by the deep-penetrating faults (8). Our interpretation suggests that the ongoing formation of the island of Taiwan is coupled with the subduction through shearing. The coupling might be spatially heterogeneous and evolve in time as subduction progresses to collision.

REFERENCES AND NOTES
15. Materials and methods are available as supplementary materials on Science Online.
25. C.-S. Ho, An Introduction to the Geology of Taiwan (Central Geological Survey of Taiwan, 1999).

ACKNOWLEDGMENTS
We thank W.-T. Liang, F. T. Wu, K.-L. Wang, T.-F. Yu, W.-S. Chen, and J. Suppe for helpful discussions and comments. T. Byrne helped clarify the geological implications in an early draft and provided inspiring discussion. We thank three reviewers for their

2D MATERIALS
Observation of tunable band gap and
anisotropic Dirac semimetal state in
black phosphorus

Jinmin Kim, Seung Su Baik, Sae Hee Ryu, Yeongsup Sohn, Soohyung Park, Byeong-Gyu Park, Jonathan Denlinger, Yeonjin Yi, Hyoun Joon Choi, Keun Su Kim

Black phosphorus consists of stacked layers of phosphorene, a two-dimensional semiconductor with promising device characteristics. We report the realization of a widely tunable band gap in few-layer black phosphorus doped with potassium using an in situ surface doping technique. Through band structure measurements and calculations, we demonstrate that a vertical electric field from dopants modulates the band gap, owing to the giant Stark effect, and tunes the material from a moderate-gap semiconductor to a band-inverted semimetal. At the critical field of this band inversion, the material becomes a Dirac semimetal with anisotropic dispersion, linear in armchair and quadratic in zigzag directions. The tunable band structure of black phosphorus may allow great flexibility in design and optimization of electronic and optoelectronic devices.

Two-dimensional (2D) atomic crystals have continued to show great potential for application in nanoscale devices (1). A key issue is controlling their electronic states to overcome the limit of natural properties. Graphene’s effectively massless state of charge carriers is a result of the conical band structure (2). However, the lack of a band gap (Eg) limits the on-off current ratio in planar field-effect transistors (3, 4), and it has been difficult to reliably achieve a sizable Eg without degrading its electronic quality (5–7). It would thus be desirable to realize a 2D system with a widely tunable Eg.

A potential candidate is few-layer black phosphorus (BP), a layered material of elemental phosphorus (5–7). The single-layer BP (or phosphorene) has a honeycomb network similar to graphene but is strongly puckered (armchair-shaped along c and zigzag-shaped along a in Fig. 1A), rendering its electronic state highly susceptible to external perturbations (7–22). The low-energy band structure of phosphorene can be approximated by a bonding and antibonding pair of mainly p3 orbitals (7, 12). The corresponding valence band (VB) and conduction band (CB) are located at the zone center and Γ7 states in Fig. 1B, with the predicted Eg of 0.7 to 1.6 eV (13–17). For multilayers, the interlayer coupling reduces Eg with increasing film thickness and reaches ~0.33 eV in bulk BP (11–14). The Eg of BP films and nanoribbons has been widely predicted to be tunable by strain (15–17) and electric field (17–21), the latter of which is more viable in gated devices. The electric field affects the real-space distribution of VB and CB states to be shifted in opposite directions to each other. Their potential difference and band mixing lead to a reduction in Eg, which is often termed the giant Stark effect (23–26). However, despite its potential importance for device applications, little is known experimentally about this effect on the surface of 2D semiconductors under a vertical electric field.

Here we report the realization of a widely tunable Eg in BP by means of the in situ deposition of potassium (K) atoms, the well-known technique to induce doping and electric field in 2D van der Waals systems (27). The K atoms on BP donate charges to the few top phosphorene layers, which are confined to form 2D electron gas near the surface (Fig. 1A, bottom). The band structure measured by angle-resolved photoemission spectroscopy (ARPES) at low K density is slightly n-doped with Eg greater than 0.6 eV (Fig. 1C). With increasing dopant density, the electric field from the ionized K donors gradually reduces Eg owing to the giant Stark effect, as supported by our density functional theory (DFT) calculations. Consequently, the electronic state of BP is widely and continuously tuned from a moderate-gap semiconductor to a band-inverted semimetal. At the critical dopant density of this band-inverted transition (21, 22), the electronic state becomes an anisotropic Dirac semimetal (Fig. 1D). This control mechanism of Eg should work in dual-gate BP devices for precisely balancing between high mobility and moderate Eg.

