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***h*-BN in the making: The surface chemistry of borazine on Rh(111)**

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ABSTRACT

Borazine is a well-established precursor molecule for the growth of hexagonal boron nitride (*h*-BN) via chemical vapor deposition on metal substrates. To understand the formation of the *h*-BN/Rh(111) moiré from borazine on a molecular level, we investigated the low-temperature adsorption and thermally induced on-surface reaction of borazine on Rh(111) *in situ* using synchrotron radiation-based high-resolution x-ray photoelectron spectroscopy (XPS), temperature-programmed XPS, and near-edge x-ray absorption fine structure measurements. We find that borazine adsorbs mainly as an intact molecule and have identified a flat-lying adsorption geometry. Borazine multilayers are observed to desorb below 200 K. Starting at about 300 K, dehydrogenation of the remaining borazine and borazine fragments takes place, and disordered boron nitride starts to grow. Above 600 K, the formation of the *h*-BN sets in. Finally, at 1100 K, the conversion to *h*-BN is complete. The *h*-BN formed by deposition and post-annealing was compared to the *h*-BN grown by an established procedure, proving the successful preparation of the desired two-dimensional material.

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I. INTRODUCTION

In 2004, a scientific milestone was reached: Geim and Novoselov were the first to prepare graphene, a two-dimensional (2D) structure built up from sp^2 -hybridized carbon atoms arranged in a honeycomb fashion.¹ This groundbreaking work laid the foundation for a flourishing research field dedicated to the prediction, synthesis, characterization, and application of 2D materials (2DM), which have been observed to exhibit outstanding physical and chemical properties. Consequently, in the last two decades, many aspects of 2DM have been theoretically and experimentally investigated.^{2–5} Hexagonal boron nitride (*h*-BN) is one of the most extensively studied representatives of this class.^{6–8} It is a graphene analog since it exhibits the same honeycomb structure but consists of sp^2 -hybridized alternating boron and nitrogen atoms. *h*-BN shows a row of startling properties, e.g., chemical inertness, high thermal stability, mechanical robustness, optical transparency, and ultraviolet lasing, which render it promising for various applications.^{9–11} Its

smooth surface allows for the growth of other 2DM on top of *h*-BN, representing a facile approach for the preparation of heterostacks.¹² In contrast to graphene, which is a zero-bandgap semiconductor, *h*-BN is insulating, characterized by a large bandgap of about 6 eV.¹³ This property, in combination with its smooth surface and structural similarity, renders it a perfect dielectric layer in graphene-based electronics.^{14,15}

In an ultra-high vacuum (UHV) environment, *h*-BN can be grown via chemical vapor deposition (CVD) on metal substrates, e.g., on Ni(111),¹⁶ Ag(111),¹⁷ Pt(111),¹⁸ Pd(111),¹⁹ Ir(111),²⁰ Ir(110),²¹ and Rh(111).²² The interaction strength between the 2DM and its support depends on the chosen metal and has a severe influence on the structure and properties of *h*-BN. CVD growth on a lattice-mismatched substrate will result in buckling of the 2D layer. In the case of Rh(111), the lattice mismatch leads to 12×12 Rh(111) unit cells being covered with 13×13 *h*-BN unit cells.²³ This moiré exhibits a highly regular structure with a periodicity of about 3.2 nm²⁴ and consists of pores and wires.²⁵ The pores are in close

contact with the substrate; that is, they experience strong interactions, while the wires are further away from the substrate and undergo only weak interactions. Due to the different chemical identities of the pores and wires, the moiré can act as a template for the selective deposition of atoms, molecules, and clusters.^{26–30} For CVD growth of *h*-BN, it is beneficial to use precursor molecules having a 1:1 B/N stoichiometry, such as ammonia borane (BH_3NH_3) or borazine ($\text{B}_3\text{H}_6\text{N}_3$), with the latter being by far the most commonly used.³¹ Borazine is isostructural and isoelectronic with benzene. Hence, it can be considered a benzene analog, despite its controversial aromaticity.³² Apart from its sensitivity toward moisture and light, it is relatively easy to synthesize and handle since it is liquid at room temperature and non-toxic.

So far, the CVD growth of *h*-BN/Rh(111) from borazine has been studied using standard UHV tools such as scanning tunneling microscopy (STM), temperature-programmed desorption (TPD), and high-resolution electron energy loss spectroscopy (HREELS).^{33,34} In our UHV study, we investigated, to our knowledge for the first time, the adsorption and reaction of borazine on Rh(111) by synchrotron radiation-based high-resolution x-ray photoelectron spectroscopy (XPS) and near edge x-ray absorption fine structure (NEXAFS) to understand the formation of *h*-BN/Rh(111) in even greater detail. The high relevance of synchrotron-based x-ray photoelectron spectroscopy for the examination of 2DM has just recently been emphasized in a review by Bignardi *et al.*³⁵ We followed the adsorption process at low temperature *in situ* by XPS, which allowed for the elucidation of the spectral fingerprint of borazine/Rh(111). In addition, the adsorption geometry of borazine on Rh(111) was evaluated using NEXAFS. The thermally induced reaction pathway of borazine was monitored by temperature-programmed XPS (TPXPS)³⁶ in a range of 130 to 1100 K. Due to the high quality of our data and a careful analysis, we were able to identify individual surface species and the gradual evolution of *h*-BN.

