Fine-Tuning the Optoelectronic Properties of Freestanding Borophene by Strain

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Supporting Information

ABSTRACT: Two-dimensional boron (borophene) is a promising, newly synthesized monolayer metal with promising electronic and optical properties. Borophene has only been recently synthesized on silver substrates, and displays a variety of crystal structures and substrate-induced strains depending on the growth conditions and surface orientation. Here, we present an extensive first-principles study of the structural and optoelectronic properties of the two proposed structures of borophene, $\beta_{12}$ and $\delta_6$, under strain. With a density functional theory analysis, we determine that the optical absorbance and electronic band structure are continuously tunable upon application of few percent of strain. Although both structures remain metallic with moderate strains of up to 6% applied, key features of the band structure, as well as the in-plane anisotropy of the complex dielectric function and optical absorption, can be significantly modified.

I. INTRODUCTION

Nanoscale conductors such as graphene and carbon nanotubes are the key functional elements in several next-generation nanotechnologies. In particular, ultrathin carbon-based films have been recently utilized in next-generation touchscreen technologies,1,2 flexible electronics,3 transparent conductive electrodes in solar cells,4−6 and low-power electronics.7,8 These materials have low production costs and scalable processing methods; however, in sub-10 nm devices, with atomically controlled interfaces, it is particularly desirable to have a defect-free atomically thin monolayer that can serve as an electrode. Although exfoliated graphene is highly promising for this application, there are remaining challenges for large-scale production. Chemical vapor deposition-grown graphene samples have micron-sized grains9 and reduced graphene oxide has residual defects10,11 which degrade the conductivity of the sheet. As an alternative, two-dimensional (2D) boron or borophene is a recently proposed monolayer material that has been predicted to display metallic properties,12−15 and form Ohmic contacts to 2D semiconductors, greatly enhancing the performance of electronic devices.16

Borophene has only been recently synthesized on silver substrates,17−20 with scanning tunneling microscopy (STM) images providing evidence of the 2D nature of the films, though the crystal structure is still undetermined due the many possible low-energy structures. Boron exists in numerous allotropes: there are four bulk boron structures,21 and as the dimensions are reduced to two,12,14,15,22−30 one,14,31−35 or zero,36−40 multiple low-energy structures have been observed and predicted. To date, the true ground state structure of the monolayer is not known.22,25,27,41−44 It is predicted that planar boron sheets form a triangular bonding configuration, which is unstable due to an excess of electrons that occupy the antibonding orbitals;12,13 this structure can be stabilized by the introduction of vacancies, an example of which is shown for the $\beta_{12}$ structure in Figure 1a, or out-of-plane buckling as shown for

![Diagram](image)

Figure 1. Atomic structure of the (a) $\beta_{12}$ and (b) $\delta_6$ borophene allotropes. The unit cell for each is shown by an orange box. The $\beta_{12}$ and $\delta_6$ phases have five and two boron atoms per unit cell, respectively, with the $\delta_6$ phase displaying an out-of-plane rippling of 0.88 Å, as shown at the bottom of (b).

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the $\delta_8$ structure in Figure 1b. Additionally, when borophene is grown on the substrates, the lattice mismatch between the substrate lattice constant and the periodicity of the boron sheet, as well as charge transfer between boron and substrate, favor the certain atomic configurations of boron atoms (boron allotropes) and rotation angles between boron and substrate (Moiré patterns). There are several experimentally observed structures for borophene grown on Ag(111) based on scanning tunneling microscopy (STM) measurements and calculations. The $\delta_8$ structure, a hexagonal lattice with out-of-plane rumpling of the central atom, was initially proposed as being consistent with the STM measurements.\(^{17}\) The $\beta_{12}$ structure, with one out of six boron atoms replaced by a vacancy, is expected to be the most abundantly grown on Ag(111) substrate,\(^{18,20,43}\) whereas at a higher growth temperatures, there is evidence for the $\chi_5$ structure,\(^{58}\) which has one out of five atoms missing and also forms a network of connected vacancies. Another structure, labeled $\alpha$-boron (one out of nine boron atoms missing),\(^{13}\) was predicted to be the lowest-energy structure in two dimensions, but has been experimentally observed as only a minor phase on Ag(111) substrates.\(^{20}\) Additionally, recent studies of borophene synthesized on Ag(110) substrates have demonstrated several new allotropes of borophene in striped phase, with varying widths of stripes.\(^{19}\)