Figure 1, E to H, shows a series of ARPES spectra taken along the armchair direction kx with different dopant density near direct Eg. As expected for pristine BP (28, 29), in Fig. 1E there...
is a well-defined VB with a nearly parabolic dispersion and with a vertex at 0.15 eV below the Fermi energy $E_F$ (30). Assuming the reported $E_g$ of 0.33 eV (12), our pristine sample is slightly hole-doped, which explains p-type conduction in transport (12). We use a $k\cdot p$ perturbation formula (31), widely accepted to fit the band dispersion of narrow-gap semiconductors, to quantify the hole effective mass $m^*_h$. The best fit (white line overlaid) yields $m^*_h = 0.08 \pm 0.03 m_e$, where $m_e$ is the electron rest mass, in good agreement with theoretical calculations (12, 14).

Upon electron doping by the K deposition on the surface, the overall band structure rigidly shifts down toward high energies (fig. S2), so that the magnitude of $E_g$ can be directly measured by ARUPS. The energy shift of surface bands is accompanied by steep band bending toward the bulk (along $z$ in Fig. 1A) to form 2D electronic states in a few phosphorene layers, as confirmed by little $k_z$ dependence (31). At low dopant density just before the CB minimum drops below $E_F$ (Fig. 1F), the VB rigidly shifts down, and $E_g$ can be estimated at $\sim 0.6$ eV or slightly greater. This $E_g$ of 2D electronic states is smaller than that predicted for monolayer phosphorene (33–37) and is comparable to those predicted for few-layer phosphorene (0.3 to 1.0 eV) (33, 14). With further increasing dopant density, this $E_g$ gradually reduces (Fig. 1G) and becomes zero (Fig. 1H), which indicates a semiconductor-semimetal transition. At the critical dopant density for this transition, where the VB and CB touch each other, the band dispersion in the armchair direction $k_x$ becomes linear (Fig. 1H), whereas that in the zigzag direction $k_y$ remains nearly parabolic (Fig. S3).

The linear dispersion in $k_x$ can be more clearly identified in high-resolution ARPES data (Fig. 2A). The peak positions follow X-shaped linear bands of the VB (red) and CB (blue) with a crossing point (Fig. 2C) that is also revealed in the intensity map at the crossing energy (Fig. 2E). The spectral simulation with linear bands and finite broadening (31) (Fig. 2B) successfully reproduces the experimental data in Fig. 2A. This suggests that BP at the critical density has a spin-degenerate Dirac state as in graphene (3) and Dirac semimetals (31, 32–34), which can be stabilized by crystalline symmetry, as explained below. A linear fit yields the velocity of charge carriers $v_x = 5.1 \pm 0.9 \times 10^5$ m/s, which is about half of that in graphene (2). Fig. 2, D to G, shows a series of constant-energy intensity maps. The ARPES intensity of band contours is modulated by the matrix-element effect that reflects the symmetry of constituent wave functions in real space (5). The maps above and below the energy of the Dirac point $E_D$ (Fig. 2, D and F) show strong suppression along $k_x$ with respect to $k_y$. The resultant twofold symmetry of intensity patterns confirms that they originate from BP rather than from K. Taking this matrix-element effect into account, the band contours are oval-shaped with the aspect ratio $r \sim 1.9$, which is related to armchair-zigzag anisotropy in Fig. 1A. Around the contour, the band dispersion gradually changes from linear along $k_x$ to quadratic along $k_y$ (fig. S4). These results support the picture of the anisotropic band crossing (Fig. 1D),

![Fig. 1. Band structure and tunable $E_g$ of few-layer BP. (A) (Top) Atomic structure of BP. The solid square is the surface unit cell, and the interlayer distance is $\sim 5$ Å. (Bottom) Density profile of a 2D electron gas decaying along $z$ toward the bulk. (B to D) Band structure of (B) pristine BP; (C) BP in the initial stage of surface doping, and (D) BP at the transition to a zero-gap semimetal. The solid square in (B) indicates the surface Brillouin zone with high symmetry points marked by red circles. (E to H) Experimental band structure of BP taken at 15 K near $E_F$ along $k_z$ with dopant density marked at the upper right of each panel. The photon energy is 104 eV for $k_z$ at the Z point of the bulk Brillouin zone (29). The dopant density is estimated in units of monolayers from simultaneously taken K 3p core-level spectra (fig. S7). The white line overlaid in (E) is a fit to the VB with the k·p perturbation formula (31).](image)

![Fig. 2. Anisotropic Dirac semimetal state at the critical density. (A) High-resolution ARPES data taken at 15 K along the armchair direction $k_x$. (B) Corresponding spectral simulation with two linearly crossing bands and finite broadening (31). (C) Normalized momentum-distribution curves (0.05-eV steps from $E_F$) with their peak positions marked by open circles. Red and blue lines are linear fits to the VB and CB, respectively. (D to G) Series of ARPES intensity maps at constant energies (marked at the bottom of each panel), shown over a whole surface Brillouin zone (Fig. 1B).](image)
which is reproduced by DFT calculations, as shown below.

