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# Raman Spectroscopy of Two-Dimensional Borophene Sheets

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Supporting Information

**ABSTRACT:** The successful fabrication of a two-dimensional boron sheet, which features a triangular lattice with periodic hole arrays, has stimulated great interest in its specific structure as well as properties such as possible superconductivity. Here, we report a study on the vibrational spectra and electron-phonon coupling (EPC) in monolayer boron sheets by *in situ* Raman and tipenhanced Raman spectroscopy (TERS) at low temperature and ultrahigh vacuum. The gap-mode TERS gives a  $3 \times 10^9$  selective enhancement on vertical vibrational Raman modes. A spatial resolution of 1 nm is achieved in this



system. Combined with first-principle calculations, the vibrational properties as well as EPC in borophene are determined. The results are helpful for further study on the mechanical, electronic, and possible superconducting properties of twodimensional boron.

**KEYWORDS:** borophene, two-dimensional materials, Raman spectroscopy, vibrational property, tip-enhanced Raman spectroscopy, electron—phonon coupling

wo-dimensional (2D) boron sheets, also called borophene, are a new type of boron allotrope experimentally discovered recently,<sup>1,2</sup> as theoretically predicted to form on certain metal surfaces.<sup>3,4</sup> The planar triangular lattice with regular hole arrays leads to intriguing properties in borophene that are dramatically different from all previously known boron allotropes. For example, borophene exhibits metallicity, in contrast to most bulk boron allotropes that are typically insulating or semiconducting.<sup>5,6</sup> Dirac electronic states have been found in borophene with  $\beta_{12}^{7}$ and  $\chi_3$  phases.<sup>8</sup> Moreover, due to the very short B–B bonds and the light mass of boron atoms, 2D borophene sheets were predicted to host advanced mechanical properties<sup>9</sup> and superconductivity with critical temperature  $(T_c)$  as high as  $10-24 \text{ K.}^{10-12}$  The high  $T_c$  is mainly due to the light mass of boron atoms in combination with strong electron-phonon coupling (EPC), similar as in the high- $T_c$  superconductor MgB<sub>2</sub>.

The polymorphism of borophene indicates that various possible structures exist with similar formation energy.<sup>14,15</sup> It is thus of critical importance to reliably determine the atomic structure of borophene sheets experimentally. So far, the most

well-known borophene structures are  $\beta_{12}$  and  $\chi_3$  phases prepared on Ag(111) substrate.<sup>1</sup> However, the only experimental proof of their structure models is the scanning tunneling microscopy (STM) images, whose resolution is not enough to visualize individual boron atoms. So far, the structure models still largely rely on theoretical simulations. Therefore, additional experiments are strongly desirable in order to further confirm the structure model, as well as to probe the physical properties of borophene, such as superconductivity.

Raman spectroscopy has been widely used to characterize bulk boron polymorphs ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -B), and the complicated chemical and structural features of different boron polymorphs are distinguishable by their distinct Raman spectra.<sup>16,17</sup> In addition, the EPC strength can be estimated by the line width of the Raman modes<sup>18,19</sup> and then used to calculate  $T_c$  according to the McMillan equation.<sup>10</sup> The Raman spectrum

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can also provide information on Debye temperature<sup>20</sup> and thermal conductance,<sup>21</sup> which are important for understanding of the thermodynamic properties of borophene. However, due to the light mass of boron atoms, the Raman scattering cross section in boron-based materials is very small as compared with graphene and silicene, making it very difficult to measure the Raman spectrum of monolayer borophene. So far, there is still no experimental report on Raman or optical spectroscopic study on monolayer borophene.

Tip-enhanced Raman spectroscopy (TERS) is a powerful technique with dramatic signal enhancement and high spatial resolution. Our recent TERS study demonstrated high performance, with 109 Raman signal enhancement and subnanometer spatial resolution, in silicene and Si cluster systems.<sup>22,23</sup> Here, combining STM, in situ Raman, and TERS, we have systematically studied the vibrational properties and the EPC in  $\beta_{12}$  and  $\chi_3$  borophene sheets. Far-field Raman and TERS spectra of borophene were obtained. The vibrational modes can be well explained with the help of first-principles calculations, supporting the assignment of these two borophene phases to  $\beta_{12}$  and  $\chi_3$  phases. The EPC in borophene was characterized and related with the possible superconductivity of borophene sheets. These results are helpful for further study on the mechanical, electronic, and intrinsic superconducting properties of borophene.

