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Multilayer Boron Films and Band Gap Transition

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We report the growth of multilayer boron films on Mo(112) surface by e-beam deposition. Subsequent annealing after deposition shows ordered structure of $c(2\times 2)$ for 1st layer, which is consistent with an earlier study. Additional deposition of boron atoms revealed no ordered structure for 2nd and 3rd layer as evident from scanning tunneling microscopy and low energy electron diffraction. Scanning tunneling spectroscopy measurements demonstrate the semiconducting nature of the 2nd and 3rd layer with a band gap of 1.2 and 1.4 eV, respectively. On the other hand, 1st layer is metallic. These results show prospects for the practical applications of boron based nanomaterials in the future.

Key words: *Boron, Mo(112), Low energy electron diffraction(LEED), Scanning tunneling microscopy(STM), Scanning tunneling spectroscopy(STS), Band gap.*

1. Introduction

Intriguing properties such as low density, extreme hardness (comparable to diamond), and melting point over 2000 °C have made boron a potential material in a variety of sectors, including high-temperature electronics and lightweight reinforcing fillers.^{1,2)} As a result, extensive studies have been accomplished in recent years on the boron-based nanomaterials. For example, multilayer boron thin-film has shown promising prospects as neutron detectors which may replace commercially used ³He neutron detectors.³⁾ In another study, boron cluster has exhibited higher capacity for storing Li and H₂, which offers to employ it as an anode material in Li-batteries and H₂ storage materials.⁴⁾ The photodetector device made of single-crystalline ultrathin boron nanosheets shows high sensitivity, dependable stability, and quick response, highlighting the material's enormous potential for field emitters, interconnects,

integrated circuits, and optoelectronic devices.⁵⁾

Due to the lack of electrons in the valence band, boron is a unique material with complicated structural characteristics. As a result, all boron allotropes are made up of large-sized unit cells that include many atoms in each case. The basic building block of these allotropes is B₁₂ icosahedra or icosahedral units. It is assumed that the three valence electrons are responsible for the bonding in B₁₂ icosahedra, where three neighboring boron atoms form a triangle in which the electron charge is concentrated.^{2,6)} While boron may create compounds with a wide range of configurations, it only occurs in four polymorphs as an element, which are α -rhombohedral, β -rhombohedral, α -tetragonal, and β -tetragonal. The first two polymorphs are well studied as they were found comparatively stable whereas the latter ones are less studied.⁷⁾ Plenty of studies have been found in determining the electronic band nature of these polymorphs from various approaches either by theoretical calculations or by experimental observations.⁸⁻¹³⁾ A comparison between these studies revealed that the bulk boron allotropes demonstrate a semiconducting nature with a band gap of 1.1 ~ 2.0 eV. However, variation in pressure and temperature induces metallicity

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and superconductivity in some allotropes.^{12,14,15} While most of the findings are based on bulk boron allotropes, electronic band nature of ultra-thin layers and boron nanostructures are comparatively rare. The recent development of boron based nanomaterials demands the search for electronic nature and/or band gap of ultra-thin boron films for practical implementation.

To extend the knowledge of the energy band of ultra-thin boron adsorbed layers on refractory metal substrates, we have investigated the band gap variation of boron layers adsorbed on Mo(112) surface in detail. Our previous work reported the formation of B₄ nanocluster on Mo(112) surface and metallic nature of the cluster.¹⁶ Therefore, this study concentrates on the additional boron layer's formation on Mo(112) surface and revealing electronic structures. Scanning tunneling spectroscopy (STS) was used to measure the corresponding band gap of boron layers, while scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) were employed to study the surface morphology and crystallinity.

2. Experimental

Experiments were performed in an ultra-high vacuum chamber with a pressure of $< 2 \times 10^{-8}$ Pa. STM and STS measurements were accomplished at room temperature with mechanically sharpened PtIr tips. Since the

PtIr tips sometimes were covered with boron during scanning, the tips were repeatedly checked by measuring $I-V$ spectra on Mo(112) substrates, which shows characteristic dI/dV curves with parabolic shapes. Once the tip was covered by boron, the tip was cleaned using 10 V pulse several times to peel off boron on it. For all the STS measurements, the set point for bias voltage was at -1 V and tunneling current at 0.3 nA. The dI/dV curves are derived from numerical derivation of $I-V$ curves.

