

A Theoretical Interpretation of NEXAFS of a Deuterated Hexagonal Boron Nitride Thin Film

Kaveenga Rasika Koswattage^{1*}, Iwao Shimoyama², Yuji Baba², Tetsuhiro Sekiguchi², Kazumichi Nakagawa³

¹ Faculty of Applied Science, Sabaragamuwa University of Sri Lanka, P.O. Box 02, Belihuloya, Sri Lanka

² Japan Atomic Energy Agency, Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan

³ Kobe University, Tsurukabuto 3-11, Nada-ku, Kobe 657-8501, Japan

* Corresponding author. : koswattagekr@appsc.sab.ac.lk, ikavee@yahoo.com

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Abstract: Near edge X-ray absorption fine structure (NEXAFS) spectroscopy was performed to study the atomic deuterium (hydrogen) adsorption behavior on hexagonal boron nitride (h-BN) epitaxial thin film as a model system to BN nanomaterial. In this research work the B and N K-edge NEXAFS spectra were analyzed by density functional theory calculations with model clusters in order to support NEXAFS experimental results as well as verify the cluster dependence of the calculation.

Key words: Boron nitride, Thin film, Deuterium (Hydrogen), NEXAFS, DV-X α

1. Introduction

There have been large amount of studies related to examine a proper media to store hydrogen especially for viable transportation. Carbon nanotubes (CNTs) were suggested as one of the most promising materials for storing hydrogen. Chemisorption of atomic hydrogen has already been reported for graphite as a model system of CNTs with regard to the degree of hydrogenation and the preferable adsorption structure [1,2]. BN nanotubes (BNNTs) also have attracted much research attention as a promising candidate for hydrogen storage and it has been reported that BNNTs are superior to CNTs for storing hydrogen. Extensive theoretical research works have been dedicated to understanding the adsorption of atomic hydrogen on BN materials. Despite the great attention paid to this subject, it is not yet clear how the adsorption mechanism works on BN materials. One of the most basic arguments of these theoretical studies is the site dependence of atomic hydrogen adsorption. However, there are a number of theoretical reports whose conclusions contradict each other [3-10]. Thus, in our previous works we have investigated the site dependence of atomic deuterium adsorption on a thin film of BN, using near-edge x-ray absorption fine structure (NEXAFS), x-ray photoelectron spectroscopy (XPS), and photon-stimulated ion desorption (PSID) in order to verify the theoretical models [11, 12].

The discrete variational (DV)-X α method is one of the density functional theory calculation which has been used to simulate the electronic structures of surfaces and interfaces [13]. The method has been successfully applied for core-hole spectroscopies such as NEXAFS to interpret experimental results [13-16]. We have also done analysis using density functional calculation (DV-X α method with a core-hole effect) to interpret the experimental results of NEXAFS and XPS employing model cluster B₂₇N₂₇H₁₈ [11]. Since there

has been an issue with the cluster size for DV-X α calculation [13], it is essential to examine reproducibility of those results of B₂₇N₂₇H₁₈ cluster. Thus, in this work we used relatively small and large clusters to conclude our NEXAFS experimental results and verify the DV-X α calculation of NEXAFS of our previous report.

2. Experimental

The BN system was represented by two cluster models of B₁₂N₁₂H₁₂ and B₄₈N₄₈H₂₄ to compare the results from B₂₇N₂₇H₁₈ cluster models which are shown in the Fig. 1. The boundaries of the clusters are terminated by hydrogen atoms. 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. A transition-state electron configuration, including a core-hole effect, was adopted in the current study. Slater's transition theory was employed by assuming that half of electron remained in an inner shell and the other half were excited or ionized. To simulate the adsorption of one H atom on BN film, an H atom was put on the top site of a central B or N atom. All model clusters were optimized by the semi-empirical AM1 method with WinMOPAC.

In the NEXAFS calculations, 1s, 2s and 2p orbitals are considered as a minimal basis set for both B and N atoms. In the case of hydrogen, 1s orbital is also considered in the minimal basis set. For the calculation of the B K-edge NEXAFS, based on the Slater's transition state, we put a half of a core hole at the B 1s state of a B atom in the central hexagon of the model cluster and put a half of an electron in the unoccupied states supposing that the B atom is excited.