To date, freestanding borophene has not yet been isolated and the optoelectronic properties of the monolayer have not yet been measured. The impact of Ag(111) substrate on the electronic structure of borophene is more complex than in the case of graphene;\(^{46}\) however, experimental measurements have confirmed the metallic character of boron adsorbed on silver substrates.\(^{47,48}\) Numerous ab initio calculations of freestanding borophene allotropes predict 2D metals with a rich set of electronic properties. Density functional theory (DFT) simulations, in particular, have demonstrated very different electronic band structures of the different borophene allotropes.\(^{12−14,22,44,48−52}\) Although all of the 2D allotropes are metallic, the band structure near the Fermi energy can take either a quadratic form as a traditional metal (e.g., for $\delta_8$ sheets), or display both quadratic and crossing linear bands, resulting in Dirac points (e.g., $\beta_{12}$ and $\chi_5$). The Dirac point is above the Fermi level in $\beta_{12}$ sheet and below the Fermi level in $\chi_5$ sheet.\(^{52}\) Additionally, phonon-mediated superconductivity\(^ {53−58}\) and low thermal conductivity\(^ {59−61}\) have been predicted for certain allotropes. Such diverse electronic properties of borophene allotropes, as well as their light weight, metallicity, and mechanical stability, suggest that it is a promising material for future applications as a monolayer conductor, a high-capacity electrode for electrochemical applications,\(^ {60−65}\) and a catalyst for hydrogen evolution reaction.\(^ {66,67}\)

This variety of experimentally synthesized borophene allotropes realized by change in substrate, the substrate crystallographic orientation, and growth conditions results in a diverse class of 2D metals. Additionally, small strains, induced by the adjustment of borophene to the substrate, can be utilized to tune the properties of borophene. Strain engineering has been extensively investigated for other 2D material systems such as graphene and transition metal dichalcogenides. As an example, homogeneous strain in graphene enhances the electron–phonon coupling\(^ {46}\) and nonuniform strain generates extremely high pseudomagnetic fields.\(^ {59,70}\) In monolayer molybdenum disulfide, small compressive (tensile) strains enhance (decrease) the fluorescence intensity,\(^ {71,72}\) and 10% tensile strain induces a semiconductor-to-metal transition.\(^ {71}\) Similar to that of these materials, mechanical strength of borophene is outstanding and the monolayer is expected to withstand high strains without the reduction in structural integrity.\(^ {52,73−79}\)

However, a systematic study of strain engineering in this system has not been performed previously. Here, we utilize the first-principle density functional theory (DFT) to understand the inplane strain dependence of electronic and optical properties of two possible boron allotropes shown in Figure 1. We demonstrate that strain engineering in borophene allows for a continuous tuning of electronic and optical properties without the structural disintegration. We predict that both borophene structures are resilient to compressive and tensile strains up to 6%, with deformation energies of less than 100 meV; and that their band structures can be significantly modified at these strains while retaining their metallic nature. Moreover, we show that both boron allotropes are weakly absorbing, with an anisotropy in the dielectric response to X- and Y-polarized light. Our study demonstrates that strain enhances the functionality of this promising 2D conductor via tuning of electronic and optical properties.

II. RESULTS

II.I. Structural Properties. We study the strain within two crystal structures of borophene, $\beta_{12}$ and $\delta_8$ as depicted in Figure 1. These structures have been predicted as candidates for borophene grown on Ag(111) based on the symmetry of scanning tunneling microscopy (STM) images. Although the $\beta_{12}$ structure has been theoretically predicted to be the most favorable geometry on noble metal substrates,\(^ {60}\) the $\delta_8$ structure is close in energy\(^ {52}\) and its $1 \times 3$ supercell displays a close lattice match to Ag(111) $1 \times \sqrt{3}$ supercell. Here, we predict that the formation energy of the $\beta_{12}$ structure on Ag(111) is 0.155 eV more favorable than that of the $\delta_8$ structure, in agreement with previous DFT-based predictions.\(^ {40}\) Figure 2 illustrates the change in total energy of borophene as a function of strain along the $x$- and $y$-axes, $\varepsilon_{xy}$, with 1% strain increments. The application of strain results in an energy penalty due to deformation (deformation energy) that we separate in three regimes—weak, moderate, or strong—based on the magnitude. We classify the deformation as weak if the energy penalty is below 50 meV/atom; moderate if the energy penalty is between 50 and 100 meV per boron atom; and strong if the deformation energies are greater than 100 meV/atom.

