Gate-tunable black phosphorus spin valve with nanosecond spin lifetimes

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Two-dimensional materials offer new opportunities for both fundamental science and technological applications, by exploiting the electron’s spin. Although graphene is very promising for spin communication due to its extraordinary electron mobility, the lack of a bandgap restricts its prospects for semiconducting spin devices such as spin diodes and bipolar spin transistors. The recent emergence of two-dimensional semiconductors could help overcome this basic challenge. In this letter we report an important step towards making two-dimensional semiconductor spin devices. We have fabricated a spin valve based on ultrathin (~5 nm) semiconducting black phosphorus (bP), and established fundamental spin properties of this spin channel material, which supports all electrical spin injection, transport, precession and detection up to room temperature. In the non-local spin valve geometry we measure Hanle spin precession and observe spin relaxation times as high as 4 ns, with spin relaxation lengths exceeding 6 μm. Our experimental results are in a very good agreement with first-principles calculations and demonstrate that the Elliott–Yafet spin relaxation mechanism is dominant. We also show that spin transport in ultrathin bP depends strongly on the charge carrier concentration, and can be manipulated by the electric field effect.

Electron spin is an important degree of freedom which can complement charge information in storage and logic devices1–3. For spin-based electronics, it is essential to have materials with long spin relaxation times at room temperature1. With respect to the material selection, semiconductors in particular offer new opportunities that are unfeasible in metal-based spintronics devices. These include: doping by the electric field effect and gate-controlled amplification/switching actions4. The boom of semiconductor spintronics started with the demonstration of electrical spin injection into GaAs by R. Fiederling et al., followed later by H. Ohno and colleagues5–8. I. Appelbaum and his colleagues further fostered this by adding silicon (Si) into the spintronics materials family7. More recently two-dimensional (2D) materials such as graphene have captured the interest of scientists on the grounds of their high electron mobility. As graphene has been investigated extensively, the first demonstration of room-temperature spin injection by N. Tombros and colleagues9. Remarkable spin lifetimes of up to ~10 ns have been reported recently, making graphene suitable for spin communication channels10. However, the zero-bandgap nature of graphene does not allow charge and spin conductance to be fully suppressed6. This makes graphene less suitable for spin rectification or amplification, and has triggered the search for alternative 2D semiconductor materials, such as transition-metal dichalcogenides and black phosphorus (bP). These materials have bandgaps in the range of 1–3 eV, which matches both Si and GaAs11,12. Their electronic densities can be tuned between the n and p regimes (without affecting the intrinsic properties of these materials), allowing for diode and transistor actions unthinkable for graphene. In addition, 2D semiconductors absorb light efficiently enough even to enable opto-spintronics devices13. Finally, and in contrast to their bulk counterparts, the 2D materials are susceptible to proximity effects and are expected to become ferromagnetic in the proximity of ferromagnetic insulators14. Optical Kerr rotation microscopy measurements suggest that long spin lifetimes up to room temperature are possible in transition-metal dichalcogenides13,15. All of the above make a strong case for pursuing 2D semiconductor spintronics.

Black phosphorus is a relatively new member in the family of 2D materials and has already been shown to be an excellent material for charge-based applications12,15. Its sizeable direct bandgap and room-temperature mobilities on the order of 1,000 cm2 V−1 s−1 (ref. 17) also make it a promising spintronics material. Moreover, phosphorus is a light element with the spin–orbit (SO) interaction strength of its p orbitals being a few tens of meV (ref. 18). Similar to Si, it is a centrosymmetric material and Dyakonov–Perel spin relaxation is expected to be inhibited19. The Elliott–Yafet (EY) mechanism remains as the primary spin scattering mechanism20 and, hence, the recent report by G. Long et al.17 on very high electron mobilities suggests long spin relaxation lengths as well.

