Surface phonon dispersion of $\mathrm{ZrB_2(0001)}\sqrt{3}\times\sqrt{3}\text{-B}$

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Abstract
Surface phonon dispersion of ZrB$_2$(0001)$\sqrt{3} \times \sqrt{3}$ (R $\pm$ 30°)-B was measured using high resolution electron energy loss spectroscopy. With adsorption of excess boron, an ordered structure of $\sqrt{3} \times \sqrt{3}$ (R $\pm$ 30°) is found at the B coverage of about 0.8 ML. Another structure of 4 × 4 appears mixed with the $\sqrt{3} \times \sqrt{3}$ phase at a higher coverage. Using the phonon dispersion relations, the $\sqrt{3} \times \sqrt{3}$ structure is inferred to consist of a planar boron network, as in the bulk. In contrast to the NbB$_2$(0001) case, no surface core level shift of B 1s is observed on this $\sqrt{3} \times \sqrt{3}$ surface, suggesting that the planar boron is not outermost.

1. Introduction

Since they were first proposed as lattice-matched and thermal-expansion-matched substrates for GaN epitaxy, ZrB$_2$(0001) surfaces have attracted wide interest [1]. This class of transition-metal diborides (MB$_2$) have crystal structure consisting of alternate stacking of a graphene-like boron layer (hereafter called 'boraphene') and a close-packed metal layer. Simple (0001) truncation therefore consists of either the metal layer or the boraphene layer.

Recently, graphene has been examined for its unique properties [2, 3]. We reported phonon dispersion of graphene in the early 1990s [4–6]. It shows considerable softening resulting from interaction with the substrate, especially in out-of-plane modes. The boraphene in MB$_2$ is isostructural with graphene; for that reason, it is interesting to investigate its properties for comparison to graphene.

On a group-5 MB$_2$(0001), for example on TaB$_2$(0001) [7] or on NbB$_2$(0001) [8], the boraphene is exposed, outermost, at the surface. On the other hand, the surface is terminated with the metal layer on a group-4 MB$_2$(0001) like HfB$_2$(0001) [9] or ZrB$_2$(0001) [10, 8]. This difference was explained theoretically by Yamamoto *et al* [11]. Their calculation shows, however, that when the chemical potential of boron is sufficiently high, as in a boron-rich condition, the boron termination is possible, even on the group-4 MB$_2$(0001).

For this study, we performed boron adsorption on ZrB$_2$(0001) to change the surface composition to the boron-rich side. Two new surface structures were found: $\sqrt{3} \times \sqrt{3}$(R $\pm$ 30°) (hereinafter $\sqrt{3}$) and 4 × 4. The boron coverage was estimated using Auger electron spectroscopy (AES). Surface phonon dispersion curves were measured using high resolution electron energy loss spectroscopy (HR-EELS) for the $\sqrt{3}$ surface.

2. Experimental details

The experiment was performed in an ultrahigh vacuum system consisting of two chambers: an HR-EELS chamber made of a high permeability alloy (PC permalloy) and a stainless-steel sample preparation chamber. The respective base pressures of the HR-EELS and the preparation chambers were 1–4 × 10^{-9} and 1–2 × 10^{-8} Pa.

The HR-EELS spectrometer (Delta 0.5; Specs GmbH) consists of a double-pass cylindrical-deflector electron monochromator and a single-pass analyzer, which was operated at an energy resolution of 2–3 meV to obtain a reasonable signal-to-noise ratio in this experiment. Because of the extreme vacuum of the HR-EELS system, the sample remains contamination-free during several hours of HR-EELS acquisition.

The sample preparation chamber is equipped with a reflection high energy electron diffraction (RHEED) system, a cylindrical mirror analyzer for AES, a miniature electron-beam heated evaporator (EFM 3; Omicron NanoTechnology GmbH), and a load-lock system. The AES spectra were taken using the RHEED gun for excitation with the primary beam energy of 15 keV and with the incidence angle of 70° from the surface normal. For boron deposition, a crystal rod of β-boron (2 mm × 2 mm × 20 mm) was used as a source

for the evaporator. After sufficient degassing, the pressure during boron deposition was less than 5×10^{-8} Pa. The XPS measurements were performed using another conventional system (Escalab 200; VG Isotech) using a Mg Kα x-ray source.