![Figure 2. Deformation energy per atom (eV) as a function of strain $\varepsilon_{xy}$ in the (a) $\beta_{12}$ and (b) $\delta_8$ boron allotropes. One pixel corresponds to a 1% increment in value of strain, and white circles mark the values of strain in 3% increments that were studied in more detail.](image-url)
The \( \beta_{12} \) structure (Figure 1a) contains five atoms per unit cell with alternating rows of empty and filled hexagons along the \( x \)-direction (forming stripes of vacancies along \( x \)-direction) and columns of continuous line of atoms alternating with incomplete hexagons along the \( y \)-direction. Evaluation of the computed charge density indicates that the boron atoms are sp-bonded with delocalized charge density along \( x \)-direction and a slightly weaker delocalization along \( y \)-direction due to the different bond lengths in each direction (see the Supporting Information Figures S1 and S2). Because the sp-type bonding in this structure is highly sensitive to the atomic orbital overlap, the density localizes upon bond stretching (for tensile strain) and results in a less free-electron-like system for states near the Fermi energy (see Figure S3 in the Supporting Information).

The deformation energy upon application of strain, shown in Figure 2a, does not reflect this anisotropy; the deformation energy has a relatively uniform behavior along the \( x \)- and \( y \)-directions. Here, small (1–2\%) tensile or compressive strain results in a small energy penalty of about \( k_B T \) (25 meV/atom); therefore, this material may easily slightly adjust its lattice constant to that of the underlying substrate. This weak deformation lasts up to strains of \( (\epsilon_x, \epsilon_y) = (\pm 3, \pm 3)\% \), with an energy penalty of about 50 meV/atom. Uniaxial strains of \( \pm 6\% \) and \( 0, \pm 6\% \) result in moderate deformations of about 100 meV/atom, whereas biaxial (6, 6)\% tensile and \( -6\% \) compressive strains result in greater than 150 meV/atom energy penalty, indicating a strong deformation. Beyond this region, the deformation energies are greater than 150 meV/atom.

By contrast, the \( \delta_b \) structure, shown in Figure 1b, contains two atoms in the hexagonal unit cell, with an out-of-plane rumpling of the central atom and no vacancy or stripe formation. Along the \( x \)-direction, the structure contains zigzag rows with boron atoms of alternating heights, whereas along the \( y \)-direction, there are continuous columns of atoms. Here, an analysis of the computed charge density suggests that the atoms bond via \( \pi \)-bonding of \( p_z \) orbitals. Due to the zigzag structure along the \( x \)-direction, the \( p_z \) orbital bonding is significantly weaker along this direction than along the \( y \)-direction, as can be seen in the charge density distribution for states near the Fermi energy (see Figure S5 in the Supporting Information).

This anisotropy is reflected in the deformation energies shown in Figure 2b: the \( \delta_b \) allotrope is soft toward deformations along the \( x \)-axis, as is expected based on the periodically buckled atomic configuration, and more difficult to deform along the \( y \)-axis. For example, with 10\% strain, the deformation energy is \( \sim \)100 meV/atom for both tensile and compressive strains along \( x \)-axis and 200 and 500 meV/atom for tensile and compressive strains along \( y \)-axis, respectively. Such large differences in the compression energies are to be expected because compression along the \( y \)-axis changes the bond lengths significantly. We predict that \( \pm 3\% \) strain results in a weak deformation and \( \pm 6\% \) strain along the \( y \)-axis and \( x \)-axis results in moderate and strong deformations, respectively.

Figure 2 indicates that \( \pm 3\% \) (weak) and \( \pm 6\% \) (moderate) strain, with few exceptions, do not result in a large deformation energy, and thus will not compromise the structural integrity of the boron monolayers. Therefore, we focus on strains up to \( \pm 6\% \) for further analysis. White circles in Figure 2 mark the values of strains for which we simulate the electronic and optical properties.