Here, we demonstrate that the necessary conditions for 2D semiconductor spintronics—that is, electrical spin injection, transport and detection up to room temperature—can all be realized in ultrathin bP devices. By taking advantage of the recent advances in van der Waals heterostructure fabrication methods, we fabricate non-local spin valve devices by fully encapsulating bP with hexagonal boron nitride (BN) layers. The BN/bP/BN structure is formed under an inert gas environment ensuring that the surfaces of bP are never exposed to air (Fig. 1a)21. The details of device fabrication and crystal growth are given in Methods. The optical image of a typical device after the deposition of ferromagnetic contacts is shown in Fig. 1b. The bottom BN (BNx) layer and the top BN (BNy) layer have crucial and distinct roles. The bottom BNx

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has been utilized as a substrate to achieve high electronic mobilities in bP by minimizing substrate-related scattering sources\(^{17}\). The ultrathin top BN\(_T\) layer has two purposes. First, it protects bP from degradation upon air exposure. Hence, this prevents the formation of chemisorbed species at the interfaces that can significantly limit the charge and spin injection\(^{21}\). It protects bP also from polymer residues formed during the device fabrication process, which has been proposed to be the source for spin relaxation in graphene\(^{22,23}\).

Equally important, this layer acts as a tunnel barrier for efficient spin injection into bP\(^{24}\). We limited the thickness of BN\(_T\) to only three layers such that it is sufficiently thin to form only a low barrier\(^{7}\). We studied a total of seven samples with thicknesses ranging from 2 nm to 10 nm. For all devices with bP thickness of 5 nm or thicker, we observed qualitatively a very similar behaviour. Here, we represent results obtained in three different junctions of the ~5-nm-thick bP sample, labelled as device A, device B...
Figure 2 | Electronic spin transport and Hanle spin precession measurements. a, Non-local signal as a function of the in-plane magnetic field. Black and red horizontal arrows represent the sweeping directions of the magnetic field. Vertical arrows represent the directions of the relative magnetization of the injector and detector electrodes. The slightly different non-local resistance signal observed at opposite sweeps is sample dependent and could be due to the different switching of the additional domains in ferromagnetic contacts present at the sides of the bP flake. b, Non-local signal as a function of the perpendicular magnetic field. Measurements are performed with an injected current of 0.5 μA at 100 K and $V_{BG}$ is fixed to 30 V. The red spheres with arrows in the schematics represent the precession of spins under the externally applied magnetic field.

and device C. The separation between injector and detector electrodes in devices A, B and C are 2.7 μm, 1.5 μm and 1.4 μm, respectively. All three devices exhibit similar low-temperature and room-temperature field effect mobilities of ~1,500 cm² V⁻¹ s⁻¹ and ~800 cm² V⁻¹ s⁻¹, respectively. Unless otherwise stated, the results shown are from device A. It is important to note that bP crystals which cleave into narrow stripes with long straight edges have been selected intentionally. This avoids additional etching steps and ensures that the spin drift diffusion is along the zigzag direction. Angular-dependent Raman measurements confirm that the long straight edges of the crystal are indeed along the zigzag direction. The latter is also known to have a higher charge mobility than the armchair direction (Fig. 1c). A key element of a semiconducting spin valve device is a high-quality tunneling barrier. It should exhibit a parabolic $V_{SD}$ dependence and a weak temperature dependence. Hence, prior to any spin transport measurements, we first characterize the charge transport properties. Figure 1d shows the $V_{SD}$ dependence of $I_{SD}$ at 2.4 K. We observe highly nonlinear $I_{SD}$-$V_{SD}$ Characteristics. Moreover, we observe nearly temperature independent $I_{SD}$-$V_{SD}$ (Fig. 1d inset). A final confirmation that the top BN₄ layer indeed acts as a high-quality, pinhole-free tunnel barrier is the scaling of the non-local resistance as a function of the channel conductance (Fig. 3d).

