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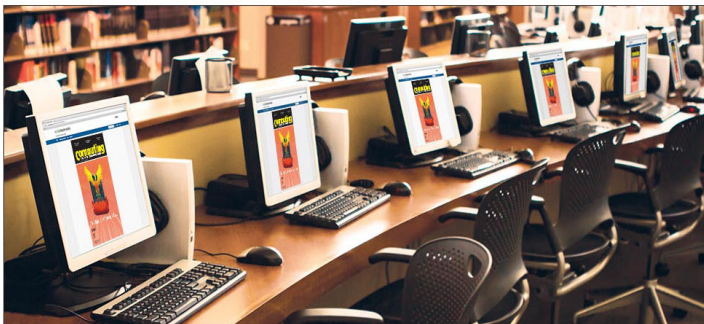
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## Variable range hopping electric and thermoelectric transport in anisotropic black phosphorus

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Black phosphorus (BP) is a layered semiconductor with a high mobility of up to  $\sim 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a narrow bandgap of  $\sim 0.3 \text{ eV}$ , and shows potential applications in thermoelectrics. In stark contrast to most other layered materials, electrical and thermoelectric properties in the basal plane of BP are highly anisotropic. To elucidate the mechanism for such anisotropy, we fabricated BP nanoribbons ( $\sim 100 \text{ nm}$  thick) along the armchair and zigzag directions, and measured the transport properties. It is found that both the electrical conductivity and Seebeck coefficient increase with temperature, a behavior contradictory to that of traditional semiconductors. The three-dimensional variable range hopping model is adopted to analyze this abnormal temperature dependency of electrical conductivity and Seebeck coefficient. The hopping transport of the BP nanoribbons, attributed to high density of trap states in the samples, provides a fundamental understanding of the anisotropic BP for potential thermoelectric applications. *Published by AIP Publishing*. [<http://dx.doi.org/10.1063/1.4985333>]

As an advanced energy harvesting technology, thermoelectrics is playing an increasingly important role in modern energy application, because it directly converts thermal energy to electricity with no moving parts.<sup>1</sup> Thermoelectric materials are usually narrow bandgap semiconductors, such as  $\text{Bi}_2\text{Te}_3$ ,  $\text{PbTe}$ , etc.<sup>2</sup> The heat-to-electricity energy conversion efficiency is a function of the dimensionless figure of merit,  $zT = S^2\sigma T/\kappa$ , where  $S$  is Seebeck coefficient,  $\sigma$  is electrical conductivity,  $T$  is absolute temperature, and  $\kappa$  is thermal conductivity of the material. Recent efforts have been focused on micro/nanostructuring of bulk materials to search for better thermoelectric materials,<sup>3,4</sup> because it is expected thermal conductivity can be reduced in low-dimensional materials when their size approaches the phonon mean free path, and their Seebeck coefficient may be also enhanced when the density of states is restructured by quantum confinement. The low dimensional materials, especially layer-structured two dimensional (2D) materials, such as transition metal dichalcogenides (TMDs), draw much attention in electronic applications.<sup>5,6</sup> In this context, these layered materials may also offer good thermoelectric properties, as their layer-structure may also be viewed as some kind of “natural nanostructuring.” Black phosphorus (BP) is a rediscovered layered semiconductor. It is found that BP has a high mobility of up to  $\sim 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Ref. 7) and a narrow bandgap of  $\sim 0.3 \text{ eV}$  (for thickness  $\geq 4 \text{ nm}$ ).<sup>8</sup> As a narrow bandgap semiconductor, BP has been evaluated for potential applications in 2D nanoelectronics.<sup>9</sup> It was reported that the Seebeck coefficient of BP is in the range of  $335\text{--}415 \mu\text{V/K}$  at  $300\text{--}385 \text{ K}$  for the bulk,<sup>10</sup> and reaches  $510 \mu\text{V/K}$  at  $210 \text{ K}$  with ion-gate tuning.<sup>11</sup> Theoretically, few-layer BP have