II.I. Optoelectronic Properties of Unstrained Borophene. Figure 3 shows the calculated band structure for both unstrained allotropes. We predict that both allotropes are metals with several bands crossing the Fermi energy (\( E_F \)), in agreement with previous calculations. The \( \beta_{12} \) allotrope contains three bands near the top of the valence band (Figure 3a) and a Dirac cone, i.e., linearly crossing bands, located near the \( S \)-point at about 0.5 eV above \( E_F \). The \( \delta_b \) allotrope shows a different character to the band structure, with two partially occupied bands, which cross \( E_F \), as shown in Figure 3b. In the vicinity of the \( \Gamma \)-point (\( k = 0 \)), there is a 4.1
The optical properties of the two boron allotropes are presented in the lower panels of Figure 3. Here, we consider only the interband transitions for optical absorption and ignore the intraband transitions that would result in modification of the spectrum at very low energies (<0.1 eV). The real ($\epsilon_1(\omega)$) and imaginary ($\epsilon_2(\omega)$) components of the dielectric function display anisotropy in response to light polarized along the $x$- and $y$-axes for both $\beta_{12}$ and $\delta_6$ allotropes. We quantify this anisotropy by the calculated bulk plasma frequency ($\omega_p$) in each direction (Table 1), $\epsilon_1$, a measure of the strength of the dynamical screening effects arising from charge excitations, shows a strong response at $\omega_p$, which is predicted to be 2.9 eV (2.4 eV) and 2.1 eV (4.4 eV) for $X$- ($Y$-) polarized light within the $\beta_{12}$ and $\delta_6$ allotropes, respectively. We note here that the 2D surface plasma will have a much smaller value than $\omega_p$ in Table 1; considering a free electron gas in 2D, the plasma frequency $\omega_{p,2D} = qL/\sqrt{2\pi}$, where $L$ is the length of the unit cell and $q$ is the wavevector of light. Considering the visible range of light, $\omega_{p,2D}$ is 1–2 orders of magnitude smaller than $\omega_p$. Interestingly, a recent study of $Pmmn$ borophene, a structure somewhat similar to $\delta_6$, has suggested that the anisotropy in the plasma frequency of borophene may be used for plasma-wave nanodevices. As we will show in Section IV, strain enhances anisotropy and therefore makes this application more feasible. $\epsilon_2$, a measure of light absorption as a consequence of neutral and plasmonic charge excitations, also shows a polarization dependence. For the $\beta_{12}$ allotrope, $\epsilon_2(\omega)$ shows an onset of $\sim0.2$ eV and contains a pronounced peak at $\omega \sim 0.8$ eV for $X$-polarized light, whereas for $Y$-polarized light, $\epsilon_2(\omega)$ slowly rises at 1 eV. For the $\delta_6$ allotrope, $\epsilon_2(\omega)$ rises from 0 at 2.5 eV due to excitations from the middle of $\Gamma-Y$ and $\Gamma-S$ regions of the $\beta_{12}$ band structure. However, our calculations for the band structure of both borophene allotropes are in agreement with published works that used similar DFT methodology. However, the discrepancy between our calculations and those presented by Peng et al. is likely due to the use of different DFT functionals (HSE06 versus Perdew–Burke–Ernzerhof (PBE)).

### Table 1. Plasma Frequencies in $\beta_{12}$ Borophene

| Strain ($\alpha_{12}/\alpha_{21}$) | $\omega_p$ of $\beta_{12}$ structure, eV | $\omega_p$ of $\delta_6$ structure, eV |
|---------------------------------|----------------|----------------|
| $(-6, 6)$                       | 3.31           | 1.34           |
| $(-6, 3)$                       | 3.39           | 1.27           |
| $(-6, 0)$                       | 3.72           | 0.64           |
| $(-6, -3)$                      | 3.73           | 1.25           |
| $(-6, -6)$                      | 3.02           | 2.92           |
| $(0, 6)$                        | 3.35           | 1.38           |
| $(0, 3)$                        | 3.05           | 1.77           |
| $(0, 0)$                        | 3.56           | 1.99           |
| $(0, -3)$                       | 3.24           | 3.28           |
| $(0, -6)$                       | 3.91           | 3.44           |
| $(3, 6)$                        | 3.02           | 1.32           |
| $(3, 3)$                        | 3.23           | 3.44           |
| $(3, 0)$                        | 3.30           | 3.44           |
| $(3, -3)$                       | 3.26           | 3.44           |
| $(3, -6)$                       | 3.26           | 3.44           |
| $(6, 6)$                        | 2.98           | 2.73           |
| $(6, 3)$                        | 2.77           | 2.73           |
| $(6, 0)$                        | 2.36           | 2.73           |
| $(6, -3)$                       | 2.46           | 2.73           |
| $(6, -6)$                       | 2.41           | 2.73           |
| $(9, 9)$                        | 0.98           | 1.56           |
| $(9, 6)$                        | 1.27           | 1.56           |
| $(9, 3)$                        | 1.24           | 1.56           |
| $(9, 0)$                        | 1.26           | 1.56           |
| $(9, -3)$                       | 1.28           | 1.56           |
| $(9, -6)$                       | 1.29           | 1.56           |
| $(2, 6)$                        | 0.94           | 1.56           |
| $(2, 3)$                        | 0.95           | 1.56           |
| $(2, 0)$                        | 0.96           | 1.56           |
| $(2, -3)$                       | 0.97           | 1.56           |
| $(2, -6)$                       | 0.98           | 1.56           |
| $(1, 6)$                        | 0.99           | 1.56           |
| $(1, 3)$                        | 1.00           | 1.56           |
| $(1, 0)$                        | 1.01           | 1.56           |
| $(1, -3)$                       | 1.02           | 1.56           |
| $(1, -6)$                       | 1.03           | 1.56           |
| $(0, 9)$                        | 0.98           | 1.56           |
| $(0, 6)$                        | 0.99           | 1.56           |
| $(0, 3)$                        | 1.00           | 1.56           |
| $(0, 0)$                        | 1.01           | 1.56           |
| $(0, -3)$                       | 1.02           | 1.56           |
| $(0, -6)$                       | 1.03           | 1.56           |
| $(3, 9)$                        | 0.97           | 1.56           |
| $(3, 6)$                        | 0.98           | 1.56           |
| $(3, 3)$                        | 0.99           | 1.56           |
| $(3, 0)$                        | 1.00           | 1.56           |
| $(3, -3)$                       | 1.01           | 1.56           |
| $(3, -6)$                       | 1.02           | 1.56           |
| $(6, 9)$                        | 0.96           | 1.56           |
| $(6, 6)$                        | 0.97           | 1.56           |
| $(6, 3)$                        | 0.98           | 1.56           |
| $(6, 0)$                        | 0.99           | 1.56           |
| $(6, -3)$                       | 1.00           | 1.56           |
| $(6, -6)$                       | 1.01           | 1.56           |
Brillouin zone and increases in strength at 4 eV due to the addition of excitations at the gap at Γ. For Y-polarized light, the onset of ϵ₂ is at 4.0 eV, with a negligibly small strength up to 6.8 eV. The Z-component of the imaginary part of the dielectric functions of both boron structures is very small, as expected for a 2D material.

