

Electronic Structure of Monolayer Hexagonal Boron Nitride Physisorbed on Metal Surfaces

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By using angle-resolved electron spectroscopic methods, we have investigated a monolayer film of hexagonal boron nitride (*h*-BN) epitaxially formed on Ni(111), Pd(111), and Pt(111). The electronic structure of the monolayer *h*-BN is almost independent of the substrate, which is in striking contrast with the case of monolayer graphite [A. Nagashima *et al.*, Phys. Rev. B **50**, 4756 (1994)]. The comparison of the present data with those for typical physisorbed systems indicates physisorption of the BN film.

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Weakly physisorbed systems, typified by rare-gas solids on metal surfaces, have been studied extensively for a long time [1–9]. Owing to the absence of strong chemical interaction with the substrate, these systems have been frequently utilized as a prototype to test the relationship between the results of various spectroscopic probes and the physical properties of adsorbates [1–3]. From a technological point of view, thin insulator films weakly bonded to flat metal surfaces would be attractive in the field of fabrication of microelectronic devices such as tunneling devices because of the spatially abrupt change of the electronic structure at the interface. Most of the so-called van der Waals solids are, however, unstable at room temperature due to the weakness of the bonding.

In this Letter, we report on a monolayer film of hexagonal boron nitride (*h*-BN) epitaxially formed on some metal surfaces. The interaction of this insulating monolayer with the substrate is very weak, and still it is highly stable against high temperature and reactive gases including the atmosphere. This is due to the strong lateral bond in the hexagonal rings of the BN film. The electronic structure of monolayer BN has been investigated precisely by using x-ray photoelectron spectroscopy (XPS), angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), and angle-resolved secondary electron emission spectroscopy (ARSEES). The energy bands of the BN film have been found to align in a similar way to the vacuum level (E_V), not to the Fermi level (E_F), as is the case for the large-gap van der Waals solids. It is very different from the case of a monolayer film of graphite, which forms a chemical bond with metal substrates [10]. The present work exhibits the first experimental evidence that BN films are physisorbed on some metal surfaces.

The experiments were done in a two-level ultrahigh vacuum (UHV) chamber with the base pressure of $\sim 1 \times 10^{-8}$ Pa. The chamber was equipped with low-energy electron diffraction (LEED) optics, an ion-bombardment gun, a gas inlet for dosing borazine ($B_3N_3H_6$) in the upper stage, a hemispherical energy analyzer, an ultraviolet discharge lamp, an x-ray source, and an electron gun in the lower stage. The unpolarized He I ($h\nu = 21.2$ eV) and He II (40.8 eV) resonance lines were used for ARUPS

and the characteristic x rays of Mg $K\alpha$ (1253.6 eV) and Al $K\alpha$ (1486.6 eV) were used for XPS. In the ARSEES measurements, primary electrons with the energy of 60–110 eV were impinged onto the sample with an incident angle of $\sim 45^\circ$. The resolution of the analyzer was 0.2 eV for the ARUPS and ARSEES, and 0.5 eV for the XPS.

Preparation of the BN film has been described in detail previously [11], and is described briefly here. The substrates used in this experiment were Ni(111), Pd(111), and Pt(111). Each specimen was cleaned by repeated cycles of Ar^+ sputtering and annealing at about 800 °C. The single-crystalline monolayer *h*-BN was grown epitaxially by thermal decomposition of borazine on the substrate at 700–800 °C. Because of the strong reduction of the surface reactivity for borazine decomposition due to the monolayer BN coating, the growth rate of the following BN layers became extremely small; for instance, an exposure necessary for depositing additional one monolayer equivalents on Ni(111) was about 300 times the exposure necessary for the first monolayer formation [11]. This enabled precise control of the film thickness. The monolayer thickness of the film has been also evaluated from the electron spectroscopic and thermal desorption mass spectroscopic studies of borazine adsorption on metal surfaces [12]. Since the lattice constant of the Ni(111) surface, 2.49 Å, is very close to the in-plane lattice constant of bulk *h*-BN (2.50 Å), monolayer BN grows commensurately with Ni(111), while the overlayer indicates incommensurate relations with the other substrates. Note that the crystallinity of the BN film is quite good even after annealing over 600 °C in UHV and after exposure to the air, as indicated by the sharp LEED patterns and the ARUPS spectra.