been predicted to be a promising thermoelectric material with a high  $zT$  when under stress or doping.<sup>12,13</sup> More interestingly, BP is a strongly anisotropic material even in the basal plane: the thermal conductivity is much higher along the zigzag than the armchair direction, while electrical conductivity shows the opposite anisotropy.<sup>14</sup> Choi *et al.*<sup>15</sup> demonstrated that the variable range hopping (VRH) dominates electrical transport in thin BP flakes ( $10\text{--}30 \text{ nm}$  thick). However, the BP flake crystal orientation was not specified in Choi and the coupling between the VRH process and the intrinsic anisotropy in BP is unclear. In this work, we elucidate and parameterize the VRH mechanism along the zigzag and armchair directions in BP. This was achieved by fabricating BP nanoribbons (thickness  $\sim 100 \text{ nm}$ ) along armchair and zigzag directions, respectively, and conducting temperature dependent measurements of electrical conductivity ( $\sigma$ ) and Seebeck coefficient ( $S$ ). Both  $\sigma$  and  $S$  increase as temperature rises, showing a behavior opposite to that of traditional semiconductors, which can be quantitatively explained by the VRH model. The hopping transport is attributed to existence of high density of trap states in the samples, which was further confirmed by artificially introducing more defects with high-energy particle irradiation.<sup>16</sup>

In BP, phosphorus atoms form a puckered honeycomb lattice with space group of  $\text{Cmca}$  (orthorhombic,  $a = 3.316 \text{ \AA}$ ,  $b = 10.484 \text{ \AA}$ ,  $c = 4.379 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ).<sup>17</sup> The schematic diagram of the crystal structure is shown in Fig. 1(a). A mechanically exfoliated BP flake is shown in Fig. 1(b), where the thickness is  $100 (\pm 2) \text{ nm}$  conformed by atomic force microscopy (AFM). The crystallographic orientations of the flake were confirmed by micro-Raman analysis, as the Raman signal depends on the angle between the laser polarization direction and the BP crystal orientation.<sup>18,19</sup> Figures 1(c)–1(e)

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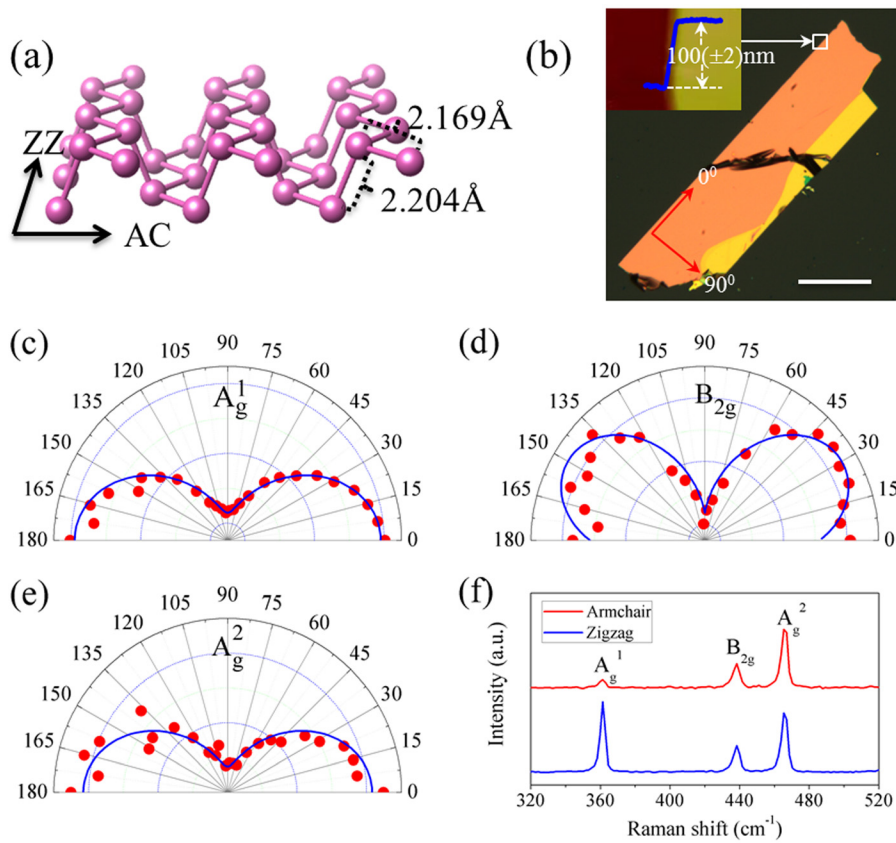