Interestingly, the $V_{BG}$ dependence of $I_{SD}$ at fixed $V_{SD}$ values exhibits a strong n-type conduction, as shown in Fig. 1e. It is in sharp contrast to the device characteristic of the adjacent junction without the BN₄ layer where typical strong p-type conduction is observed. It has been recently predicted that BN could decrease the effective work function of Co (ref. 27). It has been also shown theoretically that BN can donate electrons to bP (ref. 28). Either one of these effects could explain the dominant n-type behaviour, but the details will have to be discussed elsewhere. Last, but not least, the comparison of the $I_{SD}$-$V_{BG}$ curves of regions with and without BN shows that even such ultrathin BN layers can indeed fully encapsulate the region of interest and provide hysteresis-free transport characteristics at room temperature (Fig. 1e inset).

Now we turn our attention to spin transport measurements performed at low temperature, since in bP the charge mobility increases strongly with decreasing temperature. Here, a spin-polarized charge current is applied between electrodes 1 and 2 and a non-local voltage is measured between electrodes 3 and 4 (Fig. 1a). as a function of in-plane field $B_{||}$ at fixed gate voltage. As long as the channel is in the ‘on state’, we observe a similar behaviour for all $V_{BG}$ and all $T \leq 100$ K. Figure 2a shows a representative non-local spin valve signal measured at $T = 100$ K and $V_{BG} = 30$ V. Additional measurements are shown in the Supplementary Information. In Fig. 2a, as the magnetization directions of the ferromagnets are switched, the spin accumulation changes, giving rise to a non-local, bipolar spin signal with a change in the non-local resistance of $\Delta R \approx 15 \Omega$.

The magnetic origin of the signal is confirmed by means of Hanle spin precession measurements (Fig. 2b). For such measurement, the magnetization directions of the injector and detector electrodes are first kept parallel (antiparallel) to each other by applying an in-plane magnetic field. Then this field is removed and a magnetic field sweep perpendicular to the thin film plane ($B_{\perp}$) is performed (Fig. 2b). We observe a clear spin precession signal for both parallel and antiparallel configurations. The signal decreases (increases) for the parallel (antiparallel) configuration with increasing field, and can be fitted with the solution of the Bloch equation,

$$R_{NL} = \int_{0}^{\infty} \frac{1}{\sqrt{4\pi D_{T}t}} \exp \left( \frac{-L^2}{4D_{T}t} \right) \exp \left( \frac{-t}{\tau_{S}} \right) \cos(w_{L}t) \, dt$$

where $L \approx 2.7$ μm is the separation between the electrodes (centro-centre distance) and $w_{L}$ is the Larmor frequency. This gives a spin relaxation time of $\tau_{S} \approx 3.2 \pm 0.2$ ns, a spin diffusion constant of $D_{S} \approx 0.012 \text{ m}^2 \text{s}^{-1}$, and hence, a spin relaxation length of $L_{S} \approx 6.2$ μm. Note that $D_{S}$ extracted from such Hanle measurements is in good agreement with the value obtained from field effect mobility measurements. These spin transport parameters are very encouraging. We first note that despite having more than one order of magnitude lower mobility than state-of-the-art graphene spin valves (~20,000 cm² V⁻¹ s⁻¹) (ref. 10), $\tau_{S}$ in bP is comparable in order of magnitude.

Next, we study the magnitude of the non-local signal $R_{NL}$ itself. We observe that $V_{NL}$ increases linearly with increasing $I_{SD}$ up to 60 μA (Fig. 3b). Most of our measurements are performed with much lower $I_{SD}$ values of ~5 μA, making effects related to Joule heating negligible. We further note that although there is a sample to sample variation, we observe in all our devices a non-local signal of $R_{NL} \gg 1 \Omega$, which in one case even reaches ~320 Ω (Fig. 3c, see also Supplementary Information). At low temperature, these values compare favourably with what has been observed for...
On the other hand, temperature-dependent measurements at fixed gate bias are much less prone to extrinsic and interface related effects. Here, we discuss representative data at $V_{BG} = 30\,\text{V}$ and note that a similar behaviour is reproduced at other gate biases (see Supplementary Information). Fortunately, and unlike in graphene, $\tau_S$ in BP shows a discernible temperature dependence, and hence its correlation with momentum relaxation time ($\tau_P$) can indeed be used to identify the limiting spin dephasing mechanism. Here we determine both $\tau_S$ and $\tau_P$ directly from Hanle measurements, but we also note that the $T$ dependence of $\tau_P$ by independent four-terminal charge transport measurements is comparable to the one extracted from Hanle measurements\(^{33,37}\) (see also Supplementary Information).