The onset of absorption corresponds to the onset of ϵ₂(ω) and is negligible (<0.2 eV) for β₁₂ (Figure 3a) and 3.0 eV for δ₆ (Figure 3b), consistent with the lowest direct transition energies in the band structure. Both allotropes are predicted to be weakly absorbing; in the visible range, graphene absorbs 2.3%. We note that Peng et al. predicted a different absorption spectrum, which can again be attributed to the use of different functionals.

II.III. Band structure of Strained Borophene. II.III.I. Strained β₁₂ Borophene. Figure 4 plots the band structure of the strained β₁₂ allotrope, shown for ±6% strains to highlight the most important trends, which are observed to a lesser degree with ±3% strains. The most relevant features are highlighted in red circles (the Dirac point near S) and green ovals (the valence bands in the vicinity of the Γ-point). In general, strain along the x-axis does not significantly alter the former but does strongly influence the latter, whereas strain along the y-axis strongly influences both.

Strain along y-axis results in shifting of the Dirac point closer to E_F for compressive and farther away from E_F for tensile strains. This trend is most apparent when starting from an x-strained structure (panel (6, 0)) and straining along y-axis. Upon stretching by 6% along y-axis (panel (6, 6)), the Dirac point decreases to 0.1 eV above E_F, whereas 6% compression along y-axis (panel (6, −6)) results in the Dirac point increasing to 0.9 eV above E_F. This suggests that tensile strength can lead to the presence of massless fermions at E_F as exist in graphene, though in this case there are parabolic bands resulting in massive electrons present at E_F as well.

The gap near Γ is influenced by both x- and y-strain, with a greater influence of x-strain. The gap can open up from 0.1 eV with no strain to 0.8 eV with 6% tensile strain along x-direction. As discussed in the next section, the value of this gap influences the nature and energy of the optical absorption onset. Additionally, the influence of strain along x- and y-axes is to some extent coupled, as both strain directions affect the highlighted electronic bands to some degree. Six percent homogeneous tensile strain shifts the Dirac point to 0.1 eV above E_F and opens a 1 eV band gap at Γ, whereas 6% compressive strain shifts the Dirac point to about 0.3 eV above E_F and results in closing of the band gap in the vicinity of E_F near Γ.

II.III.II. Strained δ₆ Borophene. For the strained δ₆ allotrope, the two most relevant features are highlighted in Figure 5 by the blue arrow (gap at Γ) and red circle (unoccupied bands above the Fermi energy along Y–Γ line). As discussed in the next section, these bands contribute to optical absorption in the visible range. In general, the band gap at Γ is increased with compressive and decreased with tensile strains. Due to the anisotropic nature of the structure, there is anisotropy in this effect. Notably, a few percent deformation along the x-axis...
induces changes in the gap by up to 2 eV for 6% strain ((±6, 0)), whereas strain along y-axis does not appreciably modify the gap (by about 0.5 eV in (0, ±6)). Based on the small deformation energies for strain along x-axis, the strong response of the gap to strain in this direction may be unexpected, but can be explained based on its π-bonded nature and zigzag structure along x-axis. The $p_{\pi}$ orbitals are either pushed more out-of-plane with those of the neighboring atoms as borophene becomes more buckled under compression or pushed inplane upon tensile x-directed strain resulting in stronger interactions among the nearest neighbors.