FIG. 1. Crystal structure and characterization of black phosphorus flakes. (a) Crystal structure: zigzag direction is paralleling to the atomic ridges and armchair perpendicular to atomic ridges; (b) optical image of a BP flake:  $0^\circ$  and  $90^\circ$  indicate the angle for Raman laser polarization directions. Inset is AFM image and height data, which show that the thickness of the flake is  $100(\pm 2)$  nm. The scale bar is  $50 \mu\text{m}$ . (c)–(e) Angular dependence of intensity of typical Raman peaks for  $A_g^1$  ( $361.4 \text{ cm}^{-1}$ ),  $B_{2g}$  ( $438.4 \text{ cm}^{-1}$ ), and  $A_g^2$  ( $465.5 \text{ cm}^{-1}$ ). Solid lines are theoretical fitting results; (f) normalized intensity of BP flakes for Raman laser polarization at  $0^\circ$  and  $90^\circ$  in (b), indicating the crystal orientation: zigzag is parallel to  $0^\circ$  and armchair along  $90^\circ$ .

show the angular dependence of the intensity for the most prominent Raman peaks:  $A_g^1$  ( $361.4 \text{ cm}^{-1}$ ),  $B_{2g}$  ( $438.4 \text{ cm}^{-1}$ ), and  $A_g^2$  ( $465.5 \text{ cm}^{-1}$ ), which were fitted by the theoretically predicted angular dependences. Figure 1(f) shows the normalized (to  $A_g^2$  mode) intensity of BP flakes.

BP nanoribbons were then fabricated with  $\sim 2 \mu\text{m}$  in width and  $\sim 35 \mu\text{m}$  in length using electron beam lithography. A second lithography was used to pre-deposit four-probe metal (Ti/Au) contacts onto each of the nanoribbons.

Individual nanoribbon was then dry transferred to bridge two suspended pads<sup>20</sup> for reliable electrical and thermoelectric measurements. To further reduce the electric and thermal contact resistance, Pt metal was deposited onto the four-probe points with focused ion beam (FIB) to bond the pre-deposited metal contacts with the underlying metal electrodes [Fig. 2(h)]. During this process, the nanoribbons were minimally perturbed, such that any strain, bending, and twisting of the samples can be maximally avoided. The use