To systematically follow the evolution of the band structure, we display a 3D representation of ARPES spectra as a function of dopant density \( N \) in Fig. 3A. The constant-energy cut at \( E_v \) shows that the Fermi momentum \( k_F \) of the CB steadily increases. We estimate the electron concentration \( n \) based on Luttinger’s theorem as \( nk_F^2/\pi \) that corresponds to the area enclosed by oval-shaped contours at \( E_v \). We found that \( n \) is linearly proportional to \( N \) (fig. S6), which indicates monotonic charge transfer from dopants to phosphorene layers in the constant-momentum cut at \( k_z = 0 \). Diamonds and circles denote the positions of the VB maximum (\( E^v \)) and CB minimum (\( E^c \)), respectively. At the initial stage of doping, the \( \Gamma \rightarrow v \) state at \( E_c \) has rapidly shifted down until \( N \) is increased further, the center energy \( E_{v} = (E_{c} + E_{v})/2 \) 2 slows down, whereas the \( \Gamma \rightarrow v \) and \( \Gamma \rightarrow c \) states get progressively closer to each other and eventually cross at the critical density \( N_c \) = 0.36 monolayers (ML) (\( n = 8.3 \times 10^{13} \text{ cm}^{-2} \)), where band inversion occurs. The magnitude of \( E^c \) is calculated as \( E^c - E_v \), and is plotted as a function of \( N \) in Fig. 3B. As can be seen from the figure, \( E^c \) is widely and continuously tunable in the range of \( -0.6 \) to \( -0.2 \) eV.

We performed DFT calculations based on four-layer BP with a single K atom on each 2-by-2 surface unit cell (corresponding to \( N \sim 0.4 \text{ ML} \) in experiments). To effectively describe a lower K density, we increase the vertical distance \( d \) between K and BP (2.76 Å at equilibrium) such that the effect of K donors is gradually reduced without change in the supercell size (2D). A series of band calculations as a function of \( d \) reproduces key aspects of our experimental observations, the variation of \( E^c \) and resultant semimetal-semiconductor transition (red circles in Fig. 3B).

Furthermore, at \( E_{v} = 0 \) (\( d = 3.67 \) Å), the bands along \( k_x \) are linearly dispersing near \( E_{v} \), whereas those along \( k_y \) remain parabolic (Fig. 3C), as observed experimentally. \( N_c \) in Fig. 3B corresponds to the critical point of the band-inverted transition, where the topological invariant quantity \( Z_2 \) switches between 0 and 1 (2D), indicating an electric field generated by the ionized K donors. The \( E^c \) states, which have a positive effective mass along \( z \), freely move toward the positive electrical potential, whereas the \( E_v \) states, which have a negative effective mass along \( z \), are pushed within the body of the BP layers (2D). As stated above, this marked spatial separation of \( E^c \) and \( E_v \) states explains the variation of \( E^c \) by the giant Stark effect. Band calculations for four-layer BP under external electric field confirm the similar reduction in \( E^c \) with no change in \( E_v \) and the band crossover at the critical field of ~0.19 V/Å. From this value, we quantify the Stark coefficient \( S_{St} \) for four-layer BP as ~3 Å (24), which is comparable to those predicted for few-layer BP (19, 21) and transition metal dichalcogenides (25, 26). Because \( S_{St} \) is known to increase with film thickness (19, 21), the critical field for bulk BP (or thicker BP films) would be smaller than the practical dielectric strengths of SiO2 and A-BN. Our work thus demonstrates the giant Stark effect in BP as an efficient control mechanism of \( E^c \), which is generally attainable in 2D semiconductors and devices composed of these materials.

**Fig. 3. Quantitative analysis for the control mechanism of \( E^c \)** (A) A 3D representation of the band evolution as a function of \( N \), taken at 15 K. Diamonds and circles denote the positions of \( E^c \) and \( E^v \) respectively. (B) \( E^c \) as a function of \( N \). The negative gap in the shaded region represents the inverted gap at the \( \Gamma \) point. Overlaid red circles denote \( E^c \) from DFT band calculations where varying dopant density is simulated by changing the vertical distance \( d \) between K and BP (2D). (C) Theoretical band dispersions for K-doped BP films at \( d = 3.67 \) Å. (D) Partial charge densities of \( E^c \) and \( E^v \), points in (C), separated by a tiny gap of less than 10 meV. Light blue areas represent the isosurface, set to \( 1.76 \times 10^{-2} \text{ Å}^{-3} \), and its cross sections are shown in dark blue. Yellow and orange balls represent P and K atoms, respectively.