The unoccupied bands along the $Y$–Γ line are strongly responsive to strain along both x- and y-directions. The shape of the bands, as well as their position with respect to $E_F$, changes with strain. For example, a 6% isotropic stretch ((6, 6) panel) moves these bands by ∼1.5 eV down toward $E_F$, whereas a 6% isotropic compression ((−6, −6) panel) pushes these bands up by ∼2 eV away from $E_F$. As these bands are lowered in energy below the gap at Γ, they begin to dominate optical absorption at low energies.

This analysis of the band structure indicates that both borophene allotropes remain metallic under weak and moderate strains. The strain-related changes in band shape, as well as band position with respect to the Fermi energy, will affect the conductivity of the monolayer metal, and will also affect the energies and intensities of optical transitions, as described in the next Section II.IV.

**II.IV. Optical Properties of Strained Borophene.** With the application of strain, the weak absorbance and anisotropy of response to X-/Y-light polarization described in Section II.III are maintained. However, there are two features that can be manipulated by strain: (i) the anisotropy in response to X- and Y-polarized light; and (ii) the onset of optical absorption. As explained below, these strain-dependent trends can be related to changes in the band structure and the charge density delocalization.

**II.IV.I. Strained β_{12} Borophene.** The application of strain allows the tuning of both the real component of the dielectric function, as demonstrated by the change in calculated $\omega_2$ shown in Table 1. For X-polarized light, the $\omega_2$ ranges from 2.15 to 3.71 eV, whereas for Y-polarized light, it can vary from 0.64 to 3.44 eV. Importantly, the X-/Y-anisotropy in response can be tuned via strain as demonstrated from the change in $\omega_2$ (Table S3). This value is 1 eV for the unstrained structure. The application of tensile strain along x-axis increases the anisotropy, whereas compressive strain decreases it. Conversely, the application of tensile strain along y-axis decreases anisotropy, whereas the compressive strain decreases it. Homogeneous strain, either compressive or tensile, decreases anisotropy. These trends can be understood as due to change in anisotropy of the atomic structure; for example, with homogeneous tensile strain, the bond lengths shift such that the bond length connecting the hexagonal rows is closer to the length of the hexagonal edges, resulting in a more isotropic charge density for states near the Fermi energy (see calculated local density of states (LDOS’s) in Figures S1 and S2 in the Supporting Information).

For this structure, the application of a few percent strain does not result in a significant shift in the onset of absorption (which is close to zero) or change in absorption strength (<1% absorptivity in the UV–vis region), as shown in Figure S5a. It does, however, influence the strength of the imaginary part of dielectric function $\epsilon_2$ for X-polarized light. For example, the peak at 0.8 eV (Figure 6) is enhanced for tensile strain along the y-axis and compressive strain along the x-axis. The enhanced $\epsilon_2$ correlates with decreased delocalization of the electron density along the y-axis (see Figure S1). For the same reason, homogeneous strain, both compressive and tensile, results in decrease in the $\epsilon_2$ peak intensity and suppresses X/Y anisotropy (see Tables 1 and S3 and Figure 6a).

**II.IV.II. Strained δ_{6} Borophene.** Analogous to the $\beta_{12}$, $\omega_2$ for the $\delta_6$ allotrope can vary by a few electron volts with applied strain (0.85–3.4 eV for X-polarized light and 2.4–6.7 eV for Y-
polarized light), and strains significantly alter the X-/Y-
anisotropy, as shown in Tables 2 and S3. The trend in strain-
dependent X-/Y-anisotropy is not as clear for this structure
because of the larger deformation energy at high (6%) strain
and because of the nonplanar atomic structure. In general,
compressive (tensile) strains along y-axis increase (decrease)
anisotropy, which can be explained as due to the decreased
(increased) bond lengths and, therefore, increased (decreased)
delocalization along y-axis. For strains along x-axis, there is a
competition between change in buckling, which leads to
increased delocalization as the buckling is reduced and the
sheet becomes more planar (for tensile strain), and change in
bond lengths, which separates p₂ orbitals and reduces
delocalization. This is shown in the evolution of the charge
density for states near Γ and the position of the lowest energy of
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Table 2. Plasma Frequencies in δ₆ Borophene

| strain | ωₓ(X) of δ₆ structure, eV | ωᵧ(Y) of δ₆ structure, eV |
|--------|-------------------------|-------------------------|
| (−6, 6) | 2.02                    | 2.07                    |
| (−3, 6) | 0.85                    | 2.43                    |
| (−3, 0) | 1.84                    | 2.45                    |
| (−3, −3) | 2.33                   | 1.93                    |
| (−6, −6) | 1.97                   | 2.22                    |