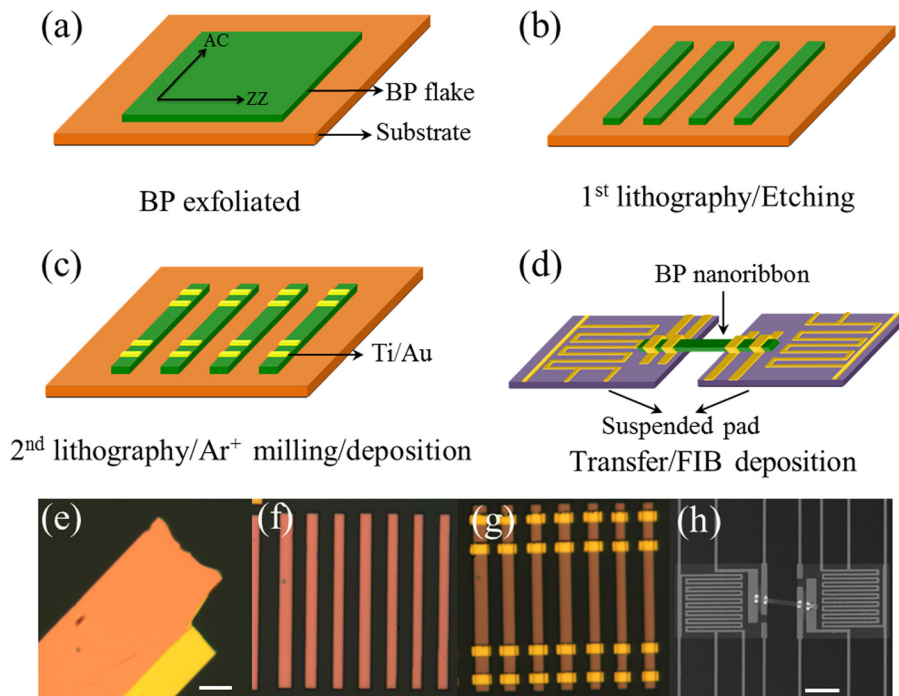


FIG. 2. Devices fabrication process. (a) BP exfoliated onto a  $\text{SiO}_2(250 \text{ nm})/\text{Si}$  substrate, then coated with PMMA; (b) the 1st electron beam lithography to tailor the nanoribbons; (c) the 2nd electron beam lithography to deposit Ti ( $10 \text{ nm}$ )/Au ( $70 \text{ nm}$ ) contacts; (d) dry transfer BP nanoribbon onto suspended pads, and deposit Pt for bonding it onto electrodes using FIB; (e)–(g) optical images of BP flake, tailored nanoribbons, and nanoribbons with pre-deposited Ti/Au; (h) SEM image of BP nanoribbons device after transfer and FIB deposition. The scale bar is  $20 \mu\text{m}$  in (e), (h).

of the suspended pads (as opposed to making devices directly on solid substrate<sup>21</sup>) helps to reduce any strain and substrate influence, as the nanoribbon body is suspended in vacuum and free to expand/shrink along its length direction. Moreover, the suspended pad method ensures a superior temperature control and sensing as heat leakage is minimized. Measurements using the suspended-pad method were described in previous reports.<sup>20,22,23</sup> All measurements were performed under low vacuum ( $<10^{-6}$  Torr) with radiation shield. (See the details of devices fabrication process and measurements in [supplementary material](#).)

Figures 3(a) and 3(c) show the temperature dependence of electrical conductivity and Seebeck coefficient of BP nanoribbons along the armchair and zigzag directions. Consistent with previous results,<sup>14</sup> these ribbons exhibit p-type conduction. The anisotropic ratio at room temperature is  $\sigma_{AC}/\sigma_{ZZ} \sim 2.2$  and  $S_{AC}/S_{ZZ} \sim 1.3$ . As a comparison, the anisotropic ratio of mobility and effective mass was reported to be  $\sim 1.5$  ( $=\mu_{AC}/\mu_{ZZ}$ )<sup>7</sup> at 300 K and  $\sim 0.16$  ( $=m_{AC}/m_{ZZ}$ ),<sup>24</sup> respectively. The thermoelectric transport is not intrinsic from the native band structure of BP, and the anisotropy of Seebeck does not necessarily match the band transport scenario. In the Mott's picture, the Seebeck is dominated by the differentiation of the density of states with respect to energy at the Fermi level; therefore, the anisotropy of that differentiation is responsible for the anisotropic Seebeck coefficient in BP. Meanwhile, in traditional semiconductors,  $\sigma$  and  $S$  generally shows opposite temperature dependence regardless of being degenerately doped or non-degenerately doped.<sup>25</sup> The fact that  $\sigma$  and  $S$  show the same trend with temperature points to unconventional charge transport, a charge dynamics that cannot be described by the conventional free electron (Drude) model in band transport.

Mott's variable range hopping (VRH) model was developed to describe hopping conduction among localized states with energies concentrated within a narrow band near the

Fermi level at relatively low temperatures.<sup>26–28</sup> The hopping process simultaneously takes into account thermally activated hopping over a potential energy barrier and phonon-assisted tunneling hopping between the localized states. The thermally activated hopping process is governed by the Boltzmann factor,  $\exp(-W/k_B T)$ , where  $W$  is the energy barrier between the localized state energies  $E_i$  and  $E_j$ . The tunneling probability is determined by the wavefunction overlap between localized states denoted as  $\exp(-2\alpha R)$ , where  $\alpha^{-1}$  is the effective radius of wavefunction of the localization states. Taken together, the hopping probability is written

$$P_{ij} = \nu_0 \exp\left(-2\alpha R_{ij} - \frac{W}{k_B T}\right), \quad (1)$$

where  $R_{ij}$  is the distance between the two localized states and  $\nu_0$  is the phonon frequency gauging interactions of the hopping carrier and the lattice. It follows that the electrical conductivity then depends on temperature as  $\sigma \sim \exp\{-1/T^{1/(d+1)}\}$ , and the Seebeck coefficient as  $S \sim T^{(d-1)/(d+1)}$ , where  $d$  is the dimensionality of the system. This model effectively explains the abnormal temperature dependencies of  $\sigma$  and  $S$ .