# **RESULTS AND DISCUSSION**

Figure 1a shows the STM topographic image of a surface with predominant  $\beta_{12}$  borophene islands, the coverage being about 0.8 monolayer (ML). The surface of these islands is characterized by moiré patterns with parallel stripes along the high-symmetry orientations of the Ag(111) substrate.<sup>1</sup> The  $\beta_{12}$  borophene has a rectangular unit cell with the lattice constants a = 0.5 nm and b = 0.3 nm, as illustrated in Figure 1b. Figure 1c is the in situ far-field Raman spectrum of nearly one monolayer  $\beta_{12}$  sheet. Multiple Raman peaks are found, especially at the low frequency region. It is distinctively different from the Raman spectrum of the boron powder as used for evaporating boron atoms (Figure S1 in the Supporting Information), which corresponds to the  $\beta$ -rhombohedral phase of bulk boron.<sup>16</sup> Note that, due to the small Raman scattering cross section of boron atoms, the far-field Raman signal of borophene on Ag(111) is very weak, and a very long accumulation time (typically 30 min) is required to obtain a reasonable signal-to-noise ratio.

To account for these Raman peaks, we calculated the phonon dispersion curves at the main symmetric points and lines in the first Brillouin zone, as shown in Figure 1d. The  $\beta_{12}$  borophene sheet processes a  $D_{2h}$  point group symmetry, by which each vibration mode is labeled. The experimental Raman peaks agree with the energies of calculated vibrational modes well, as summarized in Table S1 in the Supporting Information. The  $A_g^1$  and  $A_g^2$  modes are in-plane stretching modes. They are located in the high frequency region (~1148 and 856 cm<sup>-1</sup>) with a large full-width-at-half-maximum (fwhm) of 44 and 25 cm<sup>-1</sup>, respectively. The two strong Raman modes at 264 and 296 cm<sup>-1</sup> are  $B_{1u}^{-1}(X)$  and  $B_{1u}^{-2}$  modes. They also have large fwhm's of 29 and 27 cm<sup>-1</sup>, respectively. Although the  $B_u$  modes are normally Raman inactive, they can present due to the relaxation of the Raman selection rules, likely due to the interaction between the film and the substrate,<sup>24</sup> as will be discussed in detail later.



Figure 1. Raman spectrum and vibrational modes of  $\beta_{12}$  borophene. (a) STM topography of  $\beta_{12}$  borophene sheet on Ag(111) surface (3.9 V, 270 pA). (b) Schematic atomic structure model of  $\beta_{12}$  borophene with a rectangular unit cell of a = 0.5 nm, b = 0.3 nm. (c) In situ far-field Raman spectrum of monolayer  $\beta_{12}$  borophene (laser power 27.5 mW, data acquisition time 40 min). (d) Calculated phonon dispersion curves of  $\beta_{12}$  borophene and the corresponding vibrational density of states (VDOS). (e) Schematics of atomic displacements of each Raman mode.

The intrinsic phonon line width is usually contributed by two effects, the anharmonic phonon–phonon (ph–ph) interaction and the electron–phonon (*e*–ph) interaction. Since the anharmonic ph–ph interaction of boron is weak and negligible,<sup>25</sup> the observed large fwhm of Raman modes indicates that the *e*–ph interaction in borophene is strong.<sup>25,26</sup> According to the Allen formula,<sup>18,19</sup> the EPC constant ( $\lambda$ ) can be estimated by  $\Gamma_i = \frac{1}{g_i} \pi N(\varepsilon_f) \lambda_i \omega_i^2$ , where  $\Gamma_i$  is the Raman line width,  $g_i$  is the degeneracy of the *i* th mode,  $\omega_i$  is the unrenormalized discrete phonon frequency of the *i* th mode,



