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Atomic Structural Analysis of a Monolayer Epitaxial Film of Hexagonal Boron Nitride/Ni(111) studied by LEED Intensity Analysis

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The atomic structure of a monolayer epitaxial film of hexagonal boron nitride (h-BN) formed on a Ni(111) surface was investigated by means of LEED intensity analysis. We measured the I-V curves of the (1,0), (0,1) and (1,1) diffraction spots from a 1 × 1 atomic structure, and analyzed them by using Van Hove's analytical program based on dynamical theory. Six different atomic structural models meeting the experimental requirement of the 3-m symmetry were evaluated with Pendry's reliability factor. The final best-fit structure characterized by the minimum Pendry's reliability factor of 0.27 is as follows; the nitrogen atom in a unit cell of the h-BN overlayer is located at the on-top site of the topmost Ni atoms, while the boron atom exists at the fcc-hollow site. The spacings between the nitrogen (boron) atom and the topmost Ni layer is 2.04 Å (2.2 Å) , which is much narrower than the interlayer spacing in bulk h-BN (3.33 Å).

KEYWORDS: h-BN, LEED analysis, epitaxial film, rumpling structure, monolayer

1. Introduction

It has been known that hexagonal boron nitride overlayer is formed spontaneously on some solid surfaces at suitable temperatures, if a borazine gas ($B_3N_3H_6$) are supplied outside of the materials [1]. Since the thickness is precisely controlled by adjusting the experimental parameters such as temperature and/or gas exposure in chemical vapor deposition method, the overlayer with just one monolayer in thickness, i.e. monolayer h-BN, can be grown on surfaces of transition metals and transition metal carbides [2,3]. The monolayer h-BN exhibits specific properties of high crystalline quality, an inert feature for reaction with air [4]. Recently, large phonon-frequency shifts in the monolayer h-BN from the bulk values were found, and they originate from peculiar changes in both intra-layer and interlayer chemical bonds [5]. The experimental energy dispersion relation of the π orbitals in the monolayer h-BN/Ni (111) indicated orbital mixing with d orbitals of the substrates [3]. Kawai et al. [6] showed theoretically that a spacing between the overlayer and the substrate determines a degree of the orbital mixing.

The monolayer h-BN / Ni(111) possesses only one commensurate structure exhibiting a 1 × 1 atomic structure and was investigated from various points of view. In this paper, we have determined the structure of the monolayer h-BN / Ni(111) by means of low energy electron diffraction (LEED), which is one of the most reliable techniques to determine the overlayer structure. We have measured the Intensity-Voltage (I-V) curves of three different diffraction spots, and analyze them on the basis of a tensor LEED (TLEED) procedure [7,8].

2. Experimental

The experiments were carried out in an ultrahigh vacuum chamber equipped with a four-grid LEED optics, a XPS-UPS system, a gas inlet and an ion gun for surface cleaning. The base pressure of the vacuum chamber was $\sim 1 \times 10^{-8}$ Pa. A Ni(111) specimen was cleaned carefully by repeated cycles of ion bombardment and annealing in UHV, and the clean surface was confirmed by XPS and LEED. The epitaxial monolayer h-BN overlayer with a 1 × 1 atomic structure was grown with dissociation of borazine gas on the Ni(111) at elevated

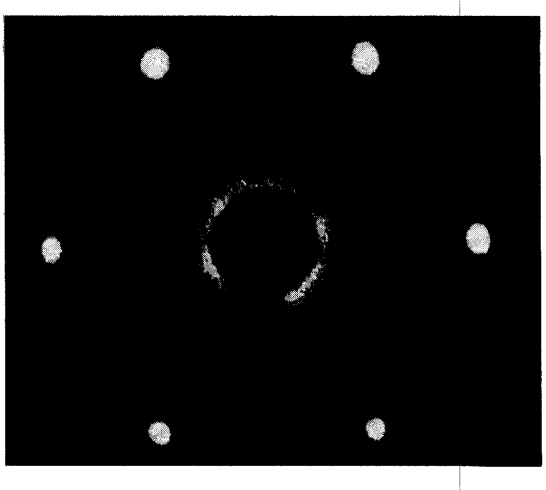

Figure 1. The tyical LEED pattern of monolayer h-BN(0001)/Ni(111).