The ZrB$_2$ single crystal used in this experiment was grown in our laboratory using the rf heated floating-zone method [12, 13]. It was oriented to the $\langle 0001 \rangle$ axis using the x-ray reflection Laue method with an accuracy of $\pm 1°$; it was sliced using a spark-erosion cutter in about 1 mm thick disks. One side of the sample was polished mechanically or mechanochemically to a mirror finish using diamond (9 and 3 μm) and alumina (1 μm) powders.

In a vacuum, the sample was heated with electron bombardment from the back. The sample temperature was measured using optical pyrometers: a two-color ($\lambda = 0.85 \ \mu$m/1.0 μm) pyrometer for a temperature range 1200–1900 K and an infrared ($\lambda = 0.9 \ \mu$m, $\epsilon = 0.16$) one for 1800–3800 K. After degas heating, the sample was finally cleaned with repeated flash heating at about 2400 K and/or ion bombardment (Kr$^+$, 3 keV). The clean surface showed a sharp 1×1 RHEED pattern with a low background; no impurity was observed in AES. The HR-EELS, AES and XPS spectra were all taken at room temperature (RT).

On boron-adsorbed ZrB$_2$(0001) surfaces, the boron coverage was estimated from the AES intensity as follows. The intensity of a B KVV peak at 181 eV is first normalized to that of a Zr MNN peak at 97 eV. Then it is reduced by the clean surface value: 2.7. Although the 181 eV peak is overlapped with one of the Zr MVV peaks at about 178 eV, this component is canceled after this subtraction if the ratio of these peaks (178 eV versus 97 eV) is constant. The absolute value for one monolayer (ML: a complete boron honeycomb on the surface) is estimated from the NbB$_2$(0001) AES data, assuming that the intensity ratio—B KVV at 181 eV versus Nb MNN at 108 eV—corresponds to 1 ML. Because the Auger efficiencies of Zr MNN and Nb MNN are not expected to vary greatly, this is expected to yield a good estimation.

3. Results and discussion

3.1. RHEED and AES observations

The RHEED pattern showing a sharp 1×1 pattern (figure 1(a)) on a clean surface gradually became diffuse with increasing background when boron was adsorbed at RT, suggesting an amorphous structure of the boron film. Because B is much lighter than Zr, the very thick amorphous boron layer is necessary to hide the substrate RHEED pattern completely. Heating the boron-adsorbed surface, a $\sqrt{3}$ RHEED pattern appeared at about 1300 K. The $\sqrt{3}$ pattern became sharper with annealing temperature, reaching the sharpest pattern at 1800 K, as shown in the inset of figure 1(b). This $\sqrt{3}$ structure was also formed with boron adsorption on a heated (1300–1800 K) surface. No structural phase transition was observed between the annealing temperature and RT. This $\sqrt{3}$ pattern is extremely clear, which suggests that not only B but also Zr contributes to this structure.

Figures 1(a) and (b) respectively portray AES spectra for the clean 1×1 and $\sqrt{3}$ surfaces. The coverage for the
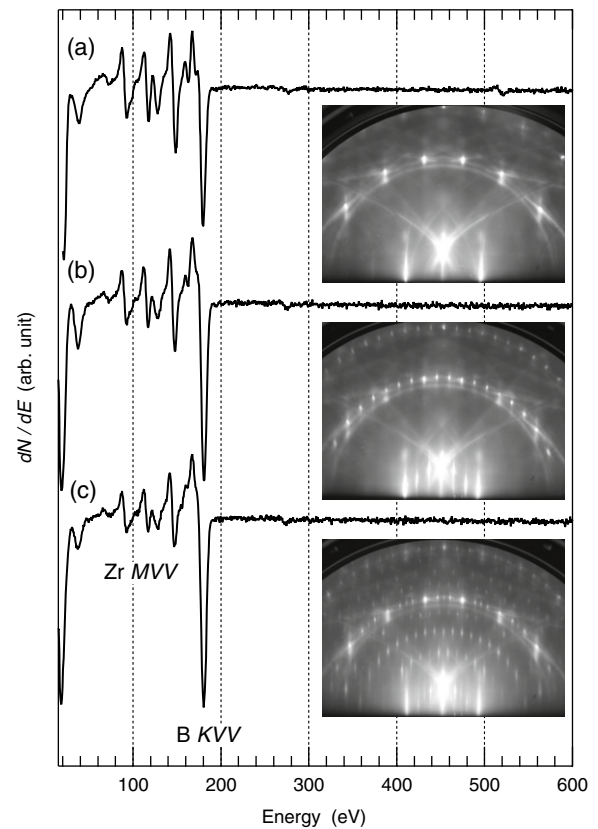
Figure 1. AES spectra and RHEED patterns (inset) for (a) clean 1×1, (b) $\sqrt{3}$ and (c) 4×4 (mixed with residual $\sqrt{3}$) structures. The primary electron energy is 15 keV. An azimuth in the RHEED is [10$\bar{1}$0].