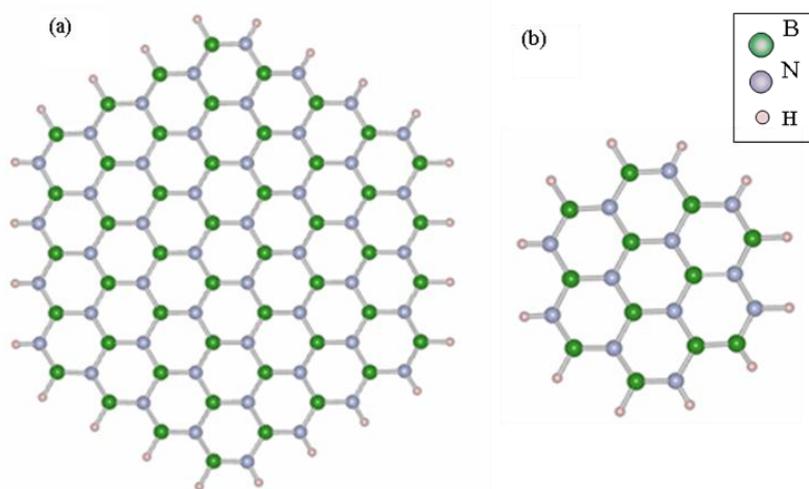


Fig. 1. Model clusters used to examine cluster dependence. Those were optimized by MOPAC with AM1 method. Green, violet and pink balls stand for B, N, and H atoms, respectively. (a) Top view of B₄₈N₄₈H₂₄ cluster for a model of h-BN. (b). Top view of B₁₂N₁₂H₁₂ cluster for a model of h-BN.

3. Results and Discussion

It has been observed through our NEXAFS experiment results as a clear spectral change in between the first π^* and σ^* resonant peaks in the B K-edge region after deuterium treatment [11]. This spectral feature modified by deuteration was assigned to out-of-plane transition by polarization dependence NEXAFS measurements. After careful analysis the change is assigned due to the formation of B-H bonds [11]. On the other hand, N K-edge spectra showed only a slight change. Following DV-X α calculations were performed in order to verify the above mentioned NEXAFS results.

In Fig. 2(a), the top shows the partial density of states (PDOS) of B for the B 1s \rightarrow LUMO transition state at the B site without H of the $B_{48}N_{48}H_{24}$ cluster. The LUMO state is indicated by an arrow in the figure. The black and red curves correspond to the PDOS of the B 2s and 2p orbitals, respectively. The black and red bars show populations of the B 2s and 2p orbitals at the each of the unoccupied states, respectively. The bottom of the figure shows the B PDOS for the B 1s \rightarrow LUMO transition state at the same B site attached by H of the $B_{48}N_{48}H_{24}$ cluster. The LUMO state is indicated by an arrow in the figure.

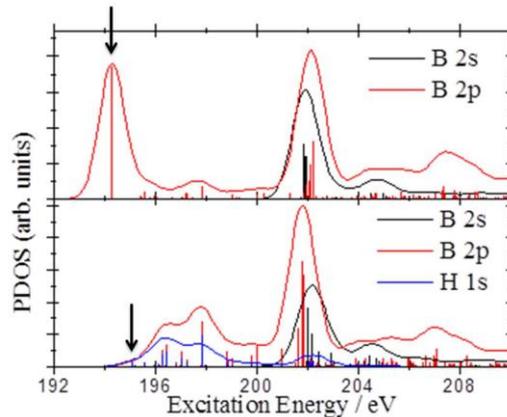


Fig. 2. NEXAFS B K-edge calculation using $B_{48}N_{48}H_{24}$ cluster. B and H PDOS for B 1s \rightarrow LUMO transition states. Excited states are indicated by arrows. Black, red, and blue curves correspond to PDOS of B 2s, B 2p, and H 1s orbitals, respectively.