Mo(112) surface was cleaned by repeated cycles of heating at 1200 °C in an oxygen pressure of 6×10^{-6} Pa to remove carbon-related impurities and subsequently Ar⁺ ion sputtering and flash heating at ~ 1500 °C. We judged the Mo(112) substrate to be clean when LEED pattern showed (1 \times 1) with low background typical for a clean surface.

Boron was deposited at room temperature from a Ta crucible using an electron beam evaporator. The samples were subsequently annealed to improve the quality of boron films. The annealing temperature required to obtain smooth films depended on the film thickness

3. Results and discussion

Fig.1 shows the growth of boron films on Mo(112) surface, which were prepared after annealing at (a) 1200 °C for 0.8 ML, (b) 900 °C for 1.6 ML and (c) 900 °C for 3.2 ML. At 0.8 ML, the surface shows clear and rather straight but

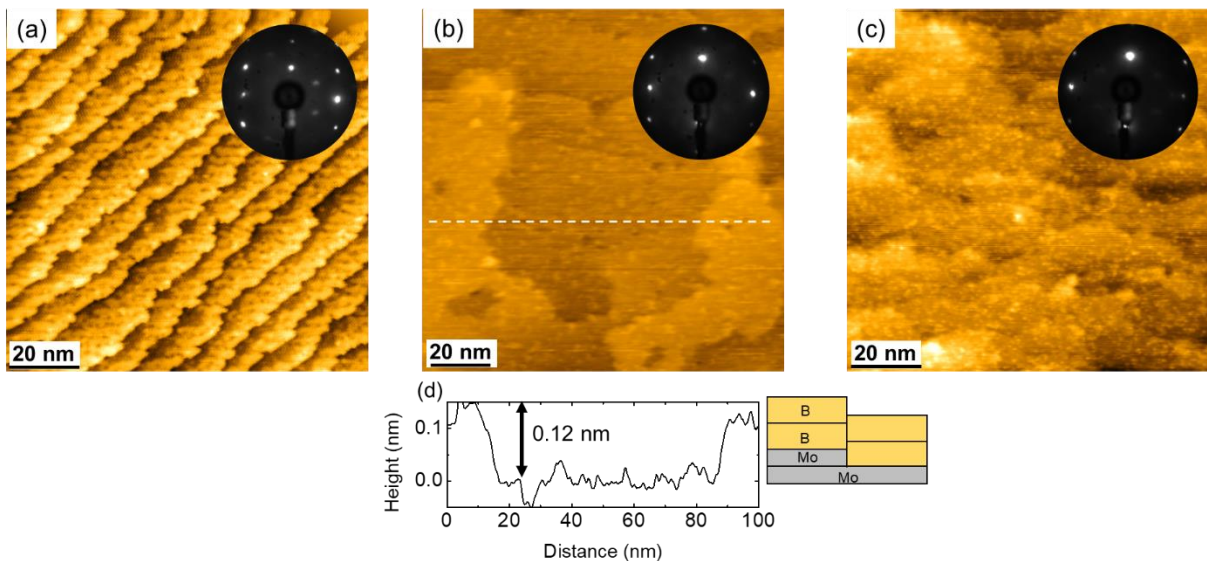


Fig.1 STM images for (a) 0.8, (b) 1.6 and (c) 3.2 ML of boron. The samples are prepared with boron deposited at room temperature and subsequently annealed to 900 – 1200 °C. Corresponding LEED patterns are shown as insets of each STM image ($E_p = 70$ eV) (d) Profile for 1.6 ML of boron along the white dashed line in (b).