temperature (≧ 600 ℃). An exposure of a few hundred Langmuir (1L=1 × 10^{-6} torr·s) was required for the monolayer h-BN formation. As we reported in a previous paper [9], the growth of the monolayer h-BN layer is automatically stopped owing to a large change in surface activity for reaction due to the monolayer h-BN formation. The experimental details concerning the monolayer h-BN formation on Ni(111) have been already described previously [9].

The LEED spot intensities were measured with a high-sensitivity chilled CCD camera connected to a Personal Computer. The spots on the screen were divided into the small pixels. The pixel intensities within the spots were integrated, and the background averaged in the frame was subtracted by the software (VGX-920). Then intensities of three different spots of (1,0), (0,1) and (1,1) were measured against the electron energy from 110 to 300 eV. The final I-V curve for each spot was obtained by averaging the curves for the symmetrically equivalent spots. Only the correct alignment of normal electron incidence provided the same I-V curves for all the symmetrically equivalent spots.

To confirm reliability of the experimental procedure used in this experiment, we have analyzed the well-known structure of a clean Ni(111) prior to the application to the monolayer h-BN / Ni(111). As a result, we obtained satisfactory results; the Pendry's reliability factor, R_p [10] for three different beams in the region of 90-300 eV decreased to 0.08 at the final best-fit structure, in which the first outermost spacing agrees with the bulk interlayer one within the experimental error of 2.03 ± 0.02 Å. This structure is in good agreement with previous reports for Ni(111) by LEED intensity analysis [11,12].

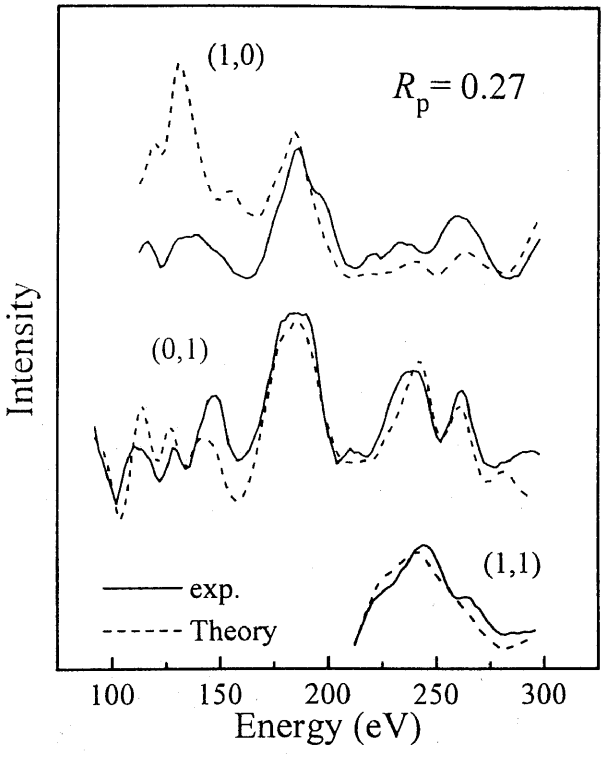

Figure 2. The observed I-V curves of the (1,0), (0,1) and (1,1) diffraction spots from the MG/Ni(111). Experimental data are shown by the solid curves, and the dotted curves represent the theoretical calculations with the minimum R_p factor.