$\sqrt{3}$ structure is estimated as 0.8 ± 0.2 ML. The desorption rate of the deposited boron depends on the surface structure. Using an amorphous film, B was desorbed more rapidly than from the $\sqrt{3}$ structure.

Upon further deposition of boron on the $\sqrt{3}$ surface at 900–1000 K, a new structure of 4×4 appeared with the $\sqrt{3}$ structure. Figure 1(c) portrays the RHEED pattern and the AES spectrum with the boron coverage of 1.2 ± 0.2 ML. The 4×4 structure was mixed with the $\sqrt{3}$ structure, and the background in the RHEED pattern was higher. The ordering in the 4×4 phase might be worse than that in the $\sqrt{3}$ phase. It was difficult to obtain the single phase of 4×4.

3.2. HR-EELS characterization

Figure 2 shows specular HR-EELS spectra. In contrast to the case for a clean 1×1 surface, where no loss peak is observed in the specular condition [8], some loss peaks are clearly observed for on the $\sqrt{3}$ and on the 4×4 surfaces.

For on the $\sqrt{3}$ surface, four clear peaks are visible at 30.4, 46.4, 66.9, and 83.0 meV, one small peak at about 95 meV, and a shoulder at about 78 meV. These peaks, except for that at 46.4 meV, can be assigned as folded-back modes from the $\bar{K}$ point in a 1×1 Brillouin zone (BZ) for a clean surface. On the other hand, the 46.4 meV mode is in the gap region for on the clean ZrB$_2$(0001): between the boron vibration modes and
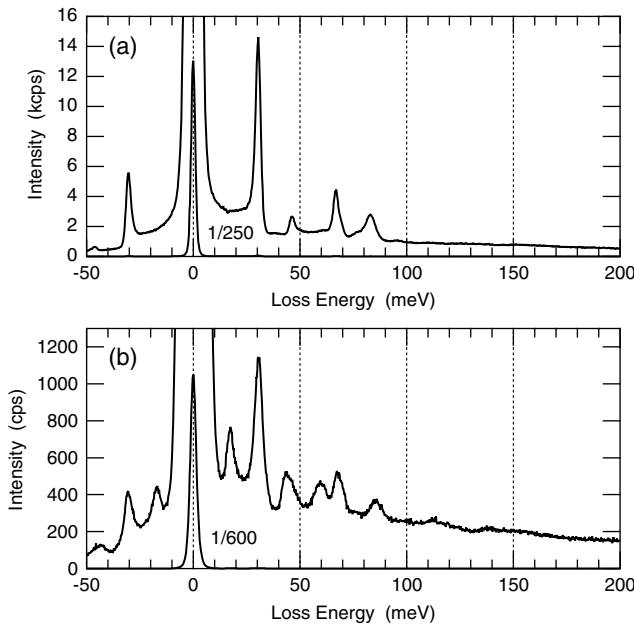
Figure 2. Specular HR-EELS spectra for (a) $\sqrt{3}$ and (b) 4×4 structures. The primary electron energies are (a) 5.8 eV and (b) 4.8 eV.

the Zr vibration modes. This mode is clearly ascribable to the adsorbed boron vibration.