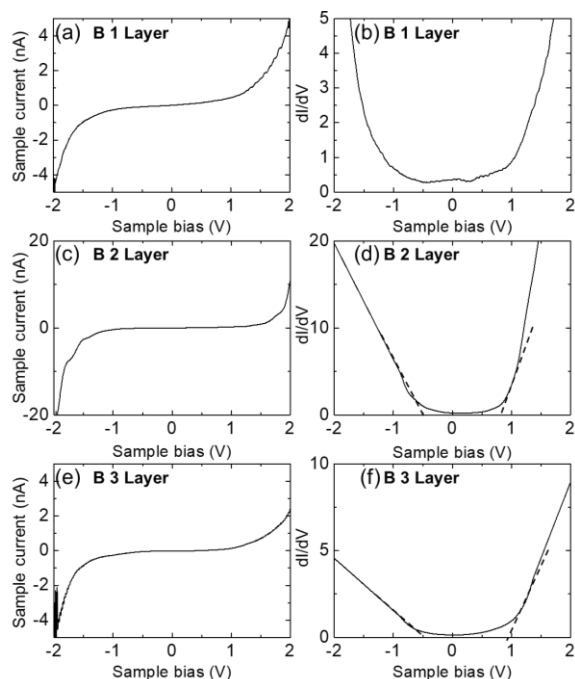


Fig.2 STS spectra for (a), (b) one, (c), (d) two, and (e), (f) three layers boron films. (a), (c), (e): $I - V$ curves. (b), (d), (f): dI/dV curves.

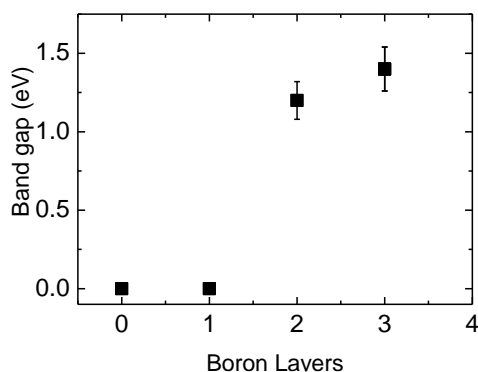


Fig.3 Band gap dependence on thickness of boron.

slightly corroded steps as shown in Fig.1(a). At 0.8 ML, 1 ML thick $c(2 \times 2)$ superstructure developed, which coexists with clean Mo(112) surface. LEED pattern in Fig. 1(a) confirms the presence of $c(2 \times 2)$ superstructure. These results are analogous to our previous report.¹⁶⁾ Fig.1(b) shows the STM image for 1.6 ML boron. At 1.6 ML, boron completely covered the surface, and regions with 1 ML and 2 ML coexisted. From the line profile shown in Fig.1(d), the surface shows a step height of 1.2 Å, almost identical to Mo(112) step height (1.28 Å), indicating that boron films grow layer-by-layer. With increasing boron coverage to 3.2 ML, the surface gets random (Fig.1(c)), but still boron grows in a layer-by-layer fashion. Boron on Mo(112) grows layer-by-layer at least up to

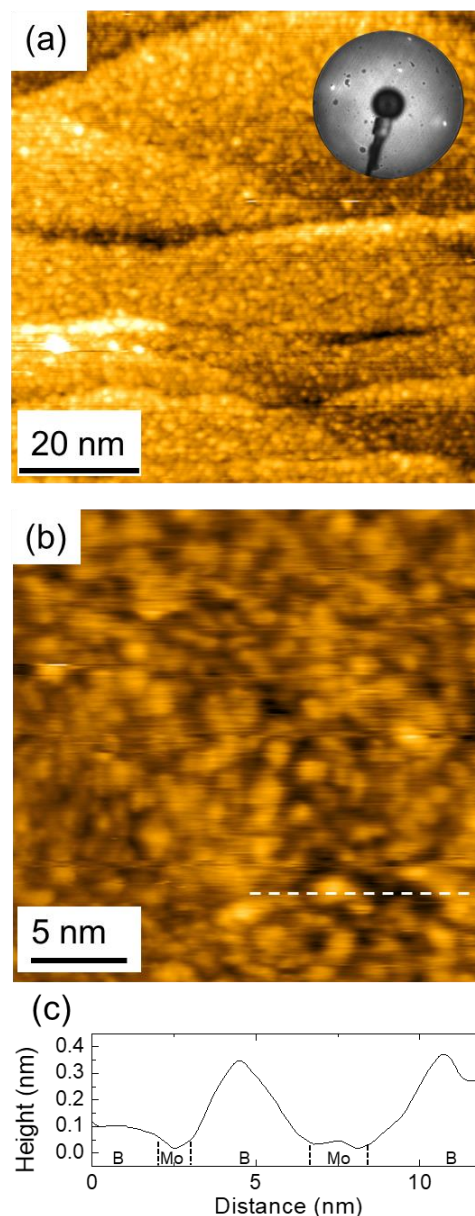


Fig.4 (a,b) STM images of boron covered Mo(112) surface after 3.2 ML deposition at room temperature. Thus, the surface is covered by isolated boron nano particles (NP). Corresponding LEED pattern ($E_p = 70$ eV) is shown as inset of STM image (a). (c) The profile along the white dashed line in (b) shows very corrugated surface.