The imaginary component of the dielectric function ε₂ in δ₆
borophene displays a weaker response to strain than in β₁₂.
The application of strain does however strongly influence the onset
of the rise in ε₂ and, therefore, absorption (shown in Figure S5b).
This strain dependence is to be expected based on the changes in the gap at Γ
and the position of the lowest energy of fully unoccupied band in the band structure, as shown in Figure 5. We predict that compressive strains along x, y, or xy
(homogeneous strain) directions increase the onset of absorption,
whereas tensile strains in the same directions decrease it. For the unstrained structure (0, 0), the onset of absorption is at 2.5 and 4.0 eV and the absorption peak is at 3.5
and 6.8 eV, for X- and Y-polarized light, respectively. The most
dramatic shift in the onset is seen with the application of homogeneous strain 6% strain; tensile strain (panel 6, 6) reduces the onsets of absorption to 1 and 3 eV (2 and 5 eV peak), whereas compression (panel −6, −6) increases the onsets to 3 and 4.5 eV (4 and 8 eV peak) for X- and Y-light polarizations, respectively.

Interestingly, at a value of strain of (−3, 6)%, there is a
qualitatively different behavior of ε₂ and absorbance (Figures 6b and S5b, respectively), which can be related to the charge
density. The local density of states shows a weak overlap of p₂ orbitals along the y-axis and consequently stronger bonding along the x-axis, whereas the density of states in the vicinity of E₀ is larger than that in the unstrained case, as shown in Figures 4 and S6. This results in larger number of states available for excitations in the vicinity of Fermi energy, therefore enhancing ε₂ at low energies. This demonstrates the sensitivity of absorption strength to modifications in charge density.

III. CONCLUSIONS

In summary, we have investigated the electronic and optical
properties of two proposed allotropes of freestanding monolayer boron (borophene) upon application of tensile
and compressive strains to simulate the influence of its
underlying substrate and assess the tunability of its optoelec-
tronic properties. We predict that the application of few percent
strain changes the total energy by <50 meV/atom, which we
expect will not compromise its structural integrity. Our DFT-
based calculations reveal that although borophene remains
metallic under up to 6% strain, the features of the band
structure can be significantly modified, and that the optical
properties of borophene strongly respond to small strains, a
feature that is correlated with enhancement of or decrease in
charge delocalization along different crystallographic directions
by the modification of bond lengths. Additionally, we demonstrate that the response of borophene to light is highly
dependent on the polarization direction of incoming light, an
anisotropy that can be tuned via strain. The ability to tune this
anisotropy may be utilized in optoelectronic applications such
as plasma-wave nanodetectors. This study demonstrates that strain can be utilized to tune the optoelectronic properties of
borophene, increasing the applicability of borophene in 2D
device architectures.

IV. METHODS

DFT and random phase approximation (RPA) calculations on the strained β₁₂ and δ₆ borophene structures were performed to
simulate the electronic and optical properties of borophene,
respectively. We utilized Quantum Espresso simulation suite, with the Perdew–Burke–Ernzerhof (PBE) approximation and Troullier–Martins norm-conserving pseudopotentials to
describe the core and nuclei of boron. To account for the
aperiodicity of the isolated monolayer, we include 12 Å of vacuum between periodic images along the direction perpendicular to borophene. Convergence of the total energy
was found to be better than 1 meV/atom for a plane wave
cutoff 100 Ry and k-point mesh of 36 × 20 × 1 and 36 × 60 × 1 for the β₁₂ and δ₆ structures, respectively, which corresponds to a k-point density of 2π × 0.01 Å⁻¹.