II. EXPERIMENTAL

All experiments were performed in a transportable two-chamber UHV apparatus attached to the open-port beamline UE56/2-PGM1 at the electron storage ring BESSY II of the Helmholtz Zentrum Berlin (HZB). The apparatus used is, *inter alia*, equipped with a hemispherical electron energy analyzer, a home-built partial yield detector for NEXAFS, and a microcapillary array dosing system that enabled the introduction of borazine into the analyzer chamber. The sample can be cooled to ~100 K using liquid nitrogen and heated, either resistively up to ~1400 K or by a tungsten filament mounted behind up to 550 K. Please refer to the literature for a more detailed description of our experimental setup.³⁷ As substrate, a Rh(111) single crystal purchased from MaTeck was used. K-type thermocouples were spot-welded to the crystal to read out its temperature. Prior to any measurements, the crystal surface was cleaned by several cycles of Ar^+ sputtering, annealing to 1200 K, and oxygen treatment at 900 K. Its cleanliness was verified using XPS. Borazine was synthesized by our group according to Sneddon³⁸ and dosed into the chamber using the microcapillary array dosing system. Exposures are given in Langmuir (L, 1 L = 1.33×10^{-6} mbar s).

To observe the adsorption and the thermally induced reaction of borazine on Rh(111) *in situ*, XP spectra were continuously measured. In the course of the TPXPS experiment, the sample was heated to 550 K using the tungsten filament for radiative heating with a heating ramp of 0.5 K/s. For temperatures >550 K, resistive heating was employed (in 50 K steps). XP spectra were measured at normal emission in the B 1s ($h\nu = 280$ eV; resolution: 200 meV), N 1s (500 eV; 200 meV), and Rh 3d (380 eV; 230 meV) regions. To avoid beam damage to the surface species, the sample was shifted by about 0.1 mm (larger than the x-ray beam diameter) between each spectrum. Processing of the XP spectra included referencing the binding energy to the Fermi edge, subtracting a linear background, and peak fitting using a convolution of Gaussian and Doniach–Šunjić functions. A table comprising the fit parameters is provided in the supplementary material. The surface coverage was determined by referring to a closed layer of *h*-BN on Rh(111), which corresponds to 1.17 ML of boron and 1.17 ML of nitrogen (12×12 Rh unit cells covered by 13×13 *h*-BN unit cells). This *h*-BN reference layer was grown by dosing $1\text{--}2 \times 10^{-8}$ mbar borazine onto the substrate held at 1050 K and is referred to as “as-prepared” *h*-BN. NEXAFS spectra at the boron and nitrogen K-edges were recorded in partial electron yield mode at incidence angles of 0° (normal incidence, NI) and 70° (grazing incidence, GI) with respect to the surface normal. Background correction was performed by subtracting the corresponding clean spectrum from each spectrum.

III. RESULTS AND DISCUSSION

The adsorption of borazine on Rh(111) was studied at 130 K by XPS. To this end, borazine was dosed into the analyzer chamber, and the adsorption process was followed *in situ* for the B 1s and N 1s core levels in individual experiments (Fig. 1).

Figure 1(a) provides the B 1s spectra recorded during adsorption of a multilayer of borazine on Rh(111) as a waterfall plot; the fit of the final B 1s spectrum is shown in Fig. 1(b). The quantitative analysis of the B 1s multilayer adsorption is depicted in Fig. S1 in the supplementary material. In the B 1s region, one major signal evolves at 189.57 eV (turquoise), shifting to 189.50 eV in the course of the adsorption process. We attribute this peak to molecular borazine (B-N_2). The shift to lower binding energies is allocated to adsorbate–adsorbate interaction, an effect that typically occurs upon increasing surface coverage. At lower binding energies, two further contributions (blue) develop at 188.66 and 187.78 eV, which we suggest belong to borazine fragments ($\text{B}_x\text{N}_y\text{H}_z$) that evolve due to the reaction of borazine with rhodium. Under the assumption that their respective binding energies depend on the number of electron-withdrawing nitrogen neighbors of the boron atom, we assign the signal at 188.66 eV to B–N fragments and the one at 187.78 eV to boron (B). Between 0.30 and 0.40 L, a new peak (yellow) starts to develop at higher binding energies, which is associated with multilayer formation. It evolves at 190.07 eV and shifts to 190.32 eV upon further exposure to borazine. At the highest exposure of 0.60 L borazine onto Rh(111), a boron coverage of 0.57 ± 0.02 ML is achieved. Interestingly, the corresponding nitrogen coverage is determined to be only 0.52 ± 0.02 ML. This unexpected deviation is larger than the estimated error. Therefore, the reaction of borazine with the rhodium surface and synchrotron radiation-induced beam