The black, red, and blue curves correspond to the PDOS of the B 2s, 2p, and H 1s orbitals, respectively. The black, red, and blue bars show populations of the B 2s, 2p, and H 1s orbitals at the each of the unoccupied states, respectively. These results show that new components appeared in the PDOS of B site attached by H of the $B_{48}N_{48}H_{24}$ cluster, which are located in between the main π^* and σ^* peaks of the $B_{48}N_{48}H_{24}$ cluster without H.

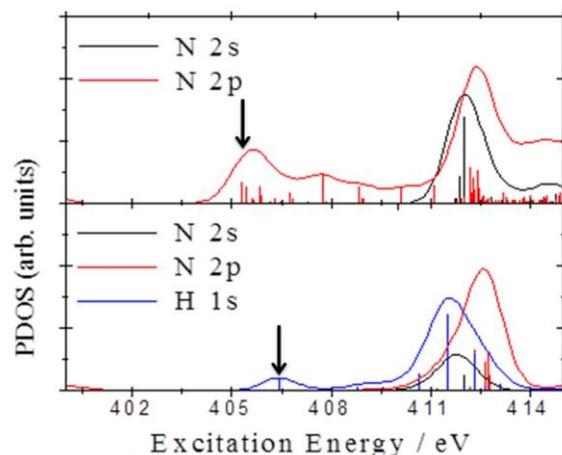


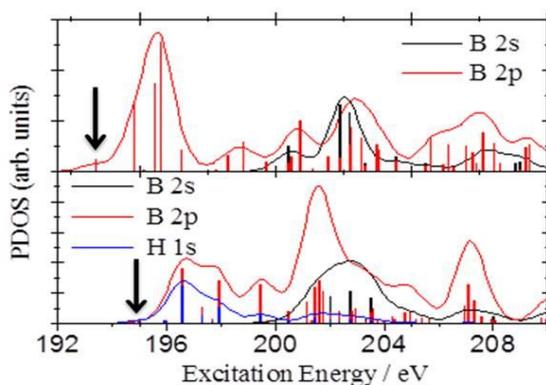
Fig. 3. NEXAFS N K-edge calculation using $B_{48}N_{48}H_{24}$ cluster. B and H PDOS for B 1s \rightarrow LUMO transition states. Excited states are indicated by arrows. Black, red, and blue curves correspond to PDOS of N 2s, N 2p, and H 1s orbitals, respectively.

It is found that H 1s contributes to the new components. This means that the new components originate from the formation of B-H bonds. This result is consistent with the NEXAFS experimental results of B K-edge of deuterated BN thin film.

In Fig. 3, the top shows the N PDOS for the N 1s → LUMO transition state at the N site without H of the $B_{48}N_{48}H_{24}$ cluster. The LUMO state is indicated by an arrow in the figure. The black and red curves correspond to the PDOS of the N 2s and 2p orbitals, respectively. The black and red bars show populations of the N 2s and 2p orbitals at the each of the unoccupied states, respectively. The bottom of the figure shows the N PDOS for the N 1s → LUMO transition state at the same N site attached by H of the $B_{48}N_{48}H_{24}$ cluster. The LUMO state is indicated by an arrow in the figure. The black, red, and blue curves correspond to the PDOS of the N 2s, 2p, and H 1s orbitals, respectively. The black, red, and blue bars show populations of the N 2s, 2p, and H 1s orbitals at the each of the unoccupied states, respectively. This is inconsistent with the NEXAFS Kedge experimental results of deuterated BN film where N K-edge spectra showed only slight change after deuterium adsorption.

We performed same calculation for cluster $B_{12}N_{12}H_{12}$ and results are shown in Figure 4(a) and Figure 4 (b). In Fig. 4 (a), the top shows the B PDOS for the B 1s → LUMO transition state at the B site without H of the $B_{12}N_{12}H_{12}$ cluster. The LUMO state is indicated by an arrow in the figure.