Figure 2. TERS spectra of  $\beta_{12}$  borophene. (a) Gap distance-dependent TERS spectra of (laser power 11.5 mW, data acquisition time 50 s). The tip–sample distance was controlled first by decreasing the tunneling current from 300 to 25 pA and then retracting the tip with 100 pm per step outward. (b) TERS intensity of  $B_{3g}^2$  mode as a function of the gap distance. The data points can be fitted well with an exponential decay with a decay length of 144 pm. The inset is an STM image with the tip at the labeled position for TERS measurement, the scalar bar being 10 nm. (c) STM image of 0.5 ML borophene on Ag(111) surface (bias voltage 0.3 V, tunneling current 50 pA). (d) TERS spectra with the tip on the terrace and at the edge of the borophene island labeled in (c), respectively. (e) TERS intensity map of the  $B_{3g}^2$  mode of the area marked by a red box in (c), with a step of 0.64 nm (0.3 V, 100 pA, 10 s). (f) TERS intensity profile along the black arrow line in (c), which was measured with a step size of 0.3 nm.

 $N(\varepsilon_f)$  is the electronic density of states (DOS) at the Fermi level, which can be modulated by doping and strain from substrate.<sup>12</sup> After subtracting a background fwhm of 10.6 cm<sup>-1</sup> (calibrated by the Raman spectrum of single crystal Si(111) at the same measurement condition) from the fwhm's of each peak to exclude the thermal and instrumental broadening, the EPC strength calculated from the far-field Raman spectrum is about 0.53 (with  $N(\varepsilon_f) = 8.02$  states/eV<sup>10</sup>). Similar EPC had been reported in graphene, as estimated from the Raman line width of the G and G' peaks.<sup>27,28</sup> Our experimental EPC is comparable but slightly smaller than the theoretically predicted EPC values in borophene,<sup>10</sup> which is reasonable since those calculations did not include effects of the Ag(111) substrate. Our EPC value is located between those of  $AlB_2$  and  $MgB_2$ . The thus estimated  $T_c$  for  $\beta_{12}$  borophene is 7.1 K, which is also slightly smaller than theoretically predicted values.<sup>10,11</sup>

When we bring the STM tip close to the surface of borophene islands, a dramatic tip-enhanced Raman spectrum is observed. Figure 2a shows a map of TERS spectra as a function of the tip-sample distance on  $\beta_{12}$  borophene. Three typical TERS spectra with different tip-sample distances were overlaid on the map as examples. Note that the data acquisition time for each TERS spectrum is only 50 s; with such a short acquisition time the far-field Raman spectra shows almost nothing, while due to the strong tip enhancement the above Raman modes are well reproduced in the TERS spectra. Interestingly, the intensity profile of the TERS spectra is dramatically different from that of far-field Raman spectrum (Figure 1c) in that the low-frequency  $B_{3g}^2$  mode is strongly enhanced and dominates the spectra. The  $B_{1u}^{-1}$  and  $B_{1u}^{-2}$  modes are also significantly enhanced, while the other modes, especially the A modes at high frequency region, show

negligible enhancement. This selective enhancement effect can be well understood as TERS mainly enhances the out-ofplane vibrational modes.<sup>22,29</sup> The  $B_{3g}^2$  phonon mode has nearly pure vertical atomic displacements, while other modes like  $A_{g}$ ,  $B_{1g}$ , and  $B_{2u}$  are all in-plane stretching modes (Figure 1e). Thus, our models for the vibrational modes agree perfectly with the observed selective enhancement in TERS. Moreover, the TERS intensity of  $B_{3g}^2$  mode exhibits a laser polarizationangle dependence (see Figure S2d in the Supporting Information), which is consistent with the fact that the gapmode TERS intensity ( $I_{TERS}$ ) is proportional to the *z* component intensity of the incident laser,  $I_{TERS} \propto EF \cdot lE_{in,z}|^2$ =  $EF \cdot I_{laser} \cos^2 \theta$ , where EF is the TERS enhancement factor.<sup>30</sup> Note that the low frequency TERS peaks exhibit larger line width compared with corresponding far-field Raman peaks, which may be due to the plasmon-phonon coupling or plasmon enhanced electron-phonon coupling.<sup>24</sup>