Here, the thickness of the BP nanoribbons is  $\sim 100$  nm, and it is much higher than the size of wavefunction of the localization states ( $\sim 25$  nm in BP, Ref. 15) and their average distance. Hence, the 3D VRH model was adopted to fit the electric and thermoelectric transport (see the comparison of 2D and 3D VRH fitting in the [supplementary material](#))

$$\sigma = \sigma_0 T^{-m} \exp\left(-\frac{A}{T^{1/4}}\right), \quad (2)$$

where  $\sigma_0$  is a pre-factor and  $m \approx 0.8$ .<sup>15,29,30</sup> If  $A$  is written as  $A = (T_0)^{1/4}$ ,  $T_0$  is related to the density of states at the Fermi level  $[D(E_F)]$  as  $T_0 = 18.1\alpha^3/k_B D(E_F)$ . In the same picture, the Seebeck coefficient is given as<sup>31</sup>

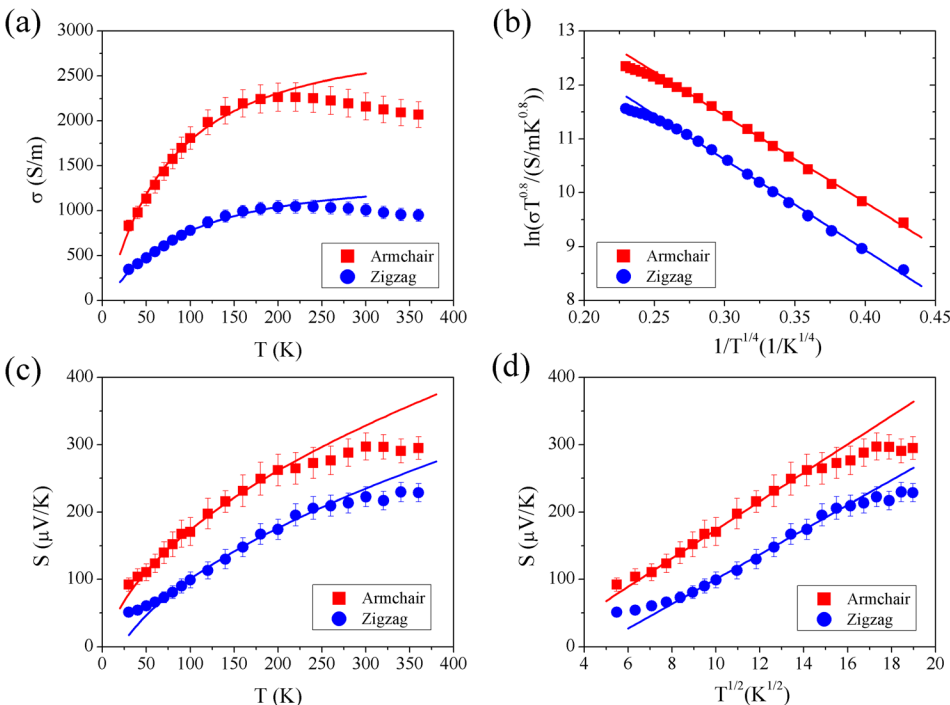


FIG. 3. Temperature dependence of electrical conductivity ( $\sigma$ ) and Seebeck coefficient ( $S$ ) of BP nanoribbons along the armchair and zigzag directions. Both the ribbons have thickness  $\sim 100$  nm. (a)  $\sigma$  versus  $T$  and (b)  $\ln(\sigma T^{0.8})$  versus  $1/T^{1/4}$ ; (c)  $S$  versus  $T$  and (d)  $S$  versus  $T^{1/2}$ . Solid lines are fitting results using 3D VRH model.

