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Revealing antiferromagnetic transition of van der Waals MnPS$_3$ via vertical tunneling electrical resistance measurement

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ABSTRACT
Understanding the correlation between the electronic and magnetic properties of materials is a crucial step to functionalize or modulate their properties. However, it is not straightforward to electrically characterize magnetic insulators, especially large-bandgap materials, due to their high resistivity. Here, we successfully performed electrical measurements of a two-dimensional (2D) antiferromagnetic insulator, van der Waals-layered MnPS$_3$, by accounting for the vertical graphene/MnPS$_3$/graphene heterostructure. Antiferromagnetic transition is observed by the variance in electrical resistance from the paramagnetic to antiferromagnetic transition near $\sim$78 K in the vertically stacked heterostructure devices, which is consistent with the magnetic moment measurement. This opens an opportunity for modulating the magnetic transition of 2D van der Waals materials via an electrical gate or surface functionalization.

I. INTRODUCTION

It has been predicted theoretically that the long-range two-dimensional (2D) magnetic order is unstable for isotropic spin systems. However, it does not interfere with the search for anisotropic 2D magnetic orders. Recently, the 2D van der Waals (vdW)-layered magnetic materials of one-atom-thick monolayers are emerging with various ferromagnetic material families, such as Cr$_2$Ge$_2$Te$_6$, CrI$_3$, Fe$_2$Te$_5$, FeSiTe$_3$, VSe$_2$, V-doped WSe$_2$, and so on. It gives rise to opportunities to control the magnetic properties via electrical gating, external magnetic field, proximity effects, as well as the attempt of several spintronic devices.

While there has been immense interest in 2D vdW-layered ferromagnetic materials, 2D vdW-layered antiferromagnetic materials are also attractive, not only for their rich physics but also for their potential applications for spintronic devices. Up to date, the main 2D vdW antiferromagnetic families are based on the compounds of transition metals, phosphorus, and chalcogenides (MPChs) such as the MPS$_3$ and MPS$_4$ families, FePS$_3$, NiPS$_3$, and MnPS$_3$. Magnetic phase transition has been revealed by direct measurement methods, such as neutron scattering and vibrating-sample magnetometer (VSM). The transition can also be detected indirectly by using vibration spectroscopy, owing to the strong spin-phonon coupling when the magnetic phase appears. In addition, an abnormal variation in resistance with temperature appears...
at the magnetic transition state, which has been observed in both ferromagnetic and antiferromagnetic metals. Nevertheless, this observation is not clarified in magnetic insulators, especially the MPS family, due to their high resistivity and contact resistance.

Here, we report the observation of antiferromagnetic phase transition for 2D vdW-layered MnPS
\textsubscript{3} via electrical resistance measurement in an h-BN/Gr/MnPS
\textsubscript{3}/Gr heterostructure. The device is constructed vertically by using top and bottom multilayer graphene sandwiched by a MnPS
\textsubscript{3} flake to overcome its low conductivity. The resistance slope clearly exhibits a phase transition, which is consistent with the magnetic susceptibility measurement. Our work demonstrates that the vdW-layered antiferromagnetic insulators can be robustly observed by means of electrical measurement under gate control as well as surface chemical doping.

II. RESULTS AND DISCUSSION

A typical MnPS
\textsubscript{3} single crystal, on the order of several millimeters, was synthesized by the chemical vapor transport method [Fig. 1(a)]. The detailed fabrication method for crystal growth is described in Sec. IV. Three dominant peaks appear at 13.7\textdegree, 27.5\textdegree, and 56.8\textdegree from X-ray diffraction (XRD) patterns, corresponding to the (001), (002), and (004) planes, which is highly consistent with the reference pattern (PDF#01-078-0495). The high-intensity XRD peaks along the c axis indicate a high-quality single crystal of MnPS
\textsubscript{3} [Fig. 1(b)]. Figure 1(c) shows the Raman spectrum of bulk MnPS
\textsubscript{3} at room temperature with an exposure time of 2 min and a laser power of 500 \textmu W. Two dominant Raman modes, (A\textsubscript{g}, B\textsubscript{g}) and (A\textsubscript{g}), are present near 273.9 and 383.3 cm\textsuperscript{-1}, respectively. Moreover, several Raman peaks appear at 155.2, 223.6, 246.3, 566.8, and 579.7 cm\textsuperscript{-1} with smaller intensities, which are congruent with the vibration modes in previous works.