The TERS intensity is very sensitive to the tip-sample distance. The tip-sample distance was varied by reducing the tunneling current from 300 to 25 pA and then retracting the tip in 100 pm per step away from the surface. The extracted intensity of the  $B_{3g}^2$  mode from Figure 2a can be fitted quantitatively very well by an exponential decay with a decay length (*D*) of 144 pm (Figure 2b). Such a short decay length is crucial for the high spatial resolution of the gap-mode TERS,<sup>22,31</sup> in which the spatial resolution can be determined by moving the tip across the step of a borophene island (Figure 2c) and measuring the Raman intensity profile as shown in Figure 2f. The TERS intensity changes more than 80% within a 0.9 nm distance, indicating a spatial resolution below 1 nm (more data are shown in Figure S2 in the Supporting Information). The enhancement factor (EF) can be



Figure 3. TERS spectra of local  $\beta_{12}$  borophene structures. (a) STM topography of  $\beta_{12}$  borophene sheet with different orientations on Ag(111) surface (bias voltage 2.3 V, tunneling current 50 pA). (b, c) Atomic structure models of the striped  $\beta_{12}$  phase (M) and the smooth  $\beta_{12}$  phase (S), respectively. The labeled black vectors are the unit vectors of  $\beta_{12}$  sheet, and the white vectors represent the crystallographic orientations of Ag(111) surface. (d) TERS spectra of  $\beta_{12}$  borophene sheets at the striped and smooth regions labeled in (a) (300 mV, 200 pA), respectively. (e) TERS spectra map along the dotted line marked in the STM topography image in the inset. The acquisition time is 50 s for each TERS spectrum, and laser power is about 10 mW.

determined by  $\text{EF} = \frac{I_{\text{near}}A_{\text{laser}}C}{I_{\text{far}}A_{\text{near}}}$ , where  $I_{\text{near}}$  and  $I_{\text{far}}$  are the Raman intensities in the near-field and far-field Raman spectra, respectively. *C* is the coverage of borophene on Ag(111) surface. The near-field and far-field intensity contrast is about 165.3 in our experiment, and the derived EF is above  $3.6 \times 10^9$  (as detailed in the Supporting Information), which are among the best records of all TERS experiments and setups so far.<sup>31,32</sup> The TERS spectrum at the edge of a borophene island was also measured, as shown in Figure 2d. It shows only a very weak B<sub>1u</sub> peak, confirming that above observed Raman modes are not edge-modes in borophene.

Furthermore, we found that TERS can also be used to distinguish different borophene phases. As reported in the literature,<sup>33</sup> two apparently different phases in STM images have been reported as the  $\beta_{12}$  sheets having different orientations on the Ag(111) substrate. When the unit vector **b** is aligned with the [112] direction (Figure 3b), the surface exhibits 1.5 nm stripes (as in Figure 1a). On the other hand, when the unit vector  $\mathbf{a}$  is aligned with the [112] direction (Figure 3c), the surface is smooth without any moiré pattern.<sup>33</sup> In the latter case, the lattice constant  $\mathbf{a} = 0.5$  nm fits the period of Ag(111) ( $\sqrt{3} \times 0.29$  nm = 0.502 nm) very well. Meanwhile the short side of lattice ( $\mathbf{b} = 0.3 \text{ nm}$ ) also matches the Ag period in the [110] direction (0.29 nm) well. The ultrahigh spatial resolution of TERS makes it possible to compare the Raman spectra of these two types of  $\beta_{12}$  domains directly. The STM image shown in Figure 3a consists of a smooth  $\beta_{12}$ domain at the upper right part of the image and a striped  $\beta_{12}$ domain at the lower-left part of the image. The TERS spectra were measured by placing the STM tip on top of each domain, as shown in Figure 3d. The two spectra are very similar, indicating that they are from intrinsically the same phase (for comparison, the TERS spectra of the  $\chi_3$  borophene is

