Synthesis of One Monolayer of Hexagonal Boron Nitride on Ni(111) from B-Trichloroborazine (ClBNH)₃

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Single-layer *h*-BN films may be grown on Ni(111) by using B-trichloroborazine (ClBNH)₃. Scanning tunneling microscopy shows perfect monolayers with a very low density of defects. This way of producing stoichiometric, ultimately thin *h*-BN layers is an alternate route to the use of borazine (HBNH)₃. The *h*-BN growth patterns indicate a reaction mechanism that proceeds via six-membered ring opening of these cyclic BN molecules. A set of density functional calculations for B-trichloroborazine, borazine, and N-trichloroborazine yields bond energies and bond lengths for these molecules.

Introduction

Hexagonal boron nitride is a layered insulator with a band gap of about 5 eV. Compared to the isoelectronic graphite the difference in electronegativities of its heteronuclear base is responsible for narrowing of the sp^2 derived π bands and the corresponding loss of conductivity. The high thermal stability is given by the strong covalent sp^2 network in the plane and the strong polarizability of the individual hexagonal layers. One layer of *h*-BN on a metal surface is an ultimately thin junction between a conductor and a nonconductor. Nagashima et al. have first synthesized one layer of *h*-BN on Ni(111) at 1000 K by using borazine (HBNH)₃ (see Figure 1) as the primary substance:[1]

$$(\text{HBNH})_3 + \text{Ni(111)} \rightarrow h\text{-BN/Ni(111)} + 3\text{H}_2 \quad (1)$$
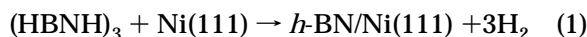
They found that after completion of the first monolayer the growth rate of *h*-BN drops by more than 2 orders of magnitude. This points to the crucial role of the Ni substrate for the reaction, i.e., its role for the hydrogen abstraction and/or the relatively high binding energy of the borazine fragments to the substrate. In subsequent experiments the Oshima group investigated the formation of *h*-BN on other substrates such as Pd(111) and Pt(111).[2] However, the films on Ni(111) were best because there is only a small lattice mismatch of about 0.5% between Ni(111) and *h*-BN. The Ni lattice is smaller than the *h*-BN lattice and the mismatch is compensated with the corrugation of *h*-BN. The structure of *h*-BN/Ni(111) is single domain (1 × 1), i.e., one BN unit has *one* orientation in the hexagonal surface unit cell of Ni(111). In this unit cell the N atom sits on top of the first layer Ni atom and the B atom on the *fcc*

Figure 1. Sketches of the two molecules borazine (HBNH)₃ and B-trichloroborazine (ClBNH)₃ that are used for the synthesis of *h*-BN/Ni(111).

site.[3−5] On the *fcc* site sits, in contrast to the *hcp* site, no Ni atom in the second Ni layer. Density functional calculations of Grad et al. confirmed this structure with N on top of Ni and B on *fcc* sites, though they found a very low energy difference of 9 meV per BN unit between B on *fcc* and B on *hcp* sites.[6] It is therefore surprising that at synthesis temperatures around 1000 K a single domain structure is formed. Recent experiments have shown that under certain conditions two domain films may be grown.[7] This is of importance for the functionality of the layers. It has, for example, to be expected that the electronic (and spintronic) properties are different for the two domains and that the growth of structures on top of *h*-BN/Ni(111) depends on the position of the second-layer Ni atoms. Domain boundaries form very long, perfect lines along densely packed [1̄10] substrate rows. They are found to be key players for intercalation and matter in processes where *h*-BN shall be used as a surfactant.[8]

The handling of borazine, a reactive liquid, is not very simple and it is therefore desirable to have alternate

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routes for the synthesis of *h*-BN films. For this purpose B-trichloroborazine is a valuable substitute. For example it is used in chemical vapor deposition (CVD) processes for the deposition of stoichiometric $200-300$ nm thick *h*-BN films.[9] This paper reports results on the use of B-trichloroborazine (ClBNH)$_3$ (see Figure 1) as the primary substance for formation of *h*-BN/Ni(111) at 1000 K from the reaction

$$(ClBNH)_3 + Ni(111) \rightarrow h\text{-BN/Ni(111)} + 3(HCl) \quad (2)$$
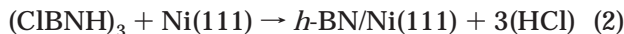
Scanning tunneling microscopy (STM) experiments show that high-quality films may be grown as for the established method that uses borazine (eq 1). It has the advantage of easier handling of B-trichloroborazine than borazine. Calculations of the thermodynamic properties of (ClBNH)$_3$ and (HBNH)$_3$ confirm the higher stability of (ClBNH)$_3$, though the comparable bond energies in the molecules rationalize the similar film morphologies and defects as observed by STM.