Figure 4a shows the temperature dependence of both $\tau_S$ and $\tau_P$ for devices A and C. In both devices, $\tau_S$ is nearly temperature independent between 2.4 K and 60 K, and decreases with increasing temperature. The extracted $\tau_S$ at 2.4 K is $\approx 3.8\,\text{ns}$ (4.8 ns) in device A (C) and decreases to $\approx 2.2\,\text{ns}$ (0.9 ns) at 250 K. Remarkably, this behaviour is qualitatively very similar to the temperature dependence of $\tau_P$. Also here, $\tau_P$ is nearly temperature independent up to 60 K and decreases monotonically from $\approx 225\,\text{fs}$ (165 fs) to $\approx 135\,\text{fs}$ (48 fs) with increasing temperature. The latter behaviour is not unique to our devices, and has been already widely reported for BP field effect transistors\(^{12,17}\). Plotting $\tau_P/\tau_S$ versus $T$, we see that $\tau_P$ is an almost linear function of $\tau_S$ (Fig. 4a bottom), pointing to a mainly EY-type spin relaxation mechanism over the entire temperature range. Such a behaviour has so far been reported only in metals; first by M. Johnson & R. H. Silsbee in aluminium\(^ {34}\), which was later also confirmed by F. J. Jedema and colleagues\(^ {35}\).

In this mechanism at low temperature, electrons can flip their spins due to the spin–orbit interaction coming from the host lattice, and impurity scattering providing momentum scattering. At higher temperatures, phonons start to dominate the spin relaxation mechanism. Our results are the first clean demonstration of the EY mechanism in a 2D material.

To shed more light on the $\tau_S$ versus $\tau_P$ result, we have performed systematic first-principles calculations of the spin relaxation rates which would be expected from the EY mechanism\(^ {35,36}\) for BP; details are discussed in Supplementary Information. In particular, we have calculated the spin-mixing probability $b^2$, which gives the
probability to find, say, the electron with a spin down if the state has the average spin pointing up. The spin-mixing probability is non-zero due to spin–orbit coupling. Since in the presence of space inversion symmetry the Bloch states are doubly spin degenerate, the calculation of \( b^2 \) involves making linear combinations of the states to diagonalize the Pauli spin matrix representing the chosen spin direction. With this, \( \tau_s \) can be calculated using

\[
\frac{1}{\tau_s} \approx \frac{b^2}{\tau_P}
\]

where \( \alpha \) is a prefactor of the order 1, being estimated up to 4, depending on the details of the impurity or phonon scattering. The momentum relaxation time \( \tau_P \) is taken from the experiment directly. We stress that the spin–orbit coupling involved is that of the host lattice (bP) only, and not of the scatterers. The presumed light scatterers (and phonons as well) yield momentum randomization only, which is necessary for spin relaxation.

The calculated magnitudes of \( b^2 \) are about \( 4 \times 10^{-3} \) for the electron spins oriented along the zigzag and armchair directions (see Supplementary Information). The extracted experimental value, using \( b^2 \approx \tau_P/\tau_s \) (taking \( \alpha \approx 1 \) from the temperature dependence in Fig. 4a, \( b^2 \) is about \( 6 \times 10^{-3} \)). Considering the uncertainty in \( \alpha \), the agreement between experiment and theory is excellent. Our theory also predicts that the spin relaxation rate is highly anisotropic—expected to be 50% higher if the injected spin is perpendicular to the phosphorene planes. For holes, the spin relaxation rate should be almost twice that of electrons, with the anisotropy reaching 100% (see Supplementary Information). Similar anisotropies were predicted for anisotropic metals. Note that since the spin in our Hanle experiment precesses in the phosphorene plane, we take the average values of \( b^2 \) for the zigzag and armchair directions (although the in-plane anisotropy is very weak (see Supplementary Information)).