The observed ARUPS spectra for the monolayer BN on Ni(111) [11], Pd(111), and Pt(111) were similar in shape to each other. Some of the spectra typical for these systems will be presented elsewhere [13]. Figure 1 shows the experimental valence-band structures of the BN films, where the binding energies are measured from E_V . Open (solid) marks denote the data obtained with He I (He II) resonance line. All the dispersion curves measured with He II agree perfectly with those obtained

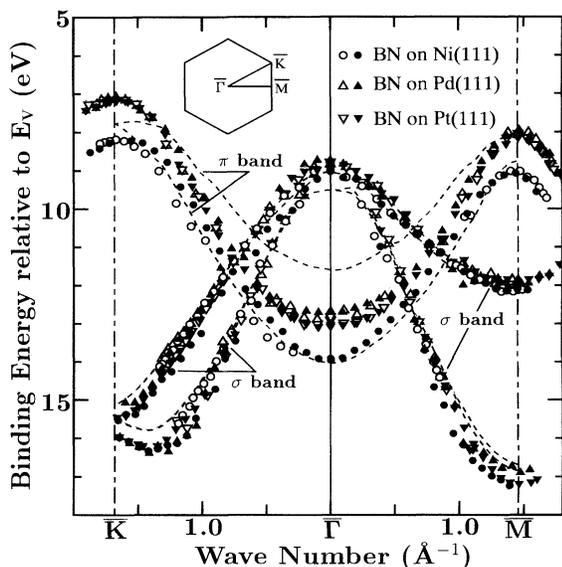


FIG. 1. Experimental valence-band structures of the monolayer *h*-BN films formed on Ni(111), Pd(111), and Pt(111). Open (solid) marks denote the data obtained with He I (He II) resonance line. Theoretical band structure of bulk *h*-BN is also indicated by broken curves [14]. The inset shows the two-dimensional Brillouin zone for the monolayer BN.

with He I, indicating a good two-dimensional character of the electronic structure of the film.

The fact that the valence-band structures observed for the BN films on the three substrates agree well with each other is in contrast to the case of monolayer graphite (MG), where the band structure depends on the substrate [10]. On chemically reactive substrates such as the (111) surfaces on Ni and transition-metal carbides (TMC's), the band structure of MG is deformed drastically from that of bulk graphite by mixing of the π states with the *d* states of the substrate, which also changes the phonon structure of MG [10,15]. In contrast, on relatively inert surfaces such as Pt(111) and the (100) surfaces of the TMC's, such changes in the physical properties have not been observed [10,15]. Compared to the case of MG, the present results for monolayer BN strongly suggest that the interaction between the BN film and the metal surface is much weaker. This striking contrast concerning the interfacial bond (i.e., the mixing of the states) between the monolayer BN and MG arises from the fact that while graphite is a semimetal, BN is an insulator with a band gap of ~ 6 eV [16]; the absence of electronic states near E_F results in no substantial mixing in the present system.

As shown in Fig. 1, the π band of the BN film on Ni(111) has a deeper binding energy by ~ 1 eV than those on the other two substrates, deviating from the trend that the valence-band structure of the monolayer BN is almost independent of the substrate. As for the shape of the dispersion curves, however, the π bands on the

three substrates are quite similar to each other and unlike the case of MG, *deformation* of the dispersion curve depending on the substrate has not occurred. In short, the difference in the band structure between the BN film on Ni(111) and those on the other substrates is the rigid energy shift of the π band. The possible reason for this phenomenon will be discussed later.

In Fig. 1, the theoretical band structure of bulk *h*-BN calculated by Catellani *et al.* [14] is also indicated by broken lines for comparison, where the whole theoretical dispersion curves were shifted rigidly to fit to the experimental data. To our knowledge, no experimental dispersion relations of the energy bands in bulk BN have been reported to date because of the nonavailability of single-crystalline samples large enough for the angle-resolved measurements. Taking into account the fact that the π band in bulk BN splits into two due to the interlayer interaction between the neighboring basal planes in a unit cell, correspondence between the theoretical band structure and the experimental one for the monolayer BN is fairly good.

