap states must be very weak (if any) because they are elevated by about 0.5 Å over the pores.¹⁷ Therefore, we suppose that the main contribution to the density of *h*-BN gap states is induced by the chemisorption in the nanomesh pores.

The observed spectra reflect the ground-state N $2p$ partial DOS distorted by the core hole in the initial state and by the valence hole in the final state. The core-hole effects cannot change the number and, as a rule, the order of the occupied and unoccupied electron states, but they can change the shape of the ground-state DOS since the ground-state wave functions are rearranged. This rearrangement strongly depends on the lifetime of the core-excited state. If this lifetime is sufficient for orbital relaxation, the spectrum may reflect, in particular, nuclear motion in the core-excited state and many-body effects (shake-ups). The many-body effects are more critical for the gapless systems (the original theory of the dynamics of the core-hole state by Mahan¹⁸ and Nozieres and Dominici¹⁹ was developed for metals) and are stronger for the states close to the Fermi level. In particular, these effects were observed in nonresonant XES of molecules chemisorbed on metal surfaces.²⁰ The shake-up singularities close to the Fermi level decrease with the decreasing core-hole lifetime. Thus, the core-hole effects cannot be a cause of the gap states, but they can strongly influence the ground-state DOS close to the Fermi level. Generally, the presence of a core hole does not prevent the application of XES for the analysis of chemical bonding in adsorbates.²¹

The orbital hybridization at a reactive *h*-BN/TM interface [e.g., *h*-BN/Ni(111)] is illustrated schematically in Fig. 2 along with the resulting spectral signatures, which can be

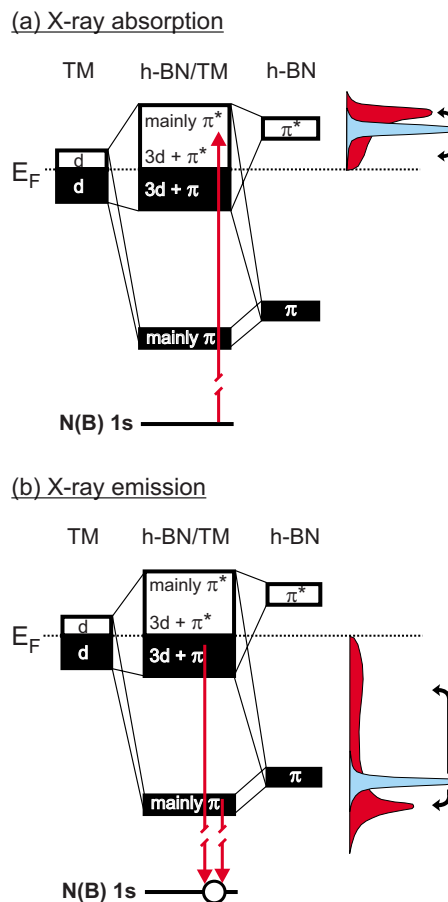


FIG. 2. (Color online) Schematic representation of the TM d -*h*-BN π hybridization and its reflection in the N $1s$ XAS and XES. Arrows at the right-hand side illustrate a modification of the corresponding spectra upon chemisorption.

expected in the N $1s$ XAS (a) and XES (b). Upon chemisorption, the unoccupied π^* band of *h*-BN is pushed upward, and the occupied π band is pushed downward relative to their positions in bulk *h*-BN. The downward shift of the π band by ~ 1 eV was observed experimentally by photoemission for *h*-BN on Ni(111),⁶ and the same amount of splitting of the π bands (denoted as “mainly π^* ” and “mainly π ”) gain some admixture of the TM d states, but essentially keep their *h*-BN nature. In turn, the TM d bands also gain an admixture of the *h*-BN $\pi(\pi^*)$ states in the vicinity of E_F . Therefore, one can expect two main signatures of orbital hybridization at the *h*-BN/TM interfaces in the XA (XE) spectra of *h*-BN: (i) an upward (downward) shift of the π^* (π) band and (ii) the formation of a hybridization-induced tail ranging down (up) to E_F , as illustrated in the right-hand side of Fig. 2. These are exactly the features observed in the XA and XE spectra of *h*-BN adsorbed on Ni(111) [Figs. 1(d) and 3(b)]. Evidently, the density of chemisorption-induced *h*-BN gap states at the *h*-BN/Ni(111) interface is quite substantial, and, in this sense, the *h*-BN monolayer is metallized.