fundamentally different, as will be discussed later). The slight differences include a 6 cm<sup>-1</sup> red shift of the B<sub>3g</sub><sup>2</sup> peak of the smooth  $\beta_{12}$  sheet as compared with that of striped  $\beta_{12}$  sheet, while the A<sub>g</sub><sup>1</sup> mode is blue-shifted. This can be well explained by the different film-substrate interaction, and different strains in the two types  $\beta_{12}$  sheets. For the smooth  $\beta_{12}$  sheet, the borophene lattice is slightly compressed in the  $[1\overline{10}]$  direction, leading to a blue shift of the in-plane stretching mode (the Ag mode).<sup>34</sup> Meanwhile, the commensuration and lattice mismatching in the smooth  $\beta_{12}$  sheet introduces a stronger film-substrate interaction, resulting in more significant enhancement of the  $B_{1u}$  and  $B_{1g}^{\ 2}$  modes at 273 and 381 cm<sup>-1</sup>. This also supports our suggestion that the Raman activity of B<sub>1u</sub> modes are due to the substrate interaction. When a rectangular borophene lattice is placed on 3-fold symmetric Ag(111) surface, the inversion and rotation symmetries are broken, leading to IR modes or Hyper Raman modes detectable by Raman spectroscopy.<sup>24</sup> The B<sub>1u</sub> mode is a typical Hyper Raman mode. According to the Hyper Raman selection rules, the B<sub>1u</sub> mode can be excited with a zpolarized laser.<sup>24</sup> This has been confirmed with our polarization-dependence experiment, where the *p*-polarized incident laser was at  $30^{\circ}$  with respect to the sample surface. Finally, we have measured TERS spectra map on an isolated island of smooth  $\beta_{12}$  sheet along the line in the inset STM image in Figure 3e. We found that at the edge of the island, the TERS spectra are similar to the striped phase, but within the terrace, the  $B_{3g}^{2}$  mode is apparently red-shifted and the  $B_{1u}$  and  $B_{1g}^{2}$ modes are stronger. These results demonstrate that TERS is a powerful technique for in situ characterization of local structures and strains in 2D materials.

We next investigated the far-field Raman and TERS spectra of the  $\chi_3$  borophene phase, which can be prepared by annealing the  $\beta_{12}$  phase at 700 K. The  $\chi_3$  phase is also inherently metallic, with a theoretically predicted EPC  $\lambda$  of 0.6–0.95 and superconducting  $T_c$  of 12–24.7 K.<sup>10,11</sup> A typical STM image of the  $\chi_3$  sheet and its structure model are shown in parts a and b, respectively, of Figure 4. We first measured the far-field



Figure 4. Vibrational properties and EPC in  $\chi_3$  borophene phase. (a) STM topography and (b) atomic structure model of  $\chi_3$  borophene sheet (bias voltage 2.9 V, tunneling current 50 pA). (c) In situ far-field Raman spectrum (25.7 mW, 50 min) and TERS spectrum (100 s, 14 mW) of the  $\chi_3$  sheet. (d) Calculated phonon dispersion curves and the corresponding vibrational density of states of the  $\chi_3$  sheet. (e) Schematics of atomic displacements of the Raman modes.

Raman spectrum of the  $\chi_3$  borophene. As shown by the black spectral line in Figure 4c, the spectrum is very different from that of  $\beta_{12}$  sheet, especially in the high frequency region. The measured Raman modes and the calculated ones are summarized in Table S2 in the Supporting Information, where the measured spectrum agrees well with the calculation. Here, the highest frequency mode is located at 1230 cm<sup>-1</sup> (Ag<sup>1</sup> mode). The weak peak at 1160 cm<sup>-1</sup> may come from the remaining  $\beta_{12}$  phase, which can coexist with the  $\chi_3$  sheet at a temperature range from 650 to 800 K.<sup>1,2</sup> From the phonon spectrum (Figure 4d) and Eliashberg spectral function,<sup>10</sup> we can see that both the  $A_u$  and  $B_g^2$  phonon branches have a flat band in the X–X' direction and strong electron–phonon coupling strength. These agree with the observed broad Raman peaks in the far-field Raman spectrum. Following the same procedure as in the  $\beta_{12}$  phase, the EPC strength has been calculated to be about 0.59 (with  $N(\varepsilon_f) = 7.71$  states/eV), and the  $T_c$  was about 9.8 K for the  $\chi_3$  borophene phase.