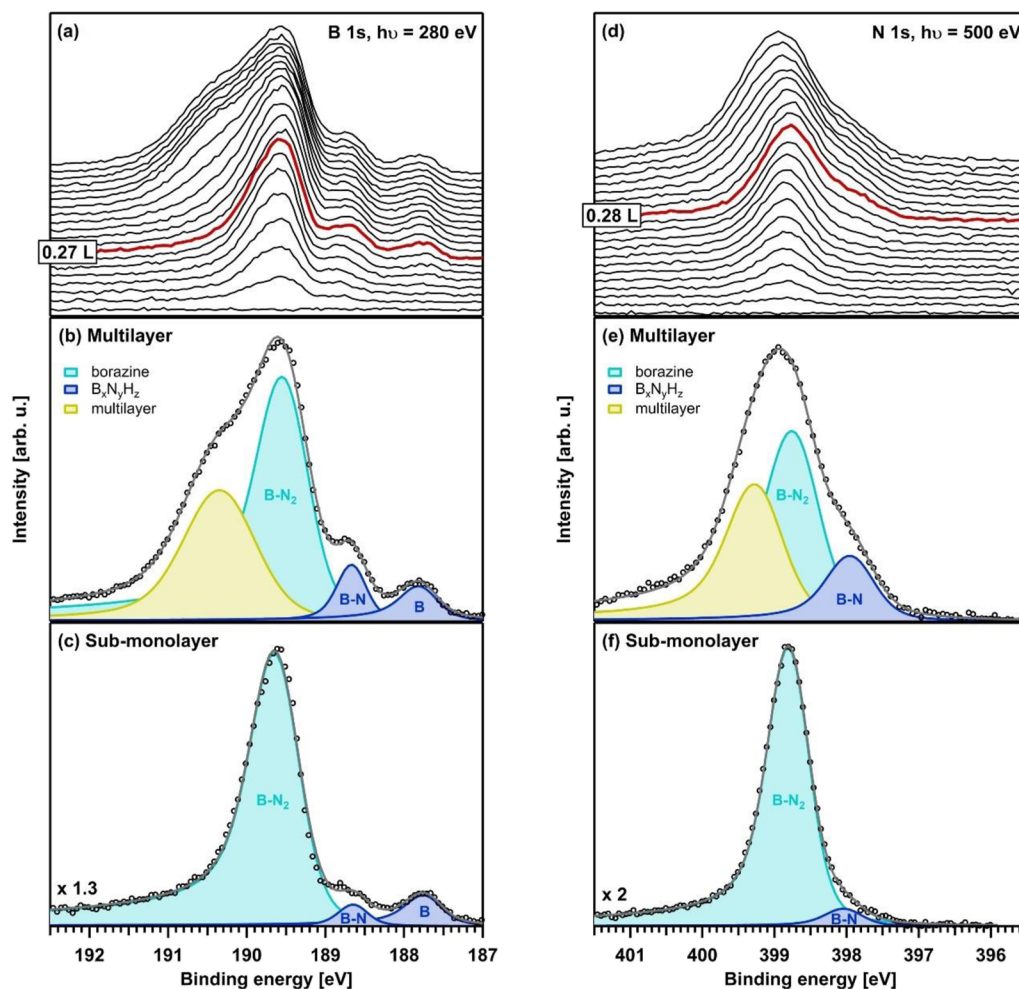


FIG. 1. (a) and (d) Waterfall plots of the B 1s and N 1s spectra recorded during the *in situ* exposure of 0.60 L borazine onto Rh(111) at 130 K. The B 1s and N 1s spectra taken after an exposure of ~ 0.28 L of borazine are marked red. (b) and (e) Fitted B 1s and N 1s spectra after adsorption of 0.60 L borazine (multilayer regime). (c) and (f) Fitted B 1s and N 1s spectra after adsorption of 0.28 L borazine (sub-monolayer regime).

damage seemingly lead to the decomposition of borazine molecules, causing N_2 desorption and boron residues (~ 0.04 ML) on the surface.

The multilayer adsorption followed in the N 1s region is visualized as a waterfall plot in Fig. 1(d), and the fit of the final N 1s spectrum is shown in Fig. 1(e). We observe a similar behavior as in the B 1s region. Initially, a major peak (turquoise) assigned to molecular borazine arises at 398.78 eV and shifts to 398.68 eV after a total exposure of 0.60 L borazine. At 0.13 L, a second signal at 398.02 eV (blue) evolves, which we attribute to borazine fragments. For high exposures >0.30 L, a third contribution is found at higher binding energies (yellow; 398.98–399.11 eV), which is again assigned to multilayer formation. Please note that, in comparison to the B 1s spectra, the data acquired in the N 1s region are more difficult to fit as the N 1s signals undergo smaller shifts in binding energy, leading to less separated peaks.

To elucidate the true fingerprint of borazine on Rh(111), multilayer formation needs to be avoided. Therefore, we also conducted an adsorption experiment with a lower borazine exposure (0.28 L), that is, in the sub-monolayer regime. Figures 1(c) and 1(f) provide the corresponding fitted B 1s (0.30 ± 0.02 ML) and N 1s (0.24 ± 0.02 ML) spectra of borazine, respectively. In Fig. S2 in the supplementary material, the B 1s spectra taken during the sub-monolayer adsorption are depicted as a waterfall plot. Both spectra reveal a dominant borazine peak and less intensive signals at lower binding energies that are assigned to borazine fragments ($B_xN_yH_z$). This behavior confirms that, at low temperatures, borazine adsorbs mainly as an intact molecule, with only small amounts of borazine being decomposed due to reaction with rhodium and/or beam damage.