(a)



(b)

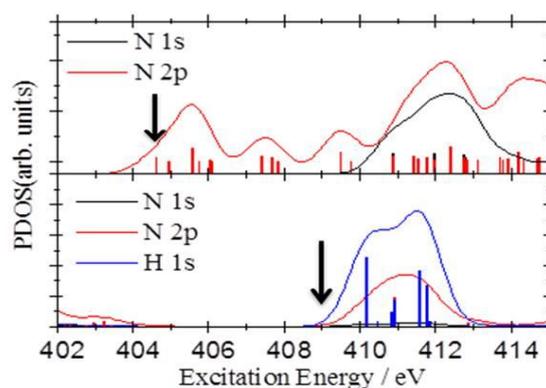


Fig. 4. NEXAFS calculation using $B_{12}N_{12}H_{12}$ cluster. (a) B and H PDOS for B 1s → LUMO transition states. (b)

N and H PDOS for N 1s → LUMO transition states. Excited states are indicated by arrows. Black, red, and blue curves correspond to PDOS of 2s, B 2p, and H 1s orbitals, respectively. Black, red, and blue bars show populations of 2s, B 2p, and H 1s at each of the states, respectively

The black and red curves correspond to the PDOS of the B 2s and 2p orbitals, respectively. The black and red bars show populations of the B 2s and 2p orbitals at the each of the unoccupied states, respectively. The bottom of the figure shows the B PDOS for the B 1s → LUMO transition state at the same B site attached by H of the $B_{12}N_{12}H_{12}$ cluster. The LUMO state is indicated by an arrow in the figure. The black, red, and blue curves correspond to the PDOS of the B 2s, 2p, and H 1s orbitals, respectively. The black, red, and blue bars

show populations of the B 2s, 2p, and H 1s orbitals at the each of the unoccupied states, respectively. In Figure 4(b), the top shows the N PDOS for the N 1s → LUMO transition state at the N site without H of the B₁₂N₁₂H₁₂ cluster. The LUMO state is indicated by an arrow in the figure. The black and red curves correspond to the PDOS of the N 2s and 2p orbitals, respectively. The black and red bars show populations of the N 2s and 2p orbitals at the each of the unoccupied states, respectively. The bottom of the figure shows the N PDOS for the N 1s → LUMO transition state at the same N site attached by H of the B₁₂N₁₂H₁₂ cluster. The LUMO state is indicated by an arrow in the figure. The black, red, and blue curves correspond to the PDOS of the N 2s, 2p, and H 1s orbitals, respectively. The black, red, and blue bars show populations of the N 2s, 2p, and H 1s orbitals at the each of the unoccupied states, respectively. These NEXAFS calculation results of B and N sites for model cluster B₁₂N₁₂H₁₂ are also almost identical to that of the B₄₈N₄₈H₂₄ cluster as shown in Fig. 2 and 3.

4. Summary

In this research work, cluster dependence NEXAFS DV-X α calculations are performed and the results of NEXAFS are supported the selective adsorption model of deuterium (hydrogen) on h-BN thin film through the NEXAFS, XPS and PSID experimental results. Thus, it can be concluded from the experimental and theoretical results that atomic deuterium (hydrogen) are preferentially adsorbed on the B sites rather than the N sites of the BN film.