It should be noted that chemisorption-induced states close to the Fermi level can often be detected by x-ray spec-

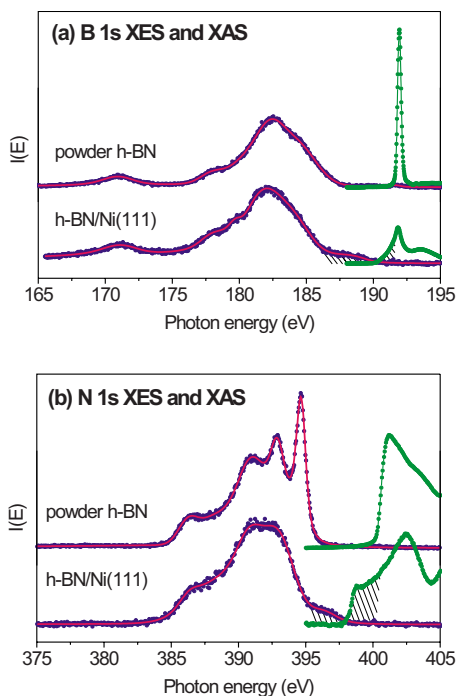


FIG. 3. (Color online) B 1s (a) and N 1s (b) x-ray absorption and x-ray emission spectra of *h*-BN on Ni(111) recorded in grazing incidence ($\Theta=20^\circ$) and compared with those of *h*-BN powder. Photon-in energies are 200 and 408 eV for B 1s and N 1s XES, respectively. Solid curves through the XES data are shown as a guide for the eye. Regions of chemisorption-induced gap states are hatched.

troscopies in molecules chemisorbed on metal surfaces.²¹ For example, such states were observed in the adsorption of molecular benzene on Ni(100) and Cu(110) and were attributed to the covalent mixing between the lowest unoccupied $\pi(e_{2u})$ orbital of benzene with the Ni *d* band and Cu *sp* band of the substrates, respectively.²³

All previous discussions have been based on the N 1s spectra of *h*-BN because we observed that the influence of metallic substrates on the boron spectra is less pronounced. This may be a consequence of the fact that nitrogen is more electronegative than boron, resulting in higher electron density on the N sites. Intuitively, these sites must be more sensitive to any disturbance, making the nitrogen spectra somewhat more informative. Nevertheless, the gap states of *h*-BN can also be observed in the B 1s XA and XE spectra, as shown in Fig. 3(a) for the *h*-BN/Ni(111) interface. The weight of the gap states is roughly the same in the N 2*p* and B 2*p* DOS, as estimated from the spectra of Fig. 3.

As mentioned above, it is much easier to observe the gap states of the chemisorbed *h*-BN monolayer with element-selective XES than with ARPES, where the substrate signal dominates in the valence band region. Nevertheless, the results obtained with these two techniques should be consistent. In order to demonstrate this consistency, we studied the valence band structure of clean and *h*-BN covered Pt(111), Rh(111), and Ni(111) surfaces with ARPES around the $\bar{\Gamma}$ point of the surface Brillouin zone. The normal emission