Finally, we study spin transport at room temperature. Note that the (spin) signal to noise ratio increases above 250 K due to a decrease in charge mobility. Nevertheless we observe a clear spin switching signal at slightly lower \( V_{BG} = 20 \) V. The spin signal becomes much cleaner in Hanle precession measurements (Fig. 4b). We reliably extract a \( \tau_s \) of \( 0.7 \) ns with a \( \lambda_s \) of \( 2.5 \) \( \mu \)m. This result is important since spin transport measurements in bulk semiconductors at high temperatures in the four-terminal non-local geometry are very rare. (There are various reports utilizing three-terminal geometry to study room-temperature spin-dependent transport). Especially our observation of a \( R_{NL} \) four orders of magnitude higher compared to what has been measured in Si (~1 mΩ) makes bP a promising semiconductor material for spintronics studies and applications. In future experiments, such large spin signals and long spin lifetimes in conjunction with the intrinsic origin of the spin relaxation mechanism will allow one to identify unambiguously the impact of the anisotropic crystal structure of bP on spin transport. If confirmed, the latter has the potential to provide directional control of spin transport. Furthermore, these properties also make bP an exciting alternative to graphene for studying proximity effects in highly interacting 2D van der Waals heterostructures. From a technology point of view, its semiconducting nature would finally also make 2D materials attractive for basic device concepts such spin diodes or spin transistors.

**Methods**

Methods, including statements of data availability and any associated accession codes and references, are available in the online version of this paper.

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Author contributions
B.O. initiated and coordinated the work. A.A. and B.O. designed the experiments. A.A. and J.Y.T. fabricated the samples. A.A. and B.O. designed the experiments. A.A. and B.O. performed transport measurements. K.W. and T.T. grew the hBN and hP crystals. M.K., M.G. and J.F. provided the theoretical work. All authors discussed the results and wrote the manuscript.

Additional information
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Competing financial interests
The authors declare no competing financial interests.
Methods

Device fabrication. Our device fabrication starts with the transfer of an ultrathin black phosphorus (bP) crystal on a ∼20 nm hexagonal boron nitride (BN) crystal by following the method developed by X. Cui and colleagues45. This bP/BN stack is encapsulated with another few layers of BN crystal. The entire transfer process has been completed under an inert gas environment, ensuring that the surface of bP was never exposed to air21. The final stack is annealed at 250 °C for 6 h under high-vacuum conditions to remove the bubbles formed during the transfer processes. This results in cleaner interfaces between 2D layers, and hence improves the bonding of bP with BN layers. We note that devices that did not undergo this annealing process show very low conductivity, most likely due to the low charge injection efficiency. A standard electron beam lithography technique is employed to create the electrode masks, which are purposely aligned along the armchair direction of the bP flake. This process is followed by the formation of Co/Ti (30 nm/5 nm) electrodes under ultrahigh vacuum conditions (∼5 × 10⁻⁷ torr). The deposition rate for both Co and Ti layers is ∼0.5 Å s⁻¹. The widths of the contact electrodes were varied from 400 nm to 1,000 nm to ensure different coercive fields. To minimize additional processing steps, we choose a single metal deposition step to form the ferromagnetic electrodes. To preserve the shape anisotropy, we introduce a number of sharp kinks in the electrode shape (see Fig. 1b), which prevents magnetization reversal due to domain wall motion. However, in bP, due to the additional height when compared to graphene, there are now sections in the device where the magnetization of the ferromagnetic contact is no longer collinear with an applied in-plane field. This design works well at low temperature and room temperature for Hanle precession measurements, but non-local magnetoresistance measurements at room temperature are noisier.

