Room-temperature ferroelectric switching of spin-to-charge conversion in germanium telluride

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The development of spintronic devices has been limited by the poor compatibility between semiconductors and ferromagnetic sources of spin. The broken inversion symmetry of some semiconductors may allow for spin–charge interconversion, but its control by electric fields is volatile. This has led to interest in ferroelectric Rashba semiconductors, which combine semiconductivity, large spin–orbit coupling and non-volatility. Here we report room-temperature, non-volatile ferroelectric control of spin-to-charge conversion in epitaxial germanium telluride films. We show that ferroelectric switching by electrical gating is possible in germanium telluride, despite its high carrier density. We also show that spin-to-charge conversion has a similar magnitude to what is observed with platinum, but the charge current sign is controlled by the orientation of ferroelectric polarization. Comparison between theoretical and experimental data suggests that the inverse spin Hall effect plays a major role in switchable conversion.

Spin-based electronics—spintronics—could potentially be used to create low-power solutions for beyond complementary metal–oxide–semiconductor (CMOS) technology1,2. Ideally, spin would be added as an extra degree of freedom into semiconductor-based electronics operating on charge, limiting the need to develop exotic materials and then integrate them into the established CMOS platform. However, combining ferromagnets (as spin generators and detectors) with semiconductors has proved challenging due to issues with material compatibility and impendence mismatch. An alternative approach is to use semiconductors doped with magnetic impurities (such as gallium manganese arsenide (Ga,Mn)As), but this technique has not yielded reproducible ferromagnetism at room temperature3, despite additional explorations with iron-doped semiconductors4.

A notable feature of zinc-blende semiconductors (such as GaAs) is their broken inversion symmetry. This leads to the splitting of some of the electronic bands by the spin–orbit interaction, coupling the direction of spins and momentum, and leading to Dresselhaus and Rashba effects. Spin–momentum locking, as well as the spin Hall effect, enables the generation of spin currents by charge currents and vice versa; therefore, semiconductor heterostructures can be used as spin generators and detectors5,6. However, unlike ferromagnets, they lack reversible non-volatile control of the spin: its direction is either fixed by the construction of the heterostructure or set by internal electric fields, and is thus volatile. The spin–charge interconversion process is also not very efficient. Recent research has shown that spin-to-charge conversion (SCC) can be tuned by an electric-field-induced ferroelectric-like state in SrTiO3 interfaces8, but this system only works at low temperatures (<50 K) and is difficult to integrate on silicon.

Ferroelectric Rashba semiconductors (FERSCs)9,10 have been identified as alternative materials for operating on spin and integrating logic and memory functionalities. FERSCs have a broken inversion symmetry, like several other semiconductors; however, because they are ferroelectric, they also display giant Rashba spin splitting of the bulk bands, with the additional effect that the spin direction in each Rashba sub-band can be reversed by switching the ferroelectric polarization11. Spin- and angle-resolved photoemission spectroscopy measurements of the prototypical FERSC—germanium telluride (GeTe)—have confirmed that the chirality of the spin texture is linked to the electric dipole12,13. Like ferromagnetics, these measurements are reconfigurable and non-volatile but can be operated by electric fields, offering reduced power consumption. FERSCs could thus potentially be used to develop all-in-one devices that integrate spin generation, manipulation and detection, similar to spin Hall effect transistors and magnetoelectric spin–orbit devices14. The compatibility of chalcogenides with germanium15 and gallium arsenide (GaAs)16 may also allow the ferroelectric control of spin injection into optically active semiconductors, leading to combined photonic and spintronic devices such as spin lasers.

In this Article, we show that epitaxial Fe/GeTe heterostructures can achieve switchable SCC at room temperature. We first demonstrate the fast ferroelectric switching of GeTe thin films using gate electrodes with voltages compatible with standard electronics, and identify an efficient, non-destructive method for the readout of the ferroelectric state. Spin pumping (SP) experiments show...
that sign of SCC reverses when switching the electric polarization. First-principles calculations are used to explore the origin of this phenomenon, and show that the inverse spin Hall effect has a major role in SCC. Notably, the SCC in Fe/GeTe is distinct from two-dimensional materials in that it involves bulk bands rather than interface or surface Rashba states. Our system has the potential to be monolithically integrated on silicon and could be of value in the development of beyond-CMOS applications such as spin transistors and spin interconnects through the substrate.