The chemical composition of the MnPS
\textsubscript{3} crystal was identified by three atoms of P, S, and Mn via photoelectron spectroscopy (XPS) [Fig. 1(d)]. The 2p peaks from the P atom can be assigned to 2p\textsubscript{1/2} near 132.8 eV and 2p\textsubscript{3/2} near 132 eV (left panel), and similarly, S 2p peaks are assigned to 2p\textsubscript{1/2} near 163.5 eV and 2p\textsubscript{3/2} near 162.3 eV (middle panel). In contrast to the single oxidation state of P and S, the oxidation state of Mn appeared in Mn\textsuperscript{2+} and Mn\textsuperscript{3+}. The XPS spectrum of Mn displays the presence of 2p\textsubscript{1/2} and 2p\textsubscript{3/2} peaks, which can be identified at, respectively, 653.5 and 652.3 eV for Mn\textsuperscript{3+} and Mn\textsuperscript{2+}, and 642.1 and 640.8 eV for Mn\textsuperscript{3+} and Mn\textsuperscript{2+} states (right panel). In addition, their satellite peaks at ~645.9 and 659.3 eV also emerged due to the interaction of 3p-3d at the optical absorption edge or Mn vacancies at the surface. The atomic ratio of Mn, P, and S is 16.07:22.31:61.62 from the XPS measurement, which is quite different from the expected value (1:1:3). While the P:S ratio is nearly 1:3, the amount of Mn is a little less than 1, indicating Mn vacancies in our synthesized MnPS
\textsubscript{3}. This may also be correlated with the appearance of two oxidation states of Mn. Nevertheless,
such defects do not strongly modify the magnetic transition temperature of MnPS₃, which appears at 78 K in the magnetic measurement later.

To study the electrical properties of MnPS₃, we first fabricated the lateral field-effect transistor configuration (see Fig. S1). The current is less than 1 pA under applied gate voltages from −30 to 30 V. The source-drain current is also too low to manifest sensible current flow. Such a high resistance of the MnPS₃ sample was also observed in other studies. It is worth noting that the lateral devices of MnPS₃ can often operate under high doping concentration via a liquid gate. However, such a highly doped regime may modulate the intrinsic properties of MnPS₃. Therefore, development of the proper device configurations is required to characterize the intrinsic magnetic properties of MnPS₃.

Figure 2(a) illustrates the schematic structure of a vertical h-BN/Gr/MnPS₃/Gr device with a multilayer MnPS₃ thickness. First, h-BN thin film was deposited on SiO₂/Si by the mechanical exfoliation method as a clean substrate. Then, the exfoliated bottom graphene, MnPS₃, and top graphene layers were successively deposited on the h-BN substrate via a dry transfer technique. Subsequently, the metal contact electrode of Cr/Au (10/50 nm) was deposited on the bottom and top graphene layers by the e-beam/thermal evaporation method, followed by e-beam patterning. Figures 2(b) and 2(c) show the optical image of the vertical device and its atomic force microscopy (AFM) topographic image, respectively. The bubbles caused by trapped ambient gas or moisture are inevitable due to the artificial transfer method for mechanical exfoliation. The inset in Fig. 2(c) indicates the height profile of the MnPS₃ flake, with the thickness estimated as approximately 5.6 nm.

The phase transition from antiferromagnetism to paramagnetism with temperature variance was observed by measuring the magnetic susceptibility of the sample (see Sec. IV). The in-plane and out-of-plane magnetic susceptibilities of multilayer MnPS₃ were measured as a function of temperature (Fig. 3, top and bottom panels). The similarity of the zero-field-cooling (ZFC) and field-cooling (FC) curves explains the well-ordered magnetic states. The derivative of out-of-plane magnetic susceptibility clearly visualizes the phase transition from paramagnetic at high temperatures to antiferromagnetic at low temperatures at approximately 78 K. A similar phase transition was observed for in-plane magnetic susceptibility. Therefore, the antiferromagnetic phase transition of MnPS₃ is clearly consistent with other reports. Interestingly, below the Néel temperature, the out-of-plane susceptibility is suppressed rapidly at 0.1 T, which is contrasted with the further rise of in-plane susceptibility. This special characteristic normally occurs in canted antiferromagnetic systems, where the spin orientation can be modulated by a high external magnetic field.

We now demonstrate that the magnetic phase transition with temperature can be identified by simply measuring the resistance of vertically stacked devices in which the MnPS₃ layer is sandwiched between the top and bottom graphene layers as the source and drain.
FIG. 3. Magnetic susceptibility of bulk MnPS₃ as a function of temperature for out-of-plane and in-plane directions at zero field cooling (ZFC) and field cooling (FC).

FIG. 4. Electrical resistance of vertical device (h-BN/Gr/MnPS₃/Gr) (left axis) and its derivative (right axis) as a function of temperature.

