Nanoscopy Reveals Surface-Metallic Black Phosphorus. YOHANNES ABATE, Georgia State University — Nanolayer and two-dimensional (2D) materials............1 such as graphene...2,3, boron nitride...1,4, transition metal dichalcogenides...1,5–8 (TMDCs), and black phosphorus (BP)...1,9–13 have intriguing fundamental physical properties and bear promise of important applications in electronics and optics...9,14,15. Of them, BP...11,12,16 is a novel layered material that has been theoretically predicted...10 to acquire plasmonic behavior for frequencies below ~0.4 eV when highly doped. The electronic properties of BP are unique due to its anisotropic structure. Advantages of BP as a material for nanoelectronics and nanooptics are due to the fact that, in contrast to metals, the free carrier density in it can be dynamically controlled by chemical or electrostatic gating, which has been demonstrated by its use in field-effect transistors....9,14,15 Despite all the interest that BP attracts, near-field and plasmonic properties of BP have not yet been investigated experimentally. Here we report the first observation of nanoscopic near-field properties of BP. We have discovered near-field patterns of outside bright fringes and high surface polarizability of nanofilm BP consistent with its surface-metallic, plasmonic behavior at mid-infrared (mid-IR) frequencies below critical frequency \( \omega_m \approx 1176 \text{ cm}^{-1} \). This has allowed us to estimate plasma frequency \( \omega_p \approx 0.4 \text{ eV} \), carrier density \( n \approx 1.1 \times 10^{11} \text{ cm}^{-2} \) and the thickness of the surface metallic layer of \( \sim 1 \text{nm} \). We have also observed similar behavior in other nanolayer semiconductors such as TMDC MoS\(_2\) and topological insulator Bi\(_2\)Te\(_3\) but not in insulators such as boron nitride. This new phenomenon is attributed to surface band-bending and charging of the semiconductor nanofilms. The surface plasmonic behavior has been found for 10-40 nm BP thickness but absent for 4 nm BP thickness. This discovery opens up a new field of research and potential applications in nanoelectronics, plasmonics, and optoelectronics.

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