In addition to the XPS measurements, we used NEXAFS to find out about the orientation of borazine on Rh(111). The

experiments were performed at the boron and nitrogen K-edges [Figs. 2(a) and 2(c)] in grazing (GI: 70°) and normal (NI: 0°) incidence right after the sub-monolayer adsorption. As a comparison, the NEXAFS spectra of “as-prepared” *h*-BN on Rh(111) are shown in Figs. 2(b) and 2(d).

The near edge structure of bulk and single-layer *h*-BN has been readily investigated in the literature.^{39–49} Our data fit these previous studies very well. At the boron K-edge [Fig. 2(b)], the spectrum measured at 70° incidence reveals a very intensive and sharp feature at 192.1 eV (I), which has been assigned to the B 1s → π^* transition.⁴⁸ The π^* contribution almost disappears for the 0° incidence spectrum. This behavior shows that, at 0° incidence, the electric field vector of the incoming light is orthogonal to the direction of the molecular orbitals of the π bonds of *h*-BN and thus cannot excite the π^* transition. From this, a flat geometry, as expected for a supported 2DM, can be derived. The small remaining π^* intensity at 0° incidence might be caused by defects in the *h*-BN overlayer.⁴⁵ Notably, even for a defect-free *h*-BN, a non-zero π^* intensity would be expected as the region between the pores and wires is tilted relative to the surface. In the π^* region, we find an additional peak at 194.9 eV (II) that has been proposed to arise due to the interaction between the 2DM and the metal substrate.^{44,46} At 0° incidence, further features (III–VI) are visible, which can hardly be seen at 70° incidence. This suggests that these peaks belong to σ^* transitions since, at 0° incidence, the electric field vector of the incoming light is parallel to the σ bonds of *h*-BN, enabling excitation of the respective transitions. This assignment is in good agreement with the literature.^{45,48} The onset of the first σ^* contribution (III) can

be taken as an approximation for the ionization potential of *h*-BN (dashed black line).⁵⁰ The analysis of the nitrogen K-edge [Fig. 2(d)] follows the interpretation of the boron K-edge: The features I'–III' are attributed to π^* transitions, while IV'–VI' correspond to σ^* contributions. As expected for a flat adsorption geometry, the π^* contributions are only observed at 70° incidence, and the σ^* contributions are enhanced at 0° incidence. In the 70° incidence spectrum, we find the most intensive peak at 401.3 eV (II'), which belongs to the N 1s → π^* transition. This feature reveals a shoulder at 402.9 eV (III') that originates from the strong binding of *h*-BN to Rh(111) in the pores.⁴⁴ In addition, a “pre-peak” at 399.2 eV (I') arises due to the distinct nitrogen-metal interaction.⁴⁶

For borazine on Rh(111), the boron K-edge at 70° incidence [Fig. 2(a)] is characterized by one major peak at 191.5 eV (B). Following the work by Doering *et al.*, which provides an analysis of the inner-shell electron energy loss spectra of gas-phase borazine,⁵¹ we assign this peak to the B 1s → π^* (e'') transition. A schematic overview of the borazine π molecular orbitals is given in Fig. S3 in the supplementary material. The shoulder at 190.0 eV (A) might result from the interaction of borazine with the Rh(111) surface. These low-photon-energy features are significantly damped for 0° incidence, indicating that borazine is adsorbed in a flat geometry on Rh(111). However, we still observe a substantial contribution in the π^* region. In the literature, this unexpected, finite π^* intensity at 0° incidence has already been described for other planar aromatic molecules adsorbed on metal substrates.^{52,53} It is attributed to conformational changes within the molecule due to bond formation with the underlying transition metal, which causes, e.g., in