Figure 2 shows the experimental conduction-band structure of the monolayer BN obtained from the ARSEES measurements, together with the theoretical one for bulk BN indicated by shaded squares [14]. Circles, upward triangles, and downward triangles represent the data for the BN films on Ni(111), Pd(111), and Pt(111), respectively. In Fig. 2, we have carefully excluded the

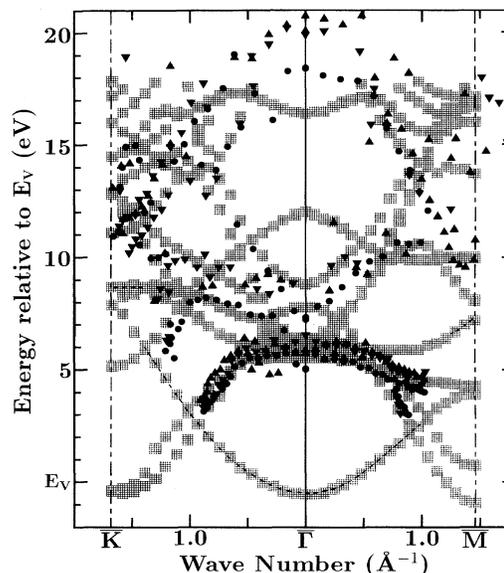


FIG. 2. Experimental conduction-band structures of the monolayer *h*-BN films measured by ARSEES. Circles, upward triangles, and downward triangles denote the data for the BN films formed on Ni(111), Pd(111), and Pt(111), respectively. Shaded squares indicate the theoretical conduction-band structure, where the broken curves represent the interlayer states peculiar to bulk BN [14].

secondary electron peaks that were observed for both the clean and BN-covered surfaces of the substrate. Typical ARSEES spectra for these systems will be published elsewhere [13]. As for the unoccupied states, the agreement between the results for the BN film on Ni(111) and those for the films on the other substrates is rather poor in general. However, as regards the lowest-energy branch, which was detected as one of the most prominent peaks in the ARSEES spectra, the agreement among the experimental results on the three substrates was relatively good. In addition, the correspondence between the experiments and the calculations was also good for the lowest branch [14,17]. Therefore, it is concluded that not only for the occupied states but also for the unoccupied states near E_V , the electronic structure of the monolayer BN is insensitive to which metal substrate is used.

It should be emphasized that the observed energy bands and core levels of the monolayer BN are aligned to E_V , not to E_F . In Table I, we tabulate the binding energies of the N $1s$ and B $1s$ XPS peaks and those of the π and σ bands at the $\bar{\Gamma}$ point together with the work function for the clean and BN-covered surfaces. These values were determined with the accuracy of ± 0.2 eV for the core levels and ± 0.1 eV for the valence bands and the work function. It is clearly seen from Table I that the binding energies referred to as E_F (E_B^F) vary from one substrate to the other, while those referred to as E_V (E_B^V) are almost the same. This is in contrast to the case of thin films of C_{60} condensed on several metal surfaces; the energy levels of C_{60} are aligned to E_F [18]. This contrast is explained as follows: The charge transfer and/or the state mixing necessary for the Fermi-level alignment could not occur sufficiently in the present system because of the much larger band gap of h -BN than that of C_{60} (~ 2 eV) [18].

The vacuum-level alignment observed for the present system suggests that the BN overlayer sits outside the surface barrier which determines the work function of the metal substrate. However, the work function of the substrate has changed upon the formation of BN, as shown in Table I. At first sight, it seems perplexing that the BN overlayer is sufficiently outside the surface barrier of the substrate to enable the vacuum-level alignment, and yet it lies sufficiently inside the barrier to generate the change in the surface dipole. To gain a better understanding of the nature of the bond between the

monolayer BN and the metal surface, a comparison with the present system and the rare-gas solid/metal system is of great value.

In Table II, we tabulate the binding energies of the $5p_{1/2}$ peak of the Xe monolayer physisorbed on some metals and the work function of the clean and Xe-covered surfaces [4–9]. As is similar to the case of the present system, the Xe monolayer exhibits the vacuum-level alignment and the work function of the substrate is changed upon physisorption. From these similarities between the monolayer BN and the rare-gas solids, it is concluded that the interaction of the BN film with Pd and Pt is physisorption.

From density-functional calculations, Lang and Williams have pointed out two important features about the closed-shell adatom/metal system [19]. First, the valence electrons in the adatom prefer to be on the interface side rather than on the vacuum side because of the deeper exchange-correlation potential on the former side due to the tail of the substrate electron density. This results in the static polarization of the adatom. Second, while it is approximately true even for the valence states that the electronic states in the adatom are effectively outside the polarization responsible for the work-function change, it is a much more justified assumption for core states. By virtue of the strong resemblance of the present system with the rare-gas solid, we infer that the monolayer BN is physisorbed onto the metal substrate to derive the maximum energy benefit from the exchange-correlation image at the substrate surface and, consequently, it changes the work function while satisfying the vacuum-level alignment.