The structure of the β₁₂ and δ₆ unit cells was optimized within the periodic directions (xy-plane) to the accuracy of 0.01
meV/atom in energy and 1 meV/Å in force tolerance. The optimized unit cells were determined to be (a₀, b₀) = (2.936 Å, 5.087 Å), where a and b are the lattice vectors in x- and y-
directions, respectively, for the β₁₂ structure and (a₀, b₀) = (2.892 Å, 1.615 Å) for the δ₆ structure. Strained unit cells were constructed with 1% strain increments, with atomic positions
reoptimized. We label strain in x- and y-directions using such
notations: (εₓ, εᵧ) = \left( \frac{a − a₀}{a₀}, \frac{b − b₀}{b₀} \right) × 100%, with a negative
strain indicating a compression and a positive indicating a
tensile. The values of these lattice constants are given in Supporting Table S1. The deformation energy was computed with ±1% strain increments as Eₐₑₙ(εₓ, εᵧ) = Eₐₑₙ(εₓ, εᵧ) − Eₐₑₙ(0, 0). Figure 2 shows a heat map of the deformation
energies for 440 values of strain for each boron allotrope.
A detailed analysis of the electronic structure of strained borophene was performed for ±3 and ±6% of strain. For band structure calculations, the coordinate of high-symmetry points in \((k_x, k_y)\) space were as follows: \(\Gamma = (0.0, 0.0), X = (\pi/a, 0.0), Y = (0.0, \pi/b), S = (\pi/a, \pi/b)\). The density of \(k\)-points along chosen high-symmetry directions was \(2\pi \times 0.005 \text{ Å}^{-1}\). The work function for each strained structure is shown in Table S2. In a separate study, we have carefully analyzed the optoelectronic properties of unstrained freestanding \(\beta_{12}\) and \(\delta_b\) borophene and the accuracy of DFT within the local density approximation (LDA) for describing these properties. We found, by comparison to many-body perturbation theory calculations within the GW \(\beta\)-Bethe–Salpeter equation approximation, that DFT-LDA and RPA can accurately describe the band structure and optical absorption properties of borophene, respectively. These studies predict that the many-body interactions are negligible, possibly due to the free-electron-like nature of electrons in this system. Accordingly, we expect that accounting for many-body interactions will not qualitatively change our conclusions on strain dependence of optoelectronic properties of borophene.

We employ the RPA to calculate the complex dielectric function \(\epsilon_i + i\epsilon_s\) of strained boron allotropes. Intraband transitions are neglected in this work. We compute the optical absorbance\(^{92}\) as \(A = \frac{\omega}{c} \epsilon_i \times 100\%\) for 25 strained geometries ranging from −6 to 6% strain. Here, \(L\) is the thickness of the simulation cell in the \(z\)-direction, i.e., perpendicular to borophene, \(\omega\) is the energy of light, and \(c\) is the speed of light. To simulate the broadening of the dielectric function due to finite temperature, we used a Gaussian smearing of width \(0.2\) eV. For the 25 strained structures, the \(k\)-point mesh was kept at \(36 \times 20 \times 1\) and \(36 \times 60 \times 1\) for the \(\beta_{12}\) and \(\delta_b\) boron allotropes, respectively. Although this \(k\)-point mesh is sufficient for capturing strain-dependent trends in optoelectronic properties, a higher-density \(k\)-point mesh of \(180 \times 100 \times 1\) and \(180 \times 300 \times 1\) for \(\beta_{12}\) and \(\delta_b\) systems, respectively, was required to eliminate noise. Due to the high computational cost, we only used this dense \(k\)-point mesh to study the unstrained structures, with the results shown in Figure 3. Strain-dependent changes in \(\epsilon_i\) and absorbance are shown in Figures 6 and S5. Within the Quantum Espresso package,\(^{89}\), the bulk plasma frequency is evaluated as an integral \(\omega_p^2 = \frac{2}{\pi} \alpha \int_0^\infty \omega \epsilon_{\omega=\omega} (\omega) d\omega\), where \(\alpha\) and \(\beta\) indicate the directions \(x, y,\) or \(z\). At this resonance frequency, the electron loss function, which is proportional to \(\epsilon_2^2/(\epsilon_1^2 + \epsilon_2^2)\), is maximized. The computed plasma frequencies for strained borophene are summarized in Tables 1 and 2.

To better understand the enhanced anisotropy of \(\epsilon_2\) in selected strained geometries of \(\beta_{12}\) borophene, we calculated the local density of states (LDOS) near the Fermi energy by summing the square of the wave functions for all of the states with eigenvalues between energies \((E_p, E_p + 100 \text{ meV})\) and \((E_p - 100 \text{ meV}, E_p)\) for all \(k\)-points. The results are plotted in Figure S1. The slices of LDOS at 0.8 Å above the atomic plane are shown in Figure S2. LDOS plots for selected values of strain in \(\delta_b\) borophene are shown in Figures S3 and S4.

## ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01232.