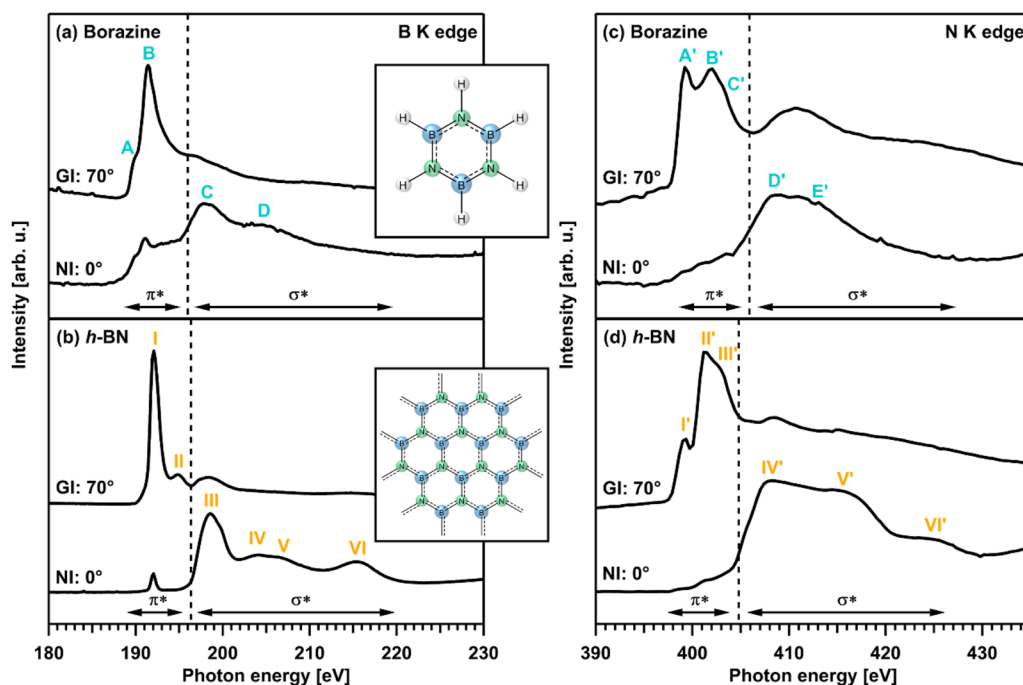


FIG. 2. GI (70°) and NI (0°) NEXAFS spectra of the (a) B K-edge of borazine/Rh(111), (b) B K-edge of *h*-BN/Rh(111), (c) N K-edge of borazine/Rh(111), and (d) N K-edge of *h*-BN/Rh(111). The dashed black lines mark the onset of the σ^* region, taken as an estimate for the ionization potential.

the case of benzene/Rh(111), rehybridization ($sp^2 \rightarrow sp^3$) and out-of-plane bending of the C–H bonds. We assume that borazine on Rh(111) behaves in a similar manner, leading to the observed residual π^* intensity. According to Doering *et al.*, the ionization potential at the boron K-edge is located at 196 eV.⁵¹ The rather broad features at photon energies >196 eV (C and D) are thus related to σ^* transitions (a_1' and e'). At the nitrogen K-edge, the spectrum for 70° incidence [Fig. 2(c)] is dominated by two peaks at 399.3 (A') and 402.0 (B') eV, with B' revealing a slight shoulder at higher photon energies (C'). We tentatively assign the sharp A' feature to the N $1s \rightarrow \pi^*$ (e'') transition. B' and C', on the other hand, might arise due to the pronounced nitrogen-metal interaction. For 0° incidence, the N K-edge shows almost no intensity in the π^* region, again indicating that borazine exhibits a flat-lying adsorption geometry. Above the ionization potential at about 406 eV, two features (C' and D') are observed that correspond to σ^* transitions (a_1' and e').⁵¹ In Fig. S4 in the supplementary material, we provide calculated boron and nitrogen K-edge NEXAFS spectra of gas-phase borazine. In the π^* region,

these show only one very intensive signal that can be associated with the B/N $1s \rightarrow \pi^*$ (e'') transition. This observation supports our assumption that the additional π^* signals seen in our experimental data probably originate from adsorbate–metal interactions.

To understand the different steps of the formation of *h*-BN, we investigated the thermally induced reaction of borazine/Rh(111) by TPXPS. After multilayer adsorption at 130 K, XP spectra were recorded during heating to 1100 K. Figure 3(a) shows the B 1s data as a waterfall plot. The corresponding B 1s density plot and the N 1s data are shown in Figs. S5 and S6 in the supplementary material, respectively. Notably, the B 1s spectra enable better insights than the N 1s spectra, which suffer from strong peak overlap.

In order to obtain detailed insights into the surface chemistry of borazine on Rh(111), we conducted a thorough fit of the B 1s spectra; exemplary spectra along with their fits are depicted in Fig. 3(b), and the resulting quantitative analysis is provided in Fig. 3(c). The spectrum at 130 K reflects the situation right after adsorption: contributions corresponding to molecular borazine (turquoise), borazine