On the 4×4 surface, some peaks appear at 17.4, 30.5, 44.2, 59.7, 67.8, 85.4, 111.8, and 138.7 meV. Among those peaks, several peaks (30.5, 44.2, 67.8, and 85.4 meV) are expected to come from the mixed $\sqrt{3}$ phase; the others are ascribed to the 4×4 phase. The 17.4 meV mode is well assigned to an acoustic surface mode that is folded back because of the 4×4 periodicity from the halfway point between $\overline{\Gamma}$ and $\overline{M}$ points, which is 16.1 meV for the clean 1×1 surface. The high energy modes (111.8 and 138.7 meV) suggest that this structure contains not only a boraphene-like sheet but also another boron network: for example, a B_6 cluster in some metal hexaborides or a B_{12} cluster in higher boride compounds. As regards the B_6 cluster, the specular HR-EELS on LaB_6 (111) gives loss peaks at 122 and 162 meV [14]. A B_{12} icosahedron cluster lattice, for example, $B_{12}As_2$ or $B_{12}P_2$, gives 115–135 meV vibration modes [15], very similarly to this case.

3.3. Phonon dispersion

To obtain the surface phonon dispersion relation of the $\sqrt{3}$ surface, off-specular HR-EELS measurements were performed with several primary electron energies. Figure 3 shows, for example, two series of off-specular HR-EELS spectra measured along (a) [$11\overline{2}0$] ($\overline{\Gamma}$–$\overline{M}$–$\overline{\Gamma}$) and (b) [$10\overline{1}0$] ($\overline{\Gamma}$–$\overline{K}$–$\overline{M}$). The loss energies are plotted versus momentum transfers along the surface, giving phonon dispersion relations as presented in figure 4.

In the observed dispersion curves, acoustic surface or surface resonance modes, labeled A and B in figure 4, are almost identical to those for on the clean 1×1 surface. The modes F, G, and K also lie close in energy to the corresponding


Figure 3. Series of off-specular HR-EELS spectra along (a) [$11\overline{2}0$] ($\overline{\Gamma}$–$\overline{M}$–$\overline{\Gamma}$) and (b) [$10\overline{1}0$] ($\overline{\Gamma}$–$\overline{K}$–$\overline{M}$) directions. The primary electron energy is 22.1 eV and the incidence angle is 75° from the surface normal. The detection angles from the surface normal are a: 69.4°, b: 64.9°, c: 60.3°, d: 55.7°, e: 51.1°, f: 47.7°, g: 44.2°, h: 40.8°, i: 37.3°, j: 35.0°, k: 32.8°, l: 30.5°, m: 28.2°, n: 68.3°, o: 62.6°, p: 58.0°, q: 53.4°, r: 50.0°, s: 46.5°, t: 43.1°, u: 39.6°, v: 36.4°, w: 33.2°, x: 30.2°, and y: 27.2°.

clean surface modes. In the $\sqrt{3}$ BZ, the $\overline{K}$ point of the 1×1 BZ is folded into the $\overline{\Gamma}$ point. Modes C and H are explainable as folded-back modes, from the $\overline{K}$ point of the 1×1 BZ, namely the $\overline{\Gamma}$ point on the right-hand side in figure 4.

The highest frequency mode K shows a slightly higher frequency than in the clean surface, but it is not much greater than 100 meV. This indicates that any boron cluster such as B_6 or B_{12} does not exist in the $\sqrt{3}$ structure.

The remaining two modes, D and E, in figure 4 lie energetically in the gap region of the clean surface phonon structure. For that reason, they cannot be any folded-back mode. On $NbB_2(0001)$, where the boraphene is outermost, similar modes are visible in this energy region, which is interpreted as the surface boraphene mode energetically lowered by losing half-bonds to Nb at the surface. Analogously, modes D and E can be assigned as horizontal and vertical modes of boraphene on the $ZrB_2(0001)\sqrt{3}$ surface.