Experimental Section

The scanning tunneling microscopy (STM) experiments were performed with a Park Scientific microprobe VPII instrument that was implemented in an electron spectrometer.[4,7] The Ni-(111) substrate was cleaned by repeated sputtering/annealing cycles and a final anneal to 1000 K after 10 μTorrs of O$_2$ exposure at room temperature. The oxygen treatment removes residual carbon traces on the surfaces and minimizes the domain mixing ratio of the *h*-BN films. The primary substances borazine (HBNH)$_3$ and B-trichloroborazine (ClBNH)$_3$ were synthesized as described in refs 10 and 11. (ClBNH)$_3$ is more stable than (HBNH)$_3$ and is therefore preferred for the *h*-BN film production. However, B-trichloroborazine is corrosive when exposed to humid air because it can hydrolyze and release HCl. As borazine it is therefore best stored at low temperatures and handeled under an inert atmosphere. The HCl gas that is released upon formation of the monolayers is of no harm for standard ultrahigh vacuum (UHV) systems. The primary substances were kept in a glass tube connected via a glass–metal adapter to a leak valve and a valve that allows differential pumping of the container down to 10^{-2} Pa. Before introduction to the UHV system the substances were further purified by freezing/melting/pumping cycles. As-received (ClBNH)$_3$ is an opaque, soft solid that melts around 350 K. Only after a melting cycle does enough vapor pressure of (ClBNH)$_3$ build up to produce the monolayer films, and the recrystallized solid becomes more transparent. The substances were introduced into the UHV system from the vapor phase via a leak valve where they were guided in a capillary onto the Ni(111) single crystal that was kept at 1000 K. Complete monolayer films were obtained after exposure of 200 μTorrs, as determined from the uncorrected readout of a hot cathode ion gauge. From X-ray photoelectron spectroscopy (XPS) and STM it is concluded that the films have perfect stoichiometry. The upper limit for Cl coverage after film production is estimated from XPS, i.e., below 3% of one monolayer.

Calculations

Calculations were performed with the state of the art complete basis set (CBS) extrapolation technique as developed by Petersson and co-workers.[12] The goal of these methods is to obtain thermodynamic properties
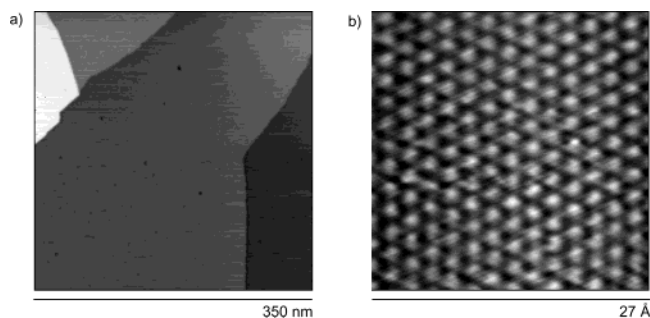

Figure 2. STM image from *h*-BN on Ni(111) as formed from B-trichloroborazine: (a) large scale image where large individual (111) terraces are seen ($V_{sample} = -0.2$ V, $I_t = 1$ nA); (b) atomic resolution zoom in ($V_{sample} = -0.2$ V, $I_t = 30$ nA, filtered).
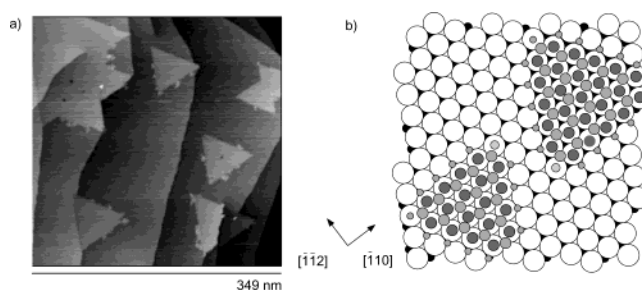

Figure 3. Single-layer *h*-BN islands on Ni(111). (a) STM image from a partial coverage of *h*-BN on Ni(111) as formed from B-trichloroborazine ($V_{sample} = -0.2$ V, $I_t = 0.5$ nA). The triangles are *h*-BN islands with B on *fcc* and B on *hcp* sites, respectively. (b) Corresponding hard sphere model for the two types of islands with *hcp* (left) and *fcc* (right) domains.

with a manageable computational effort. The estimated accuracy as tested on a set of small organic molecules is expected to be better than 9 kJ/mol (100 meV). Some geometries were calculated using the B3LYP/6–31g** method.[13,14] All ab initio calculations were done using the Gaussian98[15] program.

Results and Discussion

Figure 2 shows an STM image of a monolayer of *h*-BN on Ni(111) synthesized with B-trichloroborazine. The findings are very similar to those after film formation with borazine.[4] In Figure 2a it can be seen that large, atomically flat terraces are formed where only a small number of point-like defects are found. It has to be noted that such defects may be observed as well after borazine preparations. Figure 2b shows the regular hexagonally close-packed lattice of the *h*-BN surface where the elevations in tunneling current correspond to the N atom sites.[6]

To better understand the growth of *h*-BN on Ni(111) it is useful to investigate submonolayer coverages that were produced in interrupting the layer-forming process after 0.2 to 2 μTorrs of gas exposure. In Figure 3 such a partial coverage is shown. Triangular *h*-BN islands with fairly uniform size are observed. Counting the triangles in Figure 3 we find six triangles pointing to the right and two triangles pointing to the left. In