3 ML. The LEED patterns for 1.6 and 3.2 ML show no additional diffraction spots other than the substrate, indicating that boron films more than 2 ML are disordered even after annealing at 900 °C.

To get insights into electronic properties of boron films, we have measured STS spectra on 1st, 2nd, and 3rd layers of boron. For all boron thickness, $I - V$ spectra are relatively flat between 1 and -1 V and show steep uptake

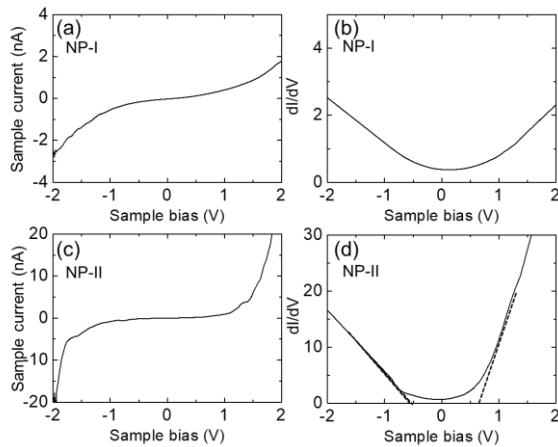


Fig.5 Two kinds of STS spectra measured on boron nanoparticle (NP) covered Mo(112) surface after 3.2 ML deposition (Fig.4). (a), (b) NP-I shows metallic nature whereas (c), (d) NP-II shows non-metallic.

beyond $|V| > 1$ eV (Fig.2(a), (c), (e)). It is difficult to evaluate the band gap from the $I - V$ curves. On the other hand, dI/dV spectra mark band gap for 2nd and 3rd layer boron as shown in Fig. 2(d) and (f), respectively. Note that on a single boron layer, dI/dV spectrum show characteristic feature of a metallic sample as shown in Fig. 2 (b), which is similar to that for Mo(112) substrate.¹⁶⁾

According to band structure calculations and optical absorption spectroscopy, boron films were known to be a semiconductor with a band gap of 1.1 ~ 2.0 eV.^{8-13,17)} Fig. 3 shows evaluation of the band gap for multilayer boron, 1.2 eV for 2nd and 1.4 eV for 3rd layer, which agrees with previous reports,^{8-13,17)} and the band gap at 1st layer is zero. The band gap formation at the 2nd layer boron indicates that the 1st layer boron is effectively connected to Mo(112) substrate and decouples the 2nd layer from the substrate.

We have also tried to measure the STS for the as-deposited boron on Mo(112) surface at room temperature. Boron forms nanoparticles (NPs) on Mo(112) when deposited at room temperature, as shown in Fig.4(a). An Enlarged STM image is shown in Fig.4(b), where the size of boron particles is 1-3 nm in width and ~ 0.4 nm in height. NPs do not coalesce at room temperature. We have measured the STS on the as-deposited sample and found two kinds of spectra. One is metallic, and the other is semiconductor-like, as shown in Fig.5. Although STS measurements have low spatial resolution on this sample because of the measurement at room temperature and the closely arranged boron nanoparticles, we

believe that the metallic one, NP-I in Fig.5(a)-(b), comes from the area where boron does not cover, and the semiconductor one, NP-II in Fig.5(c)-(d), from the area of boron clusters. The band gap from boron NPs is ~ 1.3 eV, similar to those for 2nd and 3rd layers of boron. Band gap for nanoparticle depends on its size, thickness, defects and so on, and is known to be larger than that for bulk¹⁸⁾. In our study, the difference in the band gap is small between NPs and films, and quantum effects in NPs are not significant.

4. Summary and Conclusion

Boron films prepared on Mo(112) surface show layer-by-layer growth at least up to 3 ML, and a band gap above 2 ML. 1st layer boron shows ordered structure, $c(2 \times 2)$, and is revealed as metallic. Boron nanoparticles also impart to have band gap similar to those for 2nd and 3rd layers. The band gap information is particularly interesting for future boron based nanomaterials fabrication.

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