However, the $\sqrt{3}$ ordering and the boron coverage of less than 1 ML indicate no simple boraphene on the surface, like $NbB_2(0001)1 \times 1$. Several models are possible: (A) the
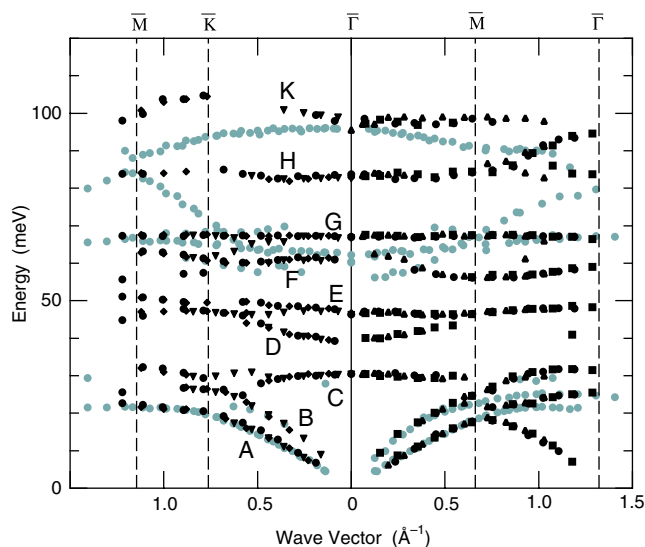
Figure 4. Measured phonon dispersion relations (black markers) of the $\sqrt{3}$ surface compared to the clean 1×1 surface data (gray circles) [8]. Primary electron energies are: solid squares, 24.4 eV; circles, 22.1 eV; diamonds, 21.3 eV; triangles, 15.6 eV; and reverse triangles, 11.5 eV.

(This figure is in colour only in the electronic version)

Figure 5. XPS spectra for the $\sqrt{3}$ surface. The detection angles are (a) surface normal and (b) 60° from surface normal. The x-ray source is Mg Kα (1253.6 eV).

modes, adsorbed boron modes appear at the gap region of the substrate. Analogously to NbB$_2$(0001) phonon structure, the gap modes are consistent with the surface boraphene, although no surface core level shift was observed in XPS. Probably, such an extra structure exists on the boraphene as a Zr adatom in each $\sqrt{3}$ unit. In contrast to the $\sqrt{3}$ structure case, some boron clusters like B$_{12}$ or B$_6$ might exist in the 4×4 structure.

Acknowledgment

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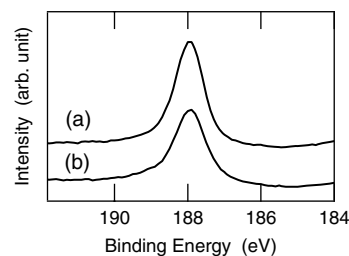
boraphene layer is not complete—for example, vacancies occur every $\sqrt{3}$ unit; (B) after boron deposition, Zr diffuses out from the bulk during heating, making an incomplete Zr layer having $\sqrt{3}$ ordering. In the simplest case, a Zr atom adheres to every $\sqrt{3}$ unit on the boraphene. The boron coverage is 0.83 ML in case A and 0.67 ML in case B.

3.4. XPS measurement

If a boraphene or boraphene-like structure was exposed outermost, some surface core level shift (SCLS) might be expected, as in the case of NbB$_2$(0001) [16]. Figure 5 shows B 1s XPS spectra of the $\sqrt{3}$ surface. The B 1s peak appears at a binding energy of 188.0 eV. The spectrum, taken from a glancing angle of 30° (figure 5(b)), shows no extra surface property compared to that taken from the surface normal (figure 5(a)). Because no SCLS exists on this surface, model A might be rejected. Further theoretical and experimental data are necessary to reveal the detailed atomic structure.

4. Summary

In summary, an ordered surface structure: $\sqrt{3} \times \sqrt{3}$ (R $\pm$ 30°) was found on boron adsorption on ZrB$_2$(0001) at coverage of about 0.8 ML. Another surface structure of 4×4 appeared at higher boron coverage mixed with the $\sqrt{3}$ structure. The phonon dispersion of the $\sqrt{3}$ surface was measured using HR-EELS. Along with some acoustic modes and folded-back