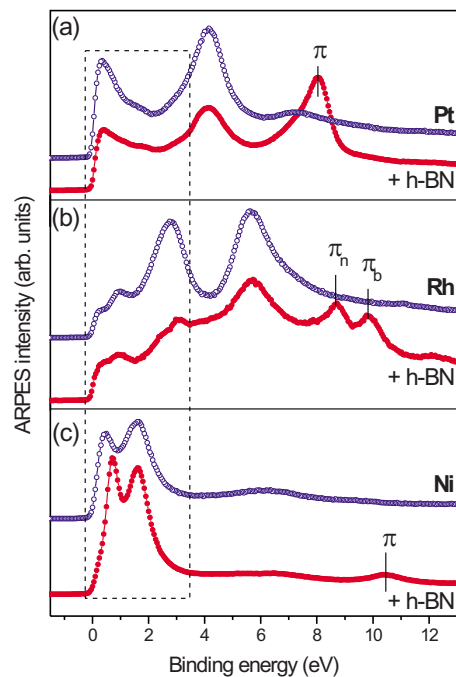


FIG. 4. (Color online) Angle-resolved valence band photoelectron spectra from clean (open circles) and *h*-BN covered (solid circles) (a) Pt(111), (b) Rh(111), and (c) Ni(111) surfaces excited with the linearly polarized photons ($h\nu=100$ eV) and collected at normal emission within $\pm 0.5^\circ$. For all spectra, the angle between the surface normal and the direction of photon polarization is set to 50° . The region where the *h*-BN gap states should be expected is marked by a rectangle.

spectra excited with $h\nu=100$ eV are shown in Fig. 4. The measured binding energies of the *h*-BN π bands at $\bar{\Gamma}$ are 10.4 eV on Ni(111), 9.8 eV (pores) and 8.7 eV (wires) on Rh(111), and 8.0 eV on Pt(111). These positions reflect trends in the chemical bonding between *h*-BN and the substrates, with higher values corresponding to stronger bonding. On the other hand, the absolute values of the π band positions should always be compared with caution because it is not quite correct to relate them to the Fermi level in physisorbed systems, such as *h*-BN/Pt(111), because in this case the monolayer is electrically decoupled from the substrate. Therefore, for such systems, it is more reasonable to refer the binding energies to the vacuum level.⁶ The σ bands are hardly visible with the chosen photon energy, but they are known to lie well below 4 eV at $\bar{\Gamma}$.^{6,16} Thus, if very few or no *h*-BN π states are mixed into the TM *d* states in the vicinity of E_F , there must be no obvious change in the shape of photoemission spectra within the first 3.5 eV below E_F upon *h*-BN adsorption. This is the situation characteristic of the *h*-BN adsorption on Pt(111) [Fig. 4(a)]. Thus, no evidence for the *h*-BN gap states can be found with ARPES for this system. In contrast, clear changes of the spectral shape can be seen in the region of the *h*-BN band gap upon *h*-BN adsorption on Rh(111) and Ni(111) [Figs. 4(b) and 4(c)]. In particular, on Ni(111), the upper 3*d* band is shifted downward at $\bar{\Gamma}$ by as much as 0.3 eV. Therefore, the Ni 3*d* and Rh 4*d* states are modified by the orbital hybridization with

the *h*-BN π states in the vicinity of E_F . This result is in clear agreement with the XES-based observation of chemisorption-induced *h*-BN gap states in *h*-BN/Ni(111) and *h*-BN/Rh(111), and the low density of these states in *h*-BN/Pt(111).

IV. CONCLUSIONS

In conclusion, our combined XES, ARPES, and XAS studies consistently reveal a finite density of *h*-BN interface gap states at E_F for several *h*-BN/TM interfaces, implying that *h*-BN is partially metallized upon chemisorption. The density of the gap states depends on the strength of the chemical interaction between *h*-BN and the substrate. At the

weakly bound *h*-BN/Pt(111) interface, the low density of gap states is associated with the very weak chemical bonding. At the strongly bound *h*-BN/Ni(111) interface, the gap states are induced by chemisorption. On Rh(111), the pores of the *h*-BN nanomesh also generate chemisorption-induced gap states. The influence of the core-hole effects on the ground-state density of gap states is expected to be stronger for stronger bound *h*-BN monolayers.

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