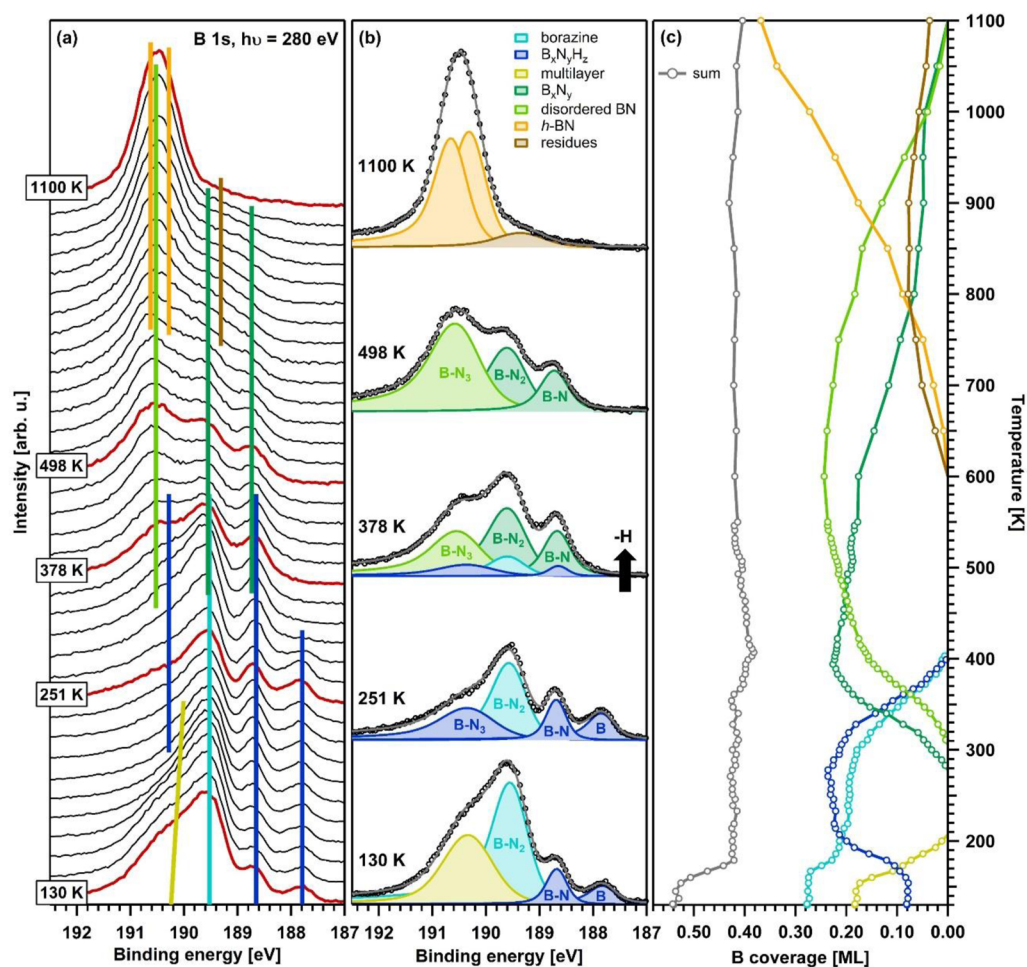


FIG. 3. B 1s data acquired during the TPXPS experiment, i.e., during heating of borazine on Rh(111) from 130 to 1100 K: (a) Waterfall plot of the B 1s spectra with the fit species being indicated by, respectively, colored lines. (b) Fits of selected B 1s spectra [marked red in (a)]. (c) Quantitative analysis.

fragments ($B_xN_yH_z$, blue), and the multilayer (yellow) are observed. Upon heating, the multilayer desorbs while borazine ($B-N_2$) and its fragments ($B-N$ and B) remain on the surface (251 K). In addition, we notice a new contribution at 190.28 eV (blue). In accordance with our suggestion that the binding energies relate to the respective number of nitrogen atoms in the compounds, we assign the new peak to boron bound to three nitrogen atoms ($B-N_3$), that is, also to a borazine fragment ($B_xN_yH_z$).

Above 280 K, strong shifts in binding energy occur. In a previous study on the decomposition of borazine on Rh(111), Farkas *et al.* used temperature-programmed desorption (TPD) to follow the desorption of borazine and hydrogen. They observed multilayer desorption below 200 K, in line with our data, and a maximum hydrogen desorption rate at ~ 130 K, which continues on a lower level up to about 800 K.³⁴ Hence, we assume that at 378 K, mostly dehydrogenated species are present on the surface and attribute the changes in binding energy and peak shape to the dehydrogenation of borazine and the subsequent formation of boron nitride. The new peaks at 189.55 and 188.66 eV are thus assigned to dehydrogenated borazine and borazine fragments (B_xN_y , dark green). The signal at higher binding energies of 190.48 eV, suggesting three nitrogen neighbors ($B-N_3$), indicates the formation of boron nitride (green), presumably growing in a disordered fashion.¹⁶ The disappearance of the peak at 187.79 eV, attributed to boron, is explained by its integration into the emerging boron nitride, as the overall surface coverage stays roughly constant above 200 K [Fig. 3(c)]. An alternative process would be the diffusion of boron into the bulk. In this case, however, a decrease in the overall boron signal would be expected. Hence, this

scenario does not appear likely. Upon further heating, at 498 K, disordered boron nitride becomes the dominating species. At 650 K, the formation of the *h*-BN moiré (orange) sets in, indicated by two peaks at 190.28 and 190.62 eV. Finally, at 1100 K, the conversion is almost complete. Besides *h*-BN, we observe a small contribution at lower binding energy (189.31 eV) that we assign to undesired boron residues (brown). The onset of *h*-BN growth at about 650 K is in line with similar studies dealing with *h*-BN evolution from borazine on Ni(111),¹⁶ Ir(111),²⁰ and Rh(111).³⁴

In the course of the TPXPS experiment, the sample was heated up to 1100 K. After cooling down to below RT, we collected XP spectra in the B 1s and N 1s regions, which are in the following compared to the spectra of “as-prepared” *h*-BN/Rh(111) (Fig. 4). Due to its strong buckling, the *h*-BN/Rh(111) moiré is characterized by two different regions, the so-called wires and pores. The wire regions weakly interact with the metal substrate, i.e., they behave almost like free-standing *h*-BN. The pore regions, on the other hand, are close to the substrate and strongly interact with the metal surface. The chemically different character of these two regions gives rise to the two distinguishable signals in XPS, as was initially reported by Preobrajenski *et al.*⁴⁴ Accordingly, the B 1s spectrum of *h*-BN [Fig. 4(b)] was fitted using two peaks at 190.69 and 190.20 eV for the pores and wires of the moiré, respectively. The separation of the two contributions is larger in the N 1s spectrum [Fig. 4(d)], where the two peaks appear at 398.82 (pores) and 398.06 (wires) eV. The latter is in good agreement with Ref. 44. Interestingly, the behavior observed for *h*-BN/Rh(111) compares well to graphene. In the case of weak interaction with the substrate, a supported graphene moiré shows