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Table 1. Calculated Gas-Phase CBS Bond Energies (E_b) and Bond Lengths (L) ($X - Y$)

molecule	bond	L (Å)	E_b (eV)[a]
H_2	H−H	0.743	4.59
HCl	H−Cl	1.286	4.55
$(ClBNH)_3$	B−Cl	1.787	5.56
$(ClBNH)_3$	N−H	1.011	5.60
$(ClBNH)_3$	B−N	1.425	6.68
$(HBNH)_3$	B−H	1.195	4.72
$(HBNH)_3$	N−H	1.010	5.38
$(HBNH)_3$	B−N	1.431	6.29
$(HBNCl)_3$	B−H	1.183	4.82
$(HBNCl)_3$	N−Cl	1.746	3.39
$(HBNCl)_3$	B−N	1.475	6.10

[a] $E_b = \Delta H^0(X) + \Delta H^0(Y) - \Delta H^0(XY)$. The B−N bond energies were determined from the enthalpy difference between the six-membered ring and the fully relaxed linear chain molecules.

combining angle scanned X-ray photoelectron diffraction (XPD) and STM it was demonstrated that the two types of islands correspond to *fcc* and *hcp* domains of *h*-BN/Ni(111).[7] This is visualized with a hard sphere model in Figure 3b. The orientation of the triangles and the stacking (*fcc* or *hcp*) of the boron atoms is inferred directly from the experiment. The termination of the island boundaries must therefore be B-type steps for the boron atoms, i.e., steps that form (11$\bar{1}$) nanofacets.

Electron counting and the calculated bond strength (see Table 1) do, however, suggest that the outer terminations of the islands are hydrogen-saturated N atoms. At the corners of the triangles we expect boron atoms which may be saturated with chlorine. From the strong energy difference between the N−Cl and the N−H bond it is seen how important the ionicity of the nitrogen is for its bonding. Furthermore, it is expected that the protons at the island rims may be substituted and used as functional bonding centers. Domain boundaries produce defect lines along [$\bar{1}$10] directions.[7] The chemical composition and geometry of the defect lines is not known in detail. The domain boundaries/defect lines act as condensation centers for adsorbates and/or as entrance channels for intercalation.[8] To date we do not have full control on the domain boundary density nor the ratio between *fcc* and *hcp* domains, although the *fcc* domains are more abundant.[7] It is sensitive and depends on the initial cleanness of the substrate and that of the primary substances (ClBNH)₃ and (HBNH)₃, respectively. The small "peninsulas" at the rim of the main islands in Figure 3a are not regularly observed. They may be of an origin similar to that of the hybrid island structures found by Michely et al. for the growth of Pt on Pt(111).[16] Therefore, we expect a rich variety of island shapes by varying the substrate temperature during synthesis.

Interestingly, the shape of the *h*-BN islands and the lack of defect lines along [$\bar{1}\bar{1}$2], i.e., 30° away from the

observed [$\bar{1}$10] directions, indicates that the six-membered rings of the molecules break up during *h*-BN formation. This is inferred from two arguments. (i) Islands as shown in Figure 3b may not be assembled from six-membered rings. (ii) A six-membered ring occupies 3 surface unit cells, and in a scenario where two remote *fcc* islands start to grow from six-membered rings [$\bar{1}\bar{1}$2] defect lines should be observed. The absence of such defect lines suggests that six-membered rings are opened and fill such defects. The opening of six-membered BN rings has been observed in related systems, i.e., the thermal decomposition of N isotope labeled (borazinylamine) polymers.[17]

In Table 1 theoretical bond lengths and bond energies are shown for some relevant molecules in the gas phase. The bond energies were determined from the enthalpies of the CBS-4 calculations and the bond distances were calculated using the B3LYP/6-31g** method. For B-trichloroborazine and borazine the B−H and B−Cl bonds are weakest while the B−N bonds in the six-membered ring are strongest. The corresponding values for N-trichloroborazine (HBNCl)₃ are shown as well for comparison, although we are not aware on successful attempts to synthesize N-trichloroborazine that is expected to be even more reactive than borazine. The trend in the B−N bond energies reflects the increasing ionicity in going from B-trichloroborazine to borazine to N-trichloroborazine. Though the difference between the B−H and the B−Cl bond is significant, the fact that similar *h*-BN island morphologies are found for both primary substances suggests an equivalent *h*-BN formation mechanism. It is likely to be initiated via hydrogen (chlorine) abstraction on bare Ni(111) that acts as a bond breaking catalyst. The detailed course of the reaction is not known but might pass via further abstraction, a para form of $Cl_2B_3N_3H_2$ or $H_2B_3N_3H_2$ and a Bergman type six-membered ring opening reaction.[18]

Summary

We have shown that single-layer *h*-BN films may be grown on Ni(111) by using B-trichloroborazine. Two different domains with *fcc* and *hcp* boron stacking have been observed. For the *h*-BN formation the orientations of defect lines indicate that the strong B−N bond in the B-trichloroborazine six-membered rings is opened. The detailed reaction mechanism can only be speculated. It most likely occurs via hydrogen and/or chlorine abstraction and a six-membered ring opening reaction.

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