TABLE I. Fitting parameters of  $\sigma$  and  $S$  using the 3D VRH model.  $\sigma_0$ ,  $A$ , and  $B$  are fitted values from  $\sigma$  and  $S$ , respectively; we calculated  $T_0$ , and estimated Density of states [ $D(E_F)$ ] and  $dD/dE$  at the Fermi level, average hopping distance ( $R$ , 200 K) and hopping energy ( $W$ , 200 K), assuming  $\alpha^{-1} = 25$  nm.

	$\sigma_0$ ( $10^7$ S/mK <sup>0.8</sup> )	$A$ (K <sup>1/4</sup> )	$T_0$ (10 <sup>4</sup> K)	$B$ ( $\mu$ V/K <sup>3/2</sup> )	$R$ (200 K) (nm)	$W$ (200 K) (meV)	$D(E_F)$ ( $10^{17}$ eV <sup>-1</sup> cm <sup>-3</sup> )	$dD/dE$ ( $E = E_F$ ) ( $10^{19}$ eV <sup>-2</sup> cm <sup>-3</sup> )
Armchair	1.176	16.156	6.813	21.170	40.276	18.528	1.973	6.895
Zigzag	0.623	16.770	7.909	18.383	41.807	19.233	1.700	4.786

$$S = \frac{k_B}{2e} \left( \frac{3}{4\pi D(E_F)} \right)^{1/2} \left( \frac{2\alpha}{3} \right)^{3/2} \left( \frac{d \ln D(E)}{dE} \right)_{E=E_F} (k_B T)^{1/2}. \quad (3)$$

When temperature approaches zero,  $S$  scales as  $S = BT^{1/2}$ , where  $B$  is pre-factor.

The 3D VRH model was used to fit the data of  $\sigma$  and  $S$  for the armchair and zigzag nanoribbons, as shown in Figs. 3(b) and 3(d). The solid lines in Fig. 3 display the fitting results, and the fitting parameters are summarized in Table I. At  $T \lesssim 200$  K, the VRH model shows good fitting with the data.  $\sigma$  deviates from the VRH prediction at  $T \gtrsim 200$  K, probably due to thermal activated band transport, as the acceptor activation energy is  $\sim 18$  meV,<sup>32</sup> and acoustic phonons scattering grows to be competitive with the VRH process at high temperatures. When temperature goes below  $\sim 50$  K, the interactions among conducting electrons may need to be considered (the Efros model).<sup>31</sup> In this scenario, the Seebeck coefficient deviates from the Mott's picture and will approach a plateau with decreasing temperature, as observed in Fig. 3(c). Based on the parameters obtained from fitting  $\sigma$  and  $S$ , we also determine the density of states and slope of the density of states at the Fermi level, listed in Table I, assuming  $\alpha^{-1} = 25$  nm (Ref. 15). The average hopping distance  $R$  is estimated from  $R \sim 0.375(T_0/T)^{1/4}\alpha^{-1}$ . At 200 K, the hopping distance  $R$  is  $\sim 40.3$  nm in armchair and  $\sim 41.8$  nm in the zigzag direction. The related average hopping energy  $W$  between localized states is calculated from  $W \sim 3/(4\pi R^3 D(E_F))$ , and at 200 K, it is  $\sim 18.5$  meV and  $19.2$  meV along the armchair and zigzag direction, respectively, which are consistent with the thermal energy at 200 K ( $k_B T \sim 17$  meV). Although we do not have an independent way to analyze the anisotropy in these parameters in the VRH model, we take the conventional band transport picture as a comparison. In the band transport, the density of states is proportional to the electron effective mass ( $m^*$ )<sup>3/2</sup>. BP has a lower effective mass for holes along the armchair than