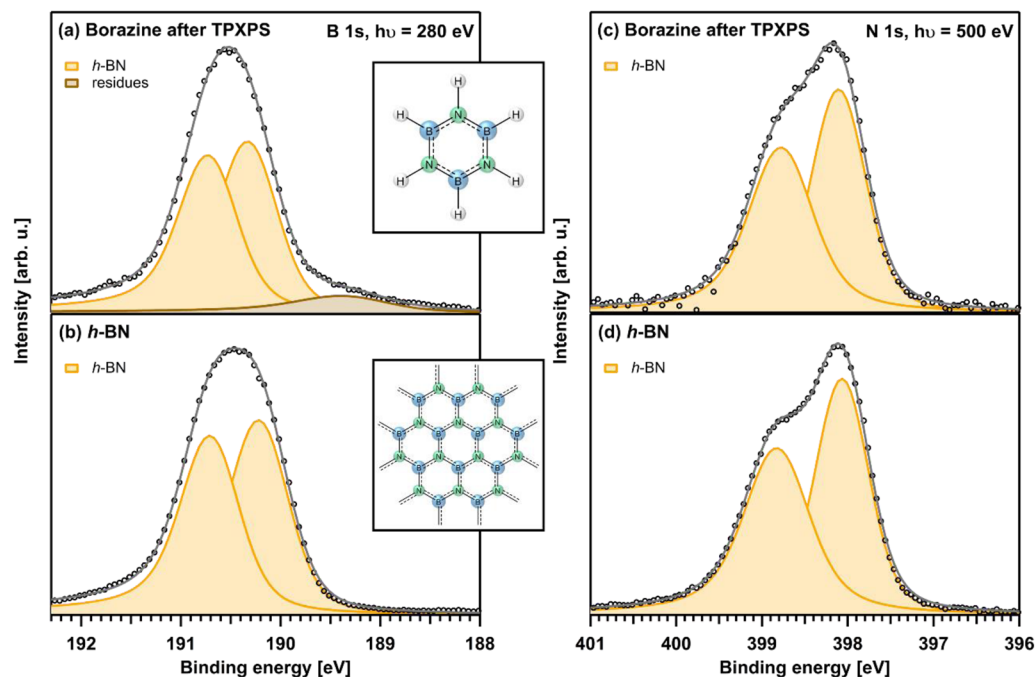


FIG. 4. Comparison between the B 1s and N 1s spectra of (a), (c) borazine/Rh(111), recorded after heating to 1100 K in the course of the TPXPS experiment, and (b), (d) *h*-BN/Rh(111).

only one signal in XPS. This applies, for example, to graphene on Ir(111).⁵⁴ On stronger interacting substrates, such as Rh(111) and Ru(0001), two components appear in the corresponding XP spectra due to the strongly interacting lower-lying parts of the moiré and the quasi-non-bonding higher-lying parts of the moiré.⁵⁵

The spectra obtained after borazine adsorption at 130 K followed by heating to 1100 K strongly resemble the spectral fingerprint of “as-prepared” *h*-BN and can be fitted using the same parameters, which clearly demonstrates that borazine has been converted to *h*-BN. Only the peak separation is somewhat smaller than observed for the “as-prepared” *h*-BN. In the B 1s spectrum [Fig. 4(a)], the peak positions are 190.71/190.31 eV for the pores/wires, while for the N 1s spectrum [Fig. 4(c)], the peaks arise at 398.77/398.10 eV. Additionally, a contribution at lower binding energies (brown; ~0.03 ML boron) is observed at the B 1s core level, indicating boron residues that have not been integrated into the 2DM. Please note that the spectra in Figs. 4(b) and 4(d) correspond to a saturated *h*-BN layer (1.17 ML boron and 1.17 ML nitrogen). In contrast, the *h*-BN obtained after heating borazine on Rh(111) covers only part of the surface (0.38 ± 0.02 ML boron and 0.37 ± 0.02 ML nitrogen).

Besides the B 1s and N 1s core levels, we also investigated the Rh 3d region to learn about the influence of borazine on the substrate. Rh 3d_{5/2} spectra were recorded prior to the adsorption [clean Rh(111)], after the adsorption of a sub-monolayer of borazine, after the adsorption of a multilayer of borazine, and after the TPXPS experiment (1100 K), i.e., after the growth of the sub-monolayer of *h*-BN. In addition, the spectrum of “as-prepared” *h*-BN/Rh(111) is shown for comparison. The fitted Rh 3d_{5/2} spectra are provided in Fig. 5.

For clean Rh(111), two well-distinguishable peaks are observed at 307.28 and 306.82 eV ($\Delta BE = 0.46$ eV). The peak at 307.28 eV belongs to the rhodium bulk (pink). However, the surface differs from the bulk due to the lower coordination of the Rh atoms in the first layer, leading to a shift of the surface-related component by the so-called surface core level shift (SCLS). The second peak at 306.82 eV is hence attributed to the clean rhodium surface (violet). The observed SCLS of 0.46 eV agrees well with the literature.⁵⁶ Adsorption of a sub-monolayer of borazine leads to a decrease in the clean surface component. At the same time, a new peak at 307.00 eV evolves that we associate with the borazine-covered surface (rose). This observation indicates a distinct interaction between borazine and the rhodium surface, leading to a significantly different SCLS. Similar adsorbate-induced SCLSs have previously been observed, e.g., for the adsorption of oxygen, nitrogen, and sulfur on Rh(100).⁵⁷ In the case of multilayer adsorption, the rhodium surface is completely covered. Consequently, the clean surface component in Fig. 5 disappears, and the adsorbate-induced peak further increases. Upon heating to 1100 K, leading to the desorption of the multilayer of borazine and the formation of a sub-monolayer of *h*-BN, the clean surface component reappears. Its large intensity is due to the fact that not even half of the surface is covered by *h*-BN. Moreover, even for a closed *h*-BN layer [topmost spectrum of “as-prepared” *h*-BN/Rh(111) in Fig. 5], the clean surface component does not disappear since the wire regions hardly interact with the Rh surface atoms and, therefore, do not influence their binding energy, which is in line with Ng *et al.*⁵⁸ The small adsorbate-induced contribution observed for the *h*-BN sub-monolayer is attributed to the