Growth. BN single crystals were obtained by using the temperature gradient method under high pressure and high temperature. Typical growth conditions were 3 GPa and 1,500 °C for 6 h. A solvent of the Ba–BN system was used to obtain high-purity crystals12. The source of BN crystals was heat treated so as to reduce oxygen impurities at 2,000 °C under a nitrogen atmosphere. The recovered BN crystals were treated by strong acid (hot aqua regia) to remove residual solvent and washed with dilute water to supply them for the exfoliation process.

bP crystals were obtained by the melt growth process under high pressure. Typical growth conditions were 2 GPa and 1,200 °C with slow cooling of 1 °C min⁻¹. The starting material of bP crystal (SN) was encapsulated in a BN capsule under an Ar atmosphere. The recovered bP crystals were mechanically removed from the BN capsule and then used for the exfoliation process. We note that similar high-quality charge and spin transport are also achieved with the crystals purchased from HQ Graphene company, the Netherlands.

Calculations. The electronic structure properties of black phosphorus were calculated within density functional theory using modern state-of-the-art codes. The crystal structure parameters were taken from X-ray diffractometry46. The atomic positions were further relaxed in all directions using the quasi-Newton variable-cell scheme as implemented in the Quantum Espresso package48, assuming for the force a convergence threshold of 10⁻⁴ Ry/a.u. with a total energy convergence condition of 10⁻¹ Ry/a.u. 217 k-points were used in sampling of the irreducible Brillouin zone wedge. A norm-conserving pseudopotential with the PBesol exchange–correlation functional47 was employed. For the kinetic energy cutoff we used 70 Ry and 540 Ry for the wavefunction and charge density, respectively.

The electronic structure calculations on the relaxed structure, including spin–orbit coupling, were then performed using the full-potential linearized augmented plane-wave method as implemented in the Wien2k package49. For the ratio of the radius of phosphorus atoms we take 2.09 bohr and a kmax parameter of 4 bohr⁻¹. For the valence electrons of the phosphorus we consider two 3s and three 3p electrons. Spin–orbit coupling has been included in a second-variational procedure in which the scalar-relativistic wavefunctions were calculated in an energy window up to 5 Ry. To correct for the standard DFT deficiency in the description of the bandgaps in semiconductors we used the modified Becke–Johnson potential50 with a parametrization allowing us to tune the bandgap to the experimental value of 0.338 eV. In the self-consistent calculation the charge density was converged for the Monkhorst–Pack k-point grid with 280 k-points in the irreducible Brillouin zone wedge.

Comparison of spin and momentum relaxation times. Several factors in our device architecture might affect the VBG dependence of spin and charge transport. These prevent us from making a precise correlation between spin and momentum relaxation times as a function of VBG alone. As discussed in the main text, the conductivity mismatch issue in our devices at low VBG values can dramatically affect the spin injection efficiency in particular. This prevents correlating the spin and momentum relaxation times to study the spin dephasing mechanism. Moreover, our devices show a surprisingly n-type dominant behaviour due to the tunnelling BN barrier compared to the typical p-type conduction dominant bP device. Such doping from contacts might cause additional p–n interfaces, which will make it difficult to determine the momentum relaxation time accurately. Further, we would like to mention that the four-terminal, long-stride device is not as ideal as Hall bar to extract the mobility accurately. For example, marked discrepancies were reported between the Hall mobilities and field effect mobility due to the underestimated values for the gate capacitances51,52. One way to overcome this challenge for the non-local spin valve geometry is to compare the temperature dependence of τs and τp at fixed VBG. Note that both parameters show a discernible temperature dependence. In Fig. 4a, τp at a fixed VBG = 30 V is directly determined from the same Hanle measurements by using the relation τp = (2D)/Vp², where Vp is the Fermi velocity calculated from first-principles for bP (see Supplementary Information). Note also that both the temperature dependence and the magnitude of the extracted momentum relaxation times are consistent with previous reports and our additional devices extracted directly from the conductivity data by using μ = (eτp)/m (see Supplementary Information for details)53,54.

Data availability. The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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