3. Results and Discussion

The observed LEED pattern shows the 3 m symmetry as shown in Fig.1. The observed I-V curves of the (1,0), (0,1) and (1,1) spots of the monolayer h-BN/Ni(111) are depicted in Fig.2. The solid curves show the observed ones from 110 to 300 eV. The curves in the energy region lower than 100 eV was not obtained in this experiment because of their low intensities. We have evaluated six different structural candidates shown in Fig.2. All the structures meet the experimental requirement of a 1 × 1 atomic structure with the 3-m symmetry observed in the LEED patterns as shown in Fig.1. In the model 1 (2), N (B) atom is located at the hcp three-fold hollow site, and another B (N) atom at the fcc three-fold hollow site. In the model 3 (4), N (B) is located at the on-top site of the topmost Ni atoms, while another B (N) exists at the hcp-hollow site. In the model 5 (6), N(B) is situated at the on-top site, and another B (N) at the fcc-hollow site.

The intensities of three diffraction beams were calculated with a TLEED analytical program supplied from Van Hove [13]. The TLEED analysis consists of two steps. Firstly, the theoretical I-V curves are calculated for a reference structure by a full dynamical theory. Secondly, the intensity deviation due to small displacement of each atom from the reference structure is evaluated

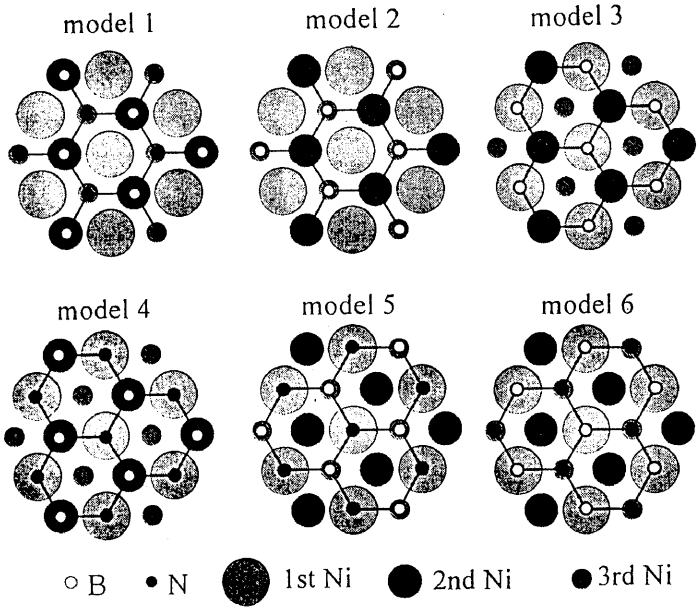

Figure 3. Six structural models meeting the experimental requirements of a 3-m symmetry. The model (a) is called Rosei model.

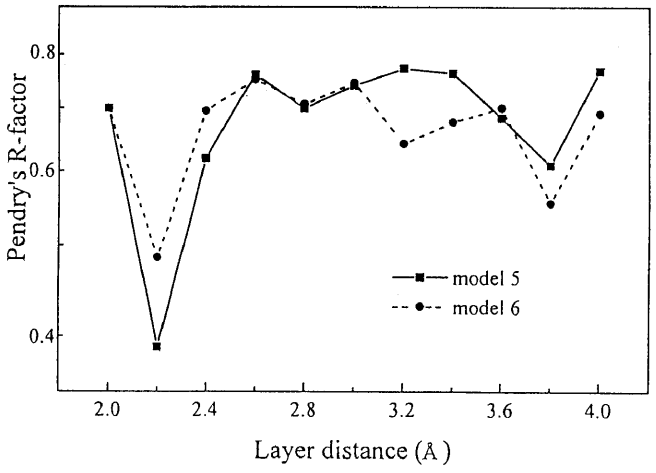

Figure 4. The R_p factor as a function of d_{Ni-BN} just after single full dynamical calculations.

by a first-order perturbation theory and the better structure exhibiting the lower R_p is obtained. In this calculation, we changed only the perpendicular displacements of surface atoms to the basal plane of monolayer h-BN, because the movement in the other directions breaks the 3-m symmetry. We changed the spacing between the monolayer h-BN and the topmost Ni layer, d_{Ni-BN} from 2.0 Å to 4.0 Å. The full dynamical calculation and the single TLEED analysis were repeated alternatively for many times until we found the final best-fit structure.

