

## Formation of *h*-BN ultrathin film on Si(111)

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### Introduction

Due to the graphite-like two-dimensional structure and wide band gap property, hexagonal boron nitride (*h*-BN) is an interesting material to achieve ultrathin insulator film. Recently, *h*-BN epitaxial monolayer films have been formed on a few single crystal surfaces of transition metals by chemical vapor deposition (CVD) with borazine ( $B_3N_3H_6$ ) gas [1]. However, this method has not been applied to semiconductor surfaces. In this report, we applied this method to the synthesis *h*-BN on Si(111). The thin films synthesized were characterized by near-edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS).

### Experimental

The experiments were performed at the BL-11A. Si(111) single crystal surface was prepared by Ar<sup>+</sup> sputtering and annealing procedures, and the surface was exposed to borazine gas ( $10^{-4}$ ~ $10^{-3}$  Pa) at high temperature in an ultrahigh vacuum chamber. Substrate temperature and borazine dose were changed as synthesis parameters. The thickness and composition ratio of the thin films were estimated by XPS measurements with monochromatic X-ray ( $\nu=450$ eV). NEXAFS spectra were measured by total electron yield method.

### Results and Discussion

Figure 1 shows the thickness of the films as functions of substrate temperature and borazine dose. The thickness reached to 6.5 Å at 1000 °C and  $10^4$  L. This thickness corresponds to two monolayers of *h*-BN. In the case of *h*-BN/Ni(111), we obtained same thickness at 800 °C and 180 L [2]. [B]/[N] ratio was larger than unity for thin films (< 3 Å), however this ratio was almost unity for thick films (>3 Å). This implies B-rich film was formed in the initial stage and stoichiometric BN film finally grew.

Figure 2 shows B K-edge NEXAFS spectra of the BN films. Top spectrum shows result for the thin film prepared at 1000 °C and  $5.4 \times 10^3$  L. Middle and bottom spectra show the results for bulk *h*-BN and *h*-BN/Ni(111), respectively. Here, magic angle is chosen for incidence angle of X-ray to cancel out the polarization dependence. The spectrum of the thin film is similar to that of bulk *h*-BN. Furthermore, the spectra of film showed graphite-like polarization dependence, namely, the sharp peak around 192 eV, which is assigned to B  $1s \rightarrow \pi^*$  transition, is enhanced at grazing incidence and suppressed at normal incidence. This gives clear evidence for formation of *h*-BN on Si(111). In the spectrum of *h*-BN/Ni(111), new  $\pi^*$  peak appears which originates from hybridisation between  $\pi^*$  orbital of *h*-BN and Ni atomic orbitals. However, the spectrum of *h*-BN/Si(111) does not show

such modification of  $\pi^*$  state. This indicates that the interaction between Si(111) and *h*-BN is weak and *h*-BN ultrathin film would keep intrinsic insulating property on Si(111).

### References

- [1] A. Nagashima et al., Phys. Rev. Lett. 75, 3918 (1995).
- [2] I. Shimoyama et al., J. Elec. Spec. Relat. Phenom. 137-140, 573 (2004).

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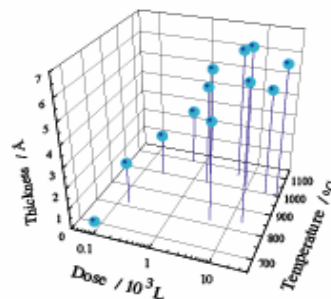


Figure 1. Thickness of *h*-BN thin films deposited on Si(111) for various substrate-temperatures and borazine doses.

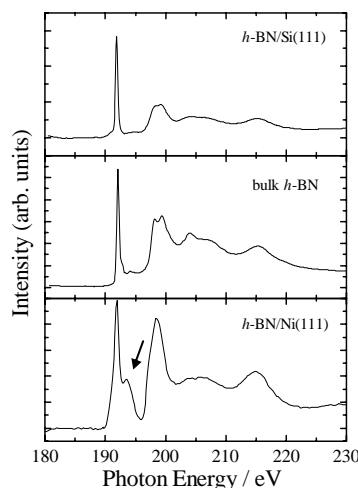


Figure 2. B K-edge NEXAFS spectra of *h*-BN/Si(111) (top), bulk *h*-BN (middle), and *h*-BN/Ni(111) (bottom). *h*-BN/Ni(111) shows new  $\pi^*$  peak (arrow) which is attributed to the hybridisation between  $\pi^*$  orbital of *h*-BN and Ni atomic orbitals. On the other hand, *h*-BN/Si(111) does not show such modification of  $\pi^*$  peak.