[see Fig. 2(a)]. The MnPS₃ layer is insulating and usually inaccessible to measure the current in the long in-plane channel due to its high resistance. In our case, however, the resistance of the vertically stacked device shrinks as the temperature increases, indicating semiconducting behavior (Fig. 4). An ultrathin layer of a few nanometers and quantum tunneling via the vdW gap in the vertical direction are the keys to the reduced resistance. Interestingly, the variation in resistance with temperature reveals a maximum value (minimum negative), which is distinct near 78 K. This critical temperature is coincident to the paramagnetic to antiferromagnetic transition in the magnetic moment curve in Fig. 3. This implies that the Néel temperature of the antiferromagnetic transition can be detected by a direct method via resistance measurement using the vertical device.

The change in the band structure between the no-spin and antiferromagnetic states could be the origin of the resistance change from the antiferromagnetic semiconducting state to the paramagnetic metallic state (Figs. S2–S4). In addition, the possibility of contributing to spin-phonon coupling and electron-phonon coupling cannot be excluded.

III. CONCLUSION

We have observed a strong correlation between the electrical and magnetic properties in MnPS₃. The change in resistance of the thin MnPS₃ flake with temperature was characterized by a vertical h-BN/Gr/MnPS₃/Gr device, which reveals the paramagnetic to antiferromagnetic transition of MnPS₃ near 78 K. This opens opportunities to study the magnetic phase transition of antiferromagnetic insulators by means of the vertical electrical transport probes in 2D vdW-heterostructure layered materials.

IV. METHOD

A. Synthesis of manganese phosphorus trisulfide (MnPS₃)

A stoichiometric amount of high-purity manganese, red phosphorus, sulfur (mole ratio Mn:P:S = 1:1:3, total amount ~2 g), and iodine (~20 mg) were mixed together and sealed in a quartz glass ampule under high vacuum (below $5 \times 10^{-3}$ Pa), then kept in a two-zone furnace (750 – 650 °C). After 10 days of heating, the ampule was cooled to room temperature and the single-crystal MnPS₃ was collected from the lower-temperature zone.

B. Sample preparation

The multilayer h-BN flake was mechanically exfoliated from bulk materials (2D semiconductors, USA) onto SiO₂ (300 nm)/Si wafers. The multilayer graphene and MnPS₃ flakes were mechanically exfoliated from bulk materials on polymethyl methacrylate (PMMA) and polyvinyl alcohol (PVA)-coated SiO₂ (300 nm)/Si wafers. To fabricate the bottom graphene layer, the multilayer graphene flake on the PPMA layer was transferred on the top of the multilayer h-BN flake on SiO₂ (300 nm)/Si wafers via a dry transfer technique. The PMMA layer was removed by acetone and
then rinsed with isopropyl alcohol. The multilayer MnPS$_3$ and other multilayer graphene flakes were successively transferred on the bottom graphene layer after the above transfer process. The electrodes were fabricated using an electron beam (e-beam) lithography method. The PMMA e-beam masks for the electrodes were patterned on the h-BN/Gr$_x$/MnPS$_3$/Gr$_y$ heterostructure flake. Finally, the electrode metals of Cr/Au (10/50 nm) were deposited using the e-beam/thermal evaporation methods, and lift-off was conducted in acetone.

C. Characterization

The topography of the sample was examined using AFM (E-sweep/Nano Navi) in noncontact mode. An optical micrograph for the bright-field mode was obtained by an optical microscope (100X, 0.9 NA, ZEISS, Axio Imager 2). Raman spectroscopy was measured under ambient conditions by using a laboratory-made confocal microscope system with 514-nm laser excitation, an objective lens (a numerical aperture of 0.95), and a laser power of 500 $\mu$W. The Raman signals were recorded with a spectrometer and a cooled charge-coupled device camera. The crystallographic structure analysis was carried out by employing an X-ray diffractometer (Rigaku, Smart Lab, Cu Ka radiation at 1.5418 Å, 45 kV, and 200 mA). X-ray photoelectron spectroscopy was examined by using an instrument (ESCA2000, VG Microtech, England) with an Al-Ka radiation source (1486.6 eV).

D. Electrical measurement method

All electrical measurements were performed with a Keithley 4200 Semiconductor Analyzer inside Quantum Design PPMS.

E. Magnetic measurement method

The magnetic measurements were performed in Quantum Design PPMS with a vibrational sample magnetometer (VSM) by increasing the magnetic field to 9 T. First, the sample at room temperature was cooled to a low temperature (2 K) without a magnetic field. The susceptibility of the sample was measured from low temperatures to 350 K with a field of 0.1 T, called zero field cooling (ZFC). The sample was then cooled with a magnetic field to low temperatures again, and the susceptibility was measured from low temperatures to 350 K with the same magnetic field, called field cooling (FC). The in-plane and out-of-plane susceptibilities were each measured independently.

SUPPLEMENTARY MATERIAL

See the supplementary material for the lateral field-effect transistor devices and details of density functional theory calculation of the electronic band structure of MnPS$_3$.

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