In Fig.4, the R_p factors obtained just after the single full dynamical culation are plotted against the spacing between the overlayer and the outer most Ni layer, d_{Ni-BN} of the models 5 and 6. The curves for these models show one large valley around 2.25 Å, and on the other hand, no clear valley appears for the curves for the other 4 models 1-4. We repeated alternatively single TLEED analysis and the full calculations for the more precise determination of d_{Ni-BN} for the models 5 and 6. The final structure with the minimum R_p factor is schematically shown in fig.5, and theoretical I-V curves of the final structure are drawn by dotted curves in Fig.2. The final R_p was 0.27 for the model 5, while the minimum R_p was 0.4 for the model 6. The obtained spacing d_{Ni-B} (d_{Ni-B}) is 2.04 (2.22) ± 0.07 Å, which is much shorter than both the bulk graphite interlayer spacing of 3.33 Å. This result is in good accordance with recent experimental results of structural analysis for monolayer graphite on Ni(111); the flat basal plane is situated 2.21 Å above the topmost Ni atoms. Theoretical calculation based on this structure in Fig.5 indicates the strong orbital mixing between the π states and the d states of Ni (111). The metallic properties of h-BN is suggested in this calculation [6]. In this experiment, we have detected a rumpling structure with 0.18 Å amplitudes, which is consistent with the results of phonon dispersion relation of h-BN/Ni(111) [5].

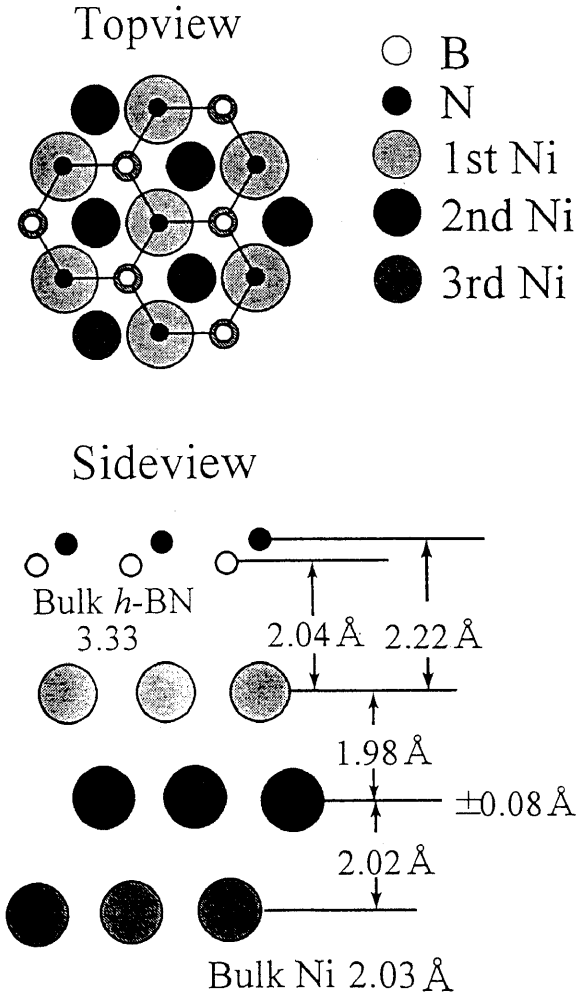

Figure 5. The final best-fit structure with the minimum R_p of 0.27.

4. Conclusion

By means of LEED, we analyzed the atomic structure of the monolayer h-BN / Ni(111) system. The best-fit structure with the minimum R_p of 0.27 is as follows; the nitrogen atoms in the unit cell exist at the on-top sites , and the boron atoms are at the fcc-hollow sites. The perpendicular spacing between B (N) and the topmost Ni is 2.04 Å (2.22 Å) , which is much small in comparison with the bulk spacing of 3.33 Å .

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