**REFERENCES AND NOTES**

Voltage-tunable circular photogalvanic effect in silicon nanowires

Sajal Dhara, Eugene J. Mele, Ritesh Agarwal

Electronic bands in crystals can support nontrivial topological textures arising from spin-orbit interactions, but purely orbital mechanisms can realize closely related dynamics without breaking spin degeneracies, opening up applications in materials containing only light elements. One such application is the circular photogalvanic effect (CPGE), which is the generation of photocurrents whose magnitude and polarity depend on the chirality of optical excitation. We show that the CPGE can arise from interband transitions at the metal contacts to silicon nanowires, where inversion symmetry is locally broken by an electric field. Bias voltage that modulates this field further controls the sign and magnitude of the CPGE. The generation of chirality-dependent photocurrents in silicon with a purely orbital-based mechanism will enable new functionalities in silicon that can be integrated with conventional electronics.

Unintentionally doped Si NWs (diameter, 100 to 150 nm; grown mostly along the (111) direction and some along the (112) direction) were used to make two-terminal devices by electron-beam lithography (section 1 in (16)). The CPGE was observed in different quantum-well (QW) geometries. For a fixed QW width and polarization of the laser (transverse electromagnetic (TEM00) mode), wavelength 680 nm, spot size ~2 µm) is incident at the metal-NW junction (see (16) for details in section 1 and figs. S1 to S5). The excitation energy (680 nm) of the laser is above the indirect bandgap of Si, and therefore contributions to the photocurrent from interband excitation (corresponding to the bulk of the Si NW) and the surface states on the [110] plane can be simultaneously present, albeit with different selection rules. Because of the geometrical anisotropy of NWs, the bulk contribution to photocurrent has two maxima with respect to linear polarization, owing to the preferential absorption of light polarized along the long axis (TM polarization) (17, 18) and in the perpendicular direction (TE polarization) to the NW at the metal-NW junction due to metal antenna effects (19, 20). In all of our experiments, we observed the usual linear polarization-dependent photocurrent variation as a function of the quarter-wave plate (QWP) [half-wave plate angle-dependent photocurrent variation is discussed in (16), sections 2 and 3 and fig. S8]. However, at the metal-NW junction, the most important contribution to the photocurrent came from the $P_{\text{circ}}$ dependence, which we observed by noticing that the maximum change in the photocurrent appeared at the left-handed (45°) and right-handed (125°) circular polarization, which has a variation of $\sin(2\alpha)$ irrespective of the physical orientation of the NW device (16), section 4 and fig. S9). As a result, the observed photocurrent at room temperature of a representative device at an applied bias of 1 V at two different spatial positions, in the metal-NW contact region (Fig. 1B), and on the bare NW (far away from the contacts, Fig. 1C) displayed different polarization dependence. At the metal-semiconductor contact, the photocurrent pattern repeated twice ($\sim \sin(2\alpha)$) as the QWP angle was changed from 0° to 360°, whereas on the NW, the pattern repeated four times ($-\cos(4\alpha + \phi)$, with a phase term $\phi$) depending on the physical orientation of the NW and laser polarization, suggesting a strong $P_{\text{circ}}$-dependent photocurrent confined to the contact region. The photocurrents can be fitted (Fig. 1B and C, solid line) with the expression $I(\alpha) = I_0 \sin(2\alpha) + I_1 \cos(4\alpha + \phi) + I_2$, where $I_0$, $I_1$, and $I_2$ are...
Observation of tunable band gap and anisotropic Dirac semimetal state in black phosphorus
Jimin Kim et al.
Science 349, 723 (2015);
DOI: 10.1126/science.aaa6486

This copy is for your personal, non-commercial use only.

If you wish to distribute this article to others, you can order high-quality copies for your colleagues, clients, or customers by clicking here.

Permission to republish or repurpose articles or portions of articles can be obtained by following the guidelines here.

The following resources related to this article are available online at www.sciencemag.org (this information is current as of September 2, 2015):

Updated information and services, including high-resolution figures, can be found in the online version of this article at:
http://www.sciencemag.org/content/349/6249/723.full.html

Supporting Online Material can be found at:
http://www.sciencemag.org/content/suppl/2015/08/12/349.6249.723.DC1.html

This article cites 36 articles, 6 of which can be accessed free:
http://www.sciencemag.org/content/349/6249/723.full.html#ref-list-1

This article appears in the following subject collections:
Physics
http://www.sciencemag.org/cgi/collection/physics