The TERS spectrum of  $\chi_3$  (red curve in Figure 4c) shows a similar shape as compared that of the striped  $\beta_{12}$  phase, with the main  $B_g^2$  peak located at 181 cm<sup>-1</sup>, which is 8 cm<sup>-1</sup> red shift from the  $\beta_{12}$  phase. In addition, the major peaks at low frequency region in the far-field Raman spectrum were well reproduced in the TERS spectrum. The selective enhancement of different Raman modes is related to the origination of the vibrational modes. The vibrated schematic of the main Raman modes of  $\chi_3$  sheet were illustrated in Figure 4e. All the modes that can be enhanced have out-of-plane vibration components, while the  $A_g$  modes at high frequencies were all in-plane vibrational modes. The selectivity of TERS enhancement agrees with the calculated vibrational properties of these modes very well.

# CONCLUSION

We have studied the vibrational properties and the electronphonon coupling of 2D borophene sheets with in situ far-field Raman and TERS spectra. Our results provide strong support to the theoretical structural models of the  $\beta_{12}$  and  $\chi_3$ borophene phases. The electron-phonon coupling strength is about 0.53-0.59, estimated by the line width of Raman peaks. The estimated  $T_c$  is about 7.1 and 9.8 K for  $\beta_{12}$  and  $\chi_3$ sheets, respectively. Moreover, we have demonstrated the high performance of our TERS spectroscopy, with  $3 \times 10^9$  signal enhancement factor and a 1 nm spatial resolution, which enables us to probe the local vibrational features of 2D borophene. For example, our TERS spectra prove that the smooth  $\beta_{12}$  phase and striped  $\beta_{12}$  phase are of the same structure but with distinguishable features arising from commensuration and strain. Our results provide a basic experimental understanding on the vibrational properties of borophene sheets, which is also important for further study on the mechanical, electronic, and intrinsic superconducting properties of two-dimensional boron.

# **METHODS**

**Experimental Setup and Sample Preparation.** All experiments were carried out in a homemade LT-UHV-STM-TERS system combined with a molecular beam epitaxy (MBE) system, details of which were described in ref 22. The samples were prepared in the MBE chamber and *in situ* transferred to the STM chamber for STM, Raman, and TERS characterizations. All experiments were performed at 78 K. The Ag(111) substrate was cleaned by Ar<sup>+</sup> sputtering and annealing cycles. Pure boron (99.9999%, Alfa) was deposited onto the Ag(111) surface by an electron beam evaporator, with the Ag substrate held at about 480 and 700 K for preparing the  $\beta_{12}$  sheet and  $\chi_3$  sheet, respectively. The STM tip used in the experiments was an electrochemically etched Ag tip, which was cleaned by deionized water before transferred into the vacuum chamber. A *p*-polarized 532 nm laser was used as Raman pumping source, with a side illumination and backscattering collection configuration.<sup>30</sup>

**Calculations.** First-principle calculations were performed using the DFT code Quantum-ESPRESSO<sup>35</sup> within the projector augmented wave method<sup>36,37</sup> and a plane-wave basis. The exchange

correlation potential was treated within the generalized gradient approximation. A 32 × 32 × 1 k-mesh was used to sample the Brillouin zone (BZ). The energy cutoff for the plane-wave basis was 400 eV. All atoms were fully relaxed until the residual force per atom was smaller than 0.001 eVÅ<sup>-1</sup>. The phonon dispersion was computed with perturbative linear response method within the density functional approximation.  $N(\varepsilon_f)$  was calculated according to ref 10.

# ASSOCIATED CONTENT

### **S** Supporting Information

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Raman spectroscopy of the boron powder used for evaporating boron, analysis of TERS enhancement factor, and laser polarization dependent behavior (PDF)

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Notes

The authors declare no competing financial interest.

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