Surface and Interface

A theoretical interpretation of NEXAFS and XPS of a deuterated hexagonal boron nitride thin film

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Introduction

Extensive theoretical research works have been dedicated to understanding the adsorption of atomic hydrogen on BN materials. One of the most basic arguments is the site dependence of atomic hydrogen adsorption. However, there are a number of theoretical reports that contradict each other. Consequently, experimental verification is needed to solve the selective adsorption of atomic hydrogen on BN materials. We have investigated site dependence of atomic deuterium adsorption on a hexagonal BN thin film as a model system for BN nanomaterials using NEXAFS and XPS [1]. In this work, we performed discrete variational (DV)-Xα theoretical calculations to interpret those experimental results of NEXAFS and XPS.

Theoretical method

NEXAFS reflects unoccupied density of state (UDOS). However, UDOS can be modified by the existence of a core hole. To take into account this core-hole effect, we adopted Slater's transition state for the DV-Xα calculations. The BN system is represented by a $B_{27}N_{27}H_{18}$ model cluster as shown in figure 1. To examine the adsorption behavior of a single H atom on the BN film, an H atom is put on the top site of a B or an N atom in the central hexagon of the cluster and these configurations are denoted as $B_{27}N_{27}H_{18}+H_B$ and $B_{27}N_{27}H_{18}+H_N$, respectively. All model clusters were optimized by AM1 method with WinMOPAC. In the DV-Xα calculations, minimal basis set were considered for all atoms.

Results and discussion

In figure 2, the top and bottom show the B partial density of state (PDOS) for the transition states from B 1s to the lowest unoccupied molecular orbitals (LUMO) at the excited B sites of the $B_{27}N_{27}H_{18}$ and $B_{27}N_{27}H_{18}+H_B$, respectively. The excited LUMO states are indicated by arrows in the figure. It is clear from the figure that new components appeared in the PDOS of $B_{27}N_{27}H_{18}+H_B$, which are located in between the main π^* and σ^* peaks of the $B_{27}N_{27}H_{18}$ and H 1s contributes to the new components. This means that the new components originate from the formation of B-H bonds. On the other hand, as shown in figure 3 that the unoccupied states of the N PDOS of $B_{27}N_{27}H_{18}+H_N$ in the π^* region almost disappear when a hydrogen atom attaches on the N site.

Experimental B K-edge NEXAFS spectra after deuterium adsorption showed clear spectral changes in between the first π^* and σ^* resonant peaks and the spectral feature modification was assigned to out-of-plane transition by polarization dependence measurement [1]. This result is consistent with the calculation result in Fig.1. On the other hand, N K-edge spectra showed only slight change after deuterium adsorption. This is inconsistent with the calculation result in Fig.2. These theoretical works support selective adsorption of atomic deuterium (hydrogen) at B sites on h-BN. Spectral change of XPS was also analyzed by the DV-Xα method, and we obtained supportive results on the selective adsorption model.
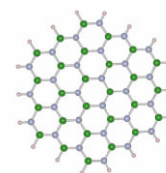

FIG.1.Top view of $B_{27}N_{27}H_{18}$ cluster. An H atom was attached on a B (green) or an N (purple) site in the central hexagon to simulate site-selective adsorption.
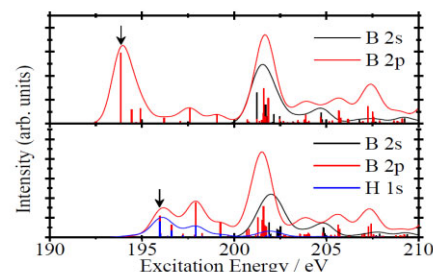

FIG.2. B and H PDOS for B 1s → LUMO transition states. Top and bottom show the results of $B_{27}N_{27}H_{18}$ and $B_{27}N_{27}H_{18}+H_B$, respectively.
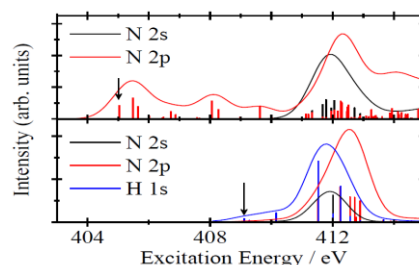

FIG.3. N and H PDOS for N 1s → LUMO transition states. Top and bottom show the results of $B_{27}N_{27}H_{18}$ and $B_{27}N_{27}H_{18}+H_N$, respectively.

Reference

[1] K. R. Koswattage *et al*., PF activity report, 27B, 59 (2010).

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