Here, we discuss the reason for the phenomenon that the π band on Ni(111) has a deeper binding energy by ~ 1 eV than those on the other substrates. Among the three substrates, Ni(111) has shown the largest work-function change upon the formation of BN and the BN film has been the most thermally stable when it was grown on Ni(111). These results suggest that the monolayer BN is bonded more strongly to Ni(111) than to the other substrates, which might stem from the stronger chemical reactivity of the Ni(111) surface and/or the 1×1 commensurate relation between the BN overlayer and Ni(111). Since BN is an insulator, the conduction electrons in the substrate may play an important role when

TABLE I. Experimental values (in eV) for the work function of the clean and BN-covered surfaces, the binding energies of the N $1s$ and B $1s$ XPS peaks, and those of the π and σ bands at the $\bar{\Gamma}$ point. E_B^F refers to the Fermi level and E_B^V to the vacuum level.

Substrate	Work function		N $1s$		B $1s$		π band (at $\bar{\Gamma}$)		σ band (at $\bar{\Gamma}$)	
	Clean	BN covered	E_B^F	E_B^V	E_B^F	E_B^V	E_B^F	E_B^V	E_B^F	E_B^V
Ni(111)	5.3	3.6	399.1	402.7	191.3	194.9	10.3	13.9	5.3	8.9
Pd(111)	5.3	4.0	398.2	402.2	190.5	194.5	8.7	12.7	4.8	8.8
Pt(111)	5.8	4.9	397.3	402.2	189.7	194.6	8.2	13.1	3.9	8.8

TABLE II. Experimental values (in eV) for the work function of the clean and Xe-covered surfaces and the binding energies of the $5p_{1/2}$ peak of the Xe atom in the physisorbed monolayer. E_B^F refers to the Fermi level and E_B^V to the vacuum level.

Substrate	Work function (eV)		Xe $5p_{1/2}$ (eV)	
	Clean	Xe covered	E_B^F	E_B^V
Al(111) ^a	4.53	4.24	7.70	11.90
Ni(100) ^b	5.30	4.90	6.83	11.73
Ga(poly) ^c	4.30	4.05	7.60	11.65
Ru(0001) ^d	5.52	5.05	6.65	11.70
Pd(110) ^e	5.20	4.28	7.33	11.61
W(100) ^f	4.65	3.66	8.10	11.76

^aChiang, Kaindl, and Eastman (Ref. [4]).

^bChristmann and Demuth (Ref. [5]).

^cJacobi (Ref. [6]).

^dWandelt, Hulse, and Küppers (Ref. [7]).

^eKüppers *et al.*; Hulse *et al.* (Ref. [8]).

^fWaclawski and Herbst (Ref. [9]).

screening the hole in the BN film created by photoemission. Therefore, one might expect that the difference in the substrate-overlayer distance would bring the difference in the screening effect. However, such an expectation can be discarded since it would introduce the energy shifts not only for the π band but also for the σ bands and, moreover, the energy bands would be shifted to *shallower* binding energies on Ni(111), which is not the case. Instead of the final-state effect, an initial-state effect should be considered. In view of the fact that the π electrons are distributed perpendicularly to the basal plane and are extended farther than the σ and core electrons, it could be concluded that because of the closer proximity to the electric dipole at the interface and stronger influence of the exchange-correlation potential, the π states do not obey the vacuum-level alignment rigorously and, hence, their energies are changed on the Ni substrate.

From the 1-eV-deeper π band, the binding energy of the BN film with Ni(111) is roughly estimated to be larger by about 1 eV/atom than that of the film with the other substrates. Semantically speaking, therefore, we should say that the BN/Ni system is in the intermediate region between the two categories of “physisorption” and “chemisorption” since the term physisorption is usually used for adsorption with binding energies below several tenths of an eV/atom.

In summary, unlike the case of MG, monolayer BN physisorbs onto metal surfaces. At the same time, the BN

film is highly stable against heat and atmospheric condition owing to the strong lateral bond, in contrast to the case of typical physisorbed systems such as the rare-gas solids. Because of the weak interfacial bonding, the electronic structure of the BN film is almost independent of the substrate, and the energies of the electronic states are aligned to E_V . The π states are, however, somewhat exceptional with respect to energy alignment because of the relatively closer proximity to the surface barrier of the substrate.

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