References

- [1] Nikitin, A., Li, X., Zhang, Z., Ogasawara, H., Dai, H., & Nilsson, A., (2008). Hydrogen Storage in Carbon Nanotubes through the Formation of Stable C–H Bonds. *Nano Lett.* 8,162-167.
- [2] Nikitin, A., Naslund, L., Zhang, Z., & Nilsson, A., (2008). C–H bond formation at the graphite surface studied with core level spectroscopy. *Surf. Sci.* 602, 2575-2580.
- [3] Mårlid, Larsson, K., & Carlsson, J.-O., (1999). Hydrogen and Fluorine Adsorption on the h-BN (001) Plane. *J. Phys. Chem. B* 103, 7637-7642.
- [4] Jia, J. F., Wang, H., Pei, X. Q., & Wu, H. S., (2007). Ab initio investigation of hydrogenation of (BN)₁₂. *Appl. Surf. Sci.* 253, 4485-4489.
- [5] Zhou, Z., Zhao, J., Chen, Z., Gao, X., Yan, T., Wen, B., & Schleyer, P., (2006). Comparative Study of Hydrogen Adsorption on Carbon and BN Nanotubes. *J. Phys. Chem. B* 110, 13363-13369.
- [6] Margulis, V. A. A., Muryumin, E. E., & Tomilin, O. B., (2007). *Proceedings of the NATO Advanced Research Workshop on Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, Vezinaichenko, T. N., Zaginaichenko, S. Y., Schur, D. V., Baranowski, B., Shpak, A. P., Skorokhod, V. V., & Kale, A., (Eds.) : Springer, (pp. 275-278).
- [7] Koi, N., & Oku, T., (2004). Molecular orbital calculations of hydrogen storage in carbon and boron nitride clusters. *Sci. Tech. Adv. Mater.* 5, 625-628.
- [8] Wu, X., Yang, J., Hou, J. G., & Zhu, Q., (2004). Hydrogen adsorption on zigzag (8,0) boron nitride nanotubes. *J. Chem. Phys.* 121, 8481.
- [9] Han, S. S., Lee, S. H., Kang, J. K., & Lee, H. M., (2005). High coverage of hydrogen on a (10,0) single-walled boron nitride nanotube. *Phys. Rev. B* 72, 113402.
- [10] Weck, P. F., Kim, E., Lepp, S. H., Naduvalath, B., & Sadeghpour, H. R., (2008). Dimer-induced stabilization of H adsorbate cluster on BN(0001) surface. *Phys. Chem. Chem. Phys.* 10 (Communication), 5184 -5187.
- [11] Koswattage, K. R., Shimoyama, I., Baba, Y., Sekiguchi, T., and Nakagawa, K., (2011). Selective adsorption of atomic hydrogen on a h-BN thin film. *J. Chem. Phys.* 135, 014706.
- [12] Koswattage, K. R., Shimoyama, I., Baba, Y., Sekiguchi, T., & Nakagawa, K., (2011). Study on selective

adsorption of deuterium on boron nitride using photon-stimulated ion-desorption. *J. Appl. Surf. Sci.* 258, 1561.

- [13] Hartree–Fock–Slater Method for Materials Science, The DV-X α Method for Design and Characterization of Materials. (2006). Adachi, H., Mukoyama, T., & Kawai, J. (Eds.), Springer.
- [14] Oji, H., Mitsumoto, R., Ito, E., Ishii, H., Ouchi, Y., Seki, K., Yokoyama, T., Ohta, T., & Kosugi, N., (1998). Core hole effect in NEXAFS spectroscopy of polycyclic aromatic hydrocarbons: Benzene, chrysene, perylene, and coronene. *J. Chem. Phys.* 109, 10409.
- [15] Tanaka, I., Araki, H., Yoshiya, M., Mizoguchi, T., Ogasawara, K., & Adachi, H., (1999). First-principles calculations of electron-energy-loss near-edge structure and near-edge x-ray-absorption fine structure of BN polytypes using model clusters. *Phys. Rev. B* 60, 4944.
- [16] Shimoyama, I., Baba, Y., Sekiguchi, T., & Nath, K. G., (2009). A theoretical interpretation of near edge X-ray absorption fine structure of hexagonal boron nitride monolayer on Ni(111). *J. Electron. Spectrosc. Relat. Phenom.* 175, 6-13.



Kaveenga Rasika Koswattage completed his PhD from Kobe University, Japan in 2012. He received his BSc degree in Physics from University of Colombo in 2004 and MSc in Physics from Kobe University in 2009, respectively. He worked as an assistant professor in Chiba University, Japan from 2012 to 2016. Currently, he is working as a senior lecturer in Sabaragamuwa University of Sri Lanka. His research interest is on surface and interface analysis and characterization of some of organic, inorganic and biomaterials using synchrotron spectroscopies in VUV and soft x-ray region.

Dr. Iwao Shimoyama is currently working as a senior principal investigator in Japan atomic energy agency. He is a surface scientist using synchrotron radiation.

Dr. Yuji Baba is currently working as a senior principal investigator in Japan atomic energy agency. His research areas are in the field of material science, solid state physics & experimental physics.

Dr. Testsuhior Sekiguchi is a senior principal investigator in Japan atomic energy agency. His research interest includes organic and inorganic material analysis using synchrotron radiation.

Prof. Kazumichi Nakagawa is a professor emeritus at Kobe University, Japan.