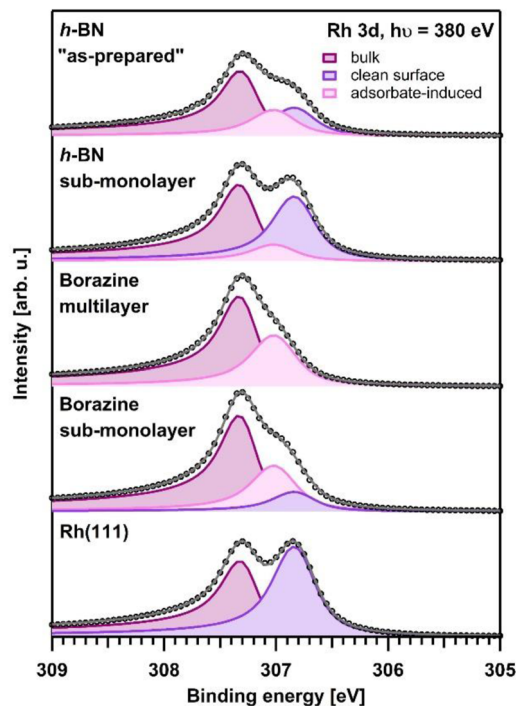


FIG. 5. Rh 3d_{5/2} spectra of, from bottom to top, clean Rh(111), Rh(111) after adsorption of a sub-monolayer of borazine, Rh(111) after adsorption of a multilayer of borazine, Rh(111) after preparation of a sub-monolayer of *h*-BN in the course of the TPXPS experiment (heating to 1100 K), and Rh(111) after preparation of a closed layer of *h*-BN (“as-prepared”).

interaction of the *h*-BN pores with the substrate. Overall, the behavior of the Rh 3d spectra, as observed upon adsorption and heating, is in good agreement with the findings by Orlando *et al.* for borazine on Ir(111).²⁰

IV. CONCLUSIONS

By means of synchrotron radiation-based surface science methods, we were able to follow the low-temperature adsorption and thermal evolution of borazine on Rh(111) *in situ*. At 130 K, borazine adsorbs on Rh(111) largely as an intact molecule, as we deduce from its spectral fingerprint in XPS. NEXAFS allowed for the elucidation of the adsorption geometry, revealing that borazine adsorbs with the plane of the six-membered ring oriented parallel to the surface. After borazine adsorption, the Rh 3d core level revealed a well-observable adsorbate-induced component, indicating a pronounced interaction between borazine and Rh(111). Temperature-programmed XPS helped us understand the thermally induced reaction pathway of borazine on Rh(111). We find that borazine multilayers desorb below 200 K. At higher temperatures, molecular borazine and several borazine fragments remain on the surface. Around room temperature, dehydrogenation sets in, and disordered boron nitride starts to emerge, which becomes the dominant species at temperatures above 500 K. At about 650 K, the XP spectra reveal the beginning formation of the *h*-BN moiré. Eventually, at 1100 K, the

conversion to *h*-BN is complete, as is deduced from the comparison to “as-prepared” *h*-BN/Rh(111). Besides the 2DM, only small amounts of boron residues are observed.

Our study complements the previously published data regarding the preparation of *h*-BN on Rh(111) via CVD of borazine. By providing detailed insight into the surface chemistry of borazine on Rh(111) on the molecular level, we contribute to a profound understanding regarding the growth process of *h*-BN/Rh(111).

SUPPLEMENTARY MATERIAL

The supplementary material contains complementary experimental XPS data, a molecular orbital diagram of the π energy levels of borazine, calculated NEXAFS spectra, and a table providing the XPS fit parameters. The supplementary material is available online as a PDF at the journal website.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Eva Marie Freiburger: Conceptualization (equal); Formal analysis (lead); Investigation (lead); Project administration (equal); Visualization (lead); Writing – original draft (lead); Writing – review & editing (equal). **Fabian Düll:** Conceptualization (equal); Investigation (supporting); Validation (supporting). **Phiona Bachmann:** Investigation (supporting). **Johann Steinhauer:** Investigation (supporting). **Federico J. Williams:** Software (lead). **Hans-Peter Steinrück:** Funding acquisition (supporting); Project administration (supporting); Supervision (supporting); Writing – review & editing (supporting). **Christian Papp:** Conceptualization (equal); Funding acquisition (lead); Project administration (equal); Resources (equal); Supervision (lead); Writing – original draft (supporting); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are presented in the manuscript and the supplementary material. Raw and meta data are provided at Zenodo: <https://zenodo.org/doi/10.5281/zenodo.10939943>.

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