along the zigzag direction (by a factor of  $\sim 0.16$ ),<sup>24</sup> resulting in a lower (by a factor of  $\sim 0.06$ ) density of states in the armchair direction. We hypothesize that such trap states arise from native defects (atomic vacancies and interstitials) and impurities formed in the pristine BP flakes during the synthesis process. To independently test the validity of the VRH model, we artificially introduce more defects by irradiating the nanoribbons with 30 keV He<sup>2+</sup> ion beams. The irradiation at this energy would allow the ions to completely go through the nanoribbon, leaving behind uniformly distributed atomic vacancies and interstitials. This is because the projected length of the ion irradiation is  $\sim 340$  nm (by SRIM simulation), deeper than the nanoribbon thickness. It is assumed that the atomic vacancies created by the irradiation are similar with the original defects for the electron hopping, and the irradiation increases the density, but not wavefunction, of the localized defect states. The electrical transports of the pristine and irradiated BP nanoribbons are shown in Fig. 4. It is expected that ion irradiation would create more atomic defects and trap states that reduce the average hopping distance  $R$ . The average hopping distance  $R$  (at 200 K) is estimated to be  $\sim 35.9$  nm after irradiated with a high dose of  $1 \times 10^{14}$  ions/cm<sup>2</sup>, lower than that in the pristine sample ( $\sim 40.3$  nm) in Fig. 4(a). The density of states of traps ( $\sim 3.1 \times 10^{17}$  eV<sup>-1</sup> cm<sup>-3</sup>) at the Fermi level also becomes larger than in pristine sample ( $\sim 2.0 \times 10^{17}$  eV<sup>-1</sup> cm<sup>-3</sup>) after the irradiation. According to Eq. (3),  $S$  is inversely proportional to the density of states.  $S$  is indeed reduced by irradiation at higher doses, as shown in Fig. 4(b) for  $S$  at 298 K, 198 K, and 78 K. Therefore, it is clear that the electrical and thermoelectric transports in BP are indeed dominated by hopping among defect states.

In conclusion, we quantify in-plane anisotropic electrical and thermoelectric transports in black phosphorus along its armchair and zigzag directions. In both directions, the electrical conductivity and Seebeck coefficient show the same trend with temperature, which cannot be explained by conventional band transport mechanism. We show that the

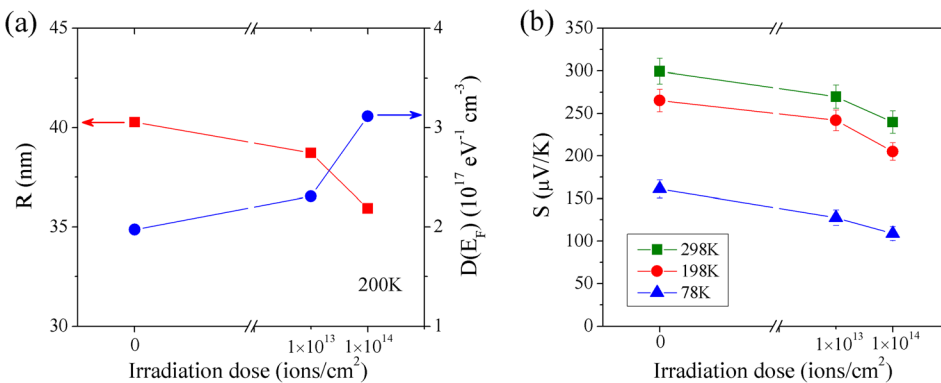


FIG. 4. Properties of a BP nanoribbon before and after He<sup>2+</sup> irradiation. (a) Irradiation dose dependence of average hopping distance and density of states of traps at the Fermi level at 200 K. (b) Irradiation dose dependence of Seebeck coefficient at 298 K, 198 K, and 78 K.

transport in BP is governed by hopping of holes among trap states distributed within a narrow band in the bandgap, and the density of trap states can be increased with energetic particle irradiation. As the electrical and thermal<sup>14</sup> transport all show strong but different anisotropies in the basal plane, BP may serve as a 2D material platform for designing exotic routing of heat and charge flows at the microscale. The intrinsic anisotropy in BP may also add insights to the idea of “phonon-glass electron-crystal” (PGEC)<sup>33</sup> in thermoelectrics. The figure of merit might be further improved in BP by carrier doping or alloying with As,<sup>34</sup> making BP a potential material basis for high-performance thermoelectrics.

See [supplementary material](#) for methods of BP nanoribbons fabrication, details of measurements, and comparison of 2D and 3D VRH fitting.

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The authors declare no competing financial interest.

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