**Ferroelectric switching of GeTe**

Ferroelectric switching of GeTe has only been previously demonstrated at the nanoscale. This has been achieved using piezoresponse force microscopy (PFM) of thin films, using transmission electron microscopy with nanometre-scale crystals and nanowires, and using X-ray spectroscopy. The common understanding of ferroelectric switching suggests that the screening of the external electric field by the large density of free carriers prevents the penetration of external electric fields, inhibiting polarization reversal and resulting in high dielectric loss. Although recent works have shown evidence of ferroelectric inversion even in polar metals, it was only achieved in the ultrathin limit. From a technical perspective, the measurement of polarization–electric field (P–E) loops via the positive-up negative-down method, commonly employed for ferroelectric oxides, cannot be performed for GeTe because it is a semiconductor with a small indirect gap (\(E_g = 0.61–0.66\text{ eV}\)) with high intrinsic p-type doping \(\left(\sigma \approx 3 \times 10^5 \text{ cm}^{-1}\text{ eV}^{-1}\right)\); therefore, displacement current peaks associated with polarization switching are overshadowed by the conduction current. Therefore, a different method for the electric readout of the ferroelectric state must be identified for narrow-gap highly doped semiconductors. To demonstrate gating, we performed a combined electric and piezo-electric experiment, following an approach similar to that used for ferroelectric oxides in ref. 29. Voltage pulses were applied by a source measure unit (SMU) to a metallic gate, deposited on the semiconductor and thin enough to permit the imaging of out-of-plane ferroelectric domains by PFM (Methods). A sketch of the device is shown in Fig. 1a.

After the application of a pulse \(V_{\text{write}}\), we recorded the resistance of the heterojunction at low voltage, and then disconnected the SMU from the gate. A portion of the gate was scanned by the PFM tip excited with an alternating current (a.c.) signal \(F_{\text{tip}}\) of ~2 V at a frequency of ~70 kHz. Tip deflection—demodulated by a lock-in amplifier, which is proportional to the piezo-/ferroelectric response of the area under the tip—was collected to map the ferroelectric domains below the gate. Figure 1b shows such domains’ configuration that progressively evolves with \(V_{\text{write}}\). Moving from +8 to ~8 V, it turns from a prevalently inward \((P_{\text{in}})\) to a fully outward \((P_{\text{out}})\) configuration, passing through intermediate states. The reversal was not complete for the positive pulse at +8 V (b1), suggesting that outward domains were favoured and that a uniform inward state would have possibly required the application of higher voltages or longer pulses.

The mean value of the PFM phase calculated over the entire \(x\)–\(y\) map for each value of \(V_{\text{write}}\) is reported in Fig. 1c. It shows a hysteretic behaviour comparable to ferroelectric loops acquired on the bare surface (Supplementary Fig. 1), with bistability and a coercivity of about 3.5 V. An asymmetry of switching is visible as a slight shift in the hysteresis loop (1.5 V) that favours the preferential orientation of outward domains for this specific interface29. Figure 1c also reports the resistance–area \((R\text{–}A)\) product of the gate/Si3N4/GeTe junction, where resistance \(R\) is measured after each writing pulse at low voltage (0.1 V), while \(A\) is the area of the electrode. The marked correlation with the PFM phase suggests that \(R\) is connected to the ferroelectric state. To better understand this relationship, in Fig. 1d, we report \(R\) versus the relative fraction of outward domains \(n_{\text{out}}\). The results can be interpreted using a simple model assuming that \(P_{\text{out}}\) and \(P_{\text{in}}\) regions have different specific resistances \(\left(\frac{1}{R_{\text{out}}} + \frac{1}{R_{\text{in}}}\right)\); therefore, \(R\) is

\[
\frac{1}{R} = \left(\frac{n_{\text{out}}}{R_{\text{out}}} + \frac{1 - n_{\text{out}}}{R_{\text{in}}}\right).
\]

Such a model reproduces the experimental data (Fig. 1d, dashed line), corroborating the ferroelectric origin of resistance modulation and providing an efficient method for the readout of the ferroelectric state.

We ascribe resistance changes to the modulation of the width of the Schottky barrier expected at the gate/semiconductor interface (Fig. 2a, inset). In the model developed for ferroelectric Schottky diodes35, the height of the Schottky barrier \(\Phi_m\) is fixed and determined by the work function of the metal \(\left(\Phi_m\right)\), electron affinity of the semiconductor \(\left(\chi_o\right)\) and its bandgap \(E_g\) (\(\Phi_m = E_g + \chi_o - \Phi_m\) (ref. 33)). In this framework, the width of the depletion region depends on the effective dielectric constant of the semiconductor, whose value is determined by the volume polarization charges associated to a certain ferroelectric state. Self-consistent calculations demonstrated that a narrower (or wider) depletion region is produced for polarization \(P\) parallel (or anti-parallel) to the built-in electric field inside the space charge region, determining a lower (or higher) electrical resistance of the junction.

We tested this mechanism for metal/GeTe junctions: arrays of squared Ti (100 nm) contacts were deposited on 22-nm-thick GeTe(111) on Si(111) (Methods). Voltage pulses were applied at the electrode to pole the ferroelectric GeTe film. Figure 2a reports the current–voltage \((I\text{–}V)\) curves collected at low voltages after poling with \(\pm 10 \text{ V}\). Due to the high p-type intrinsic doping of GeTe (ref. 34), the metal/semiconductor junction behaves as an ohmic contact (the Schottky barrier width is of the order of a few nanometres). The conductance is hysteretic (Fig. 2b), showing a modulation of about 50% on this junction, whereas a maximum of 300% was found in some devices (Supplementary Fig. 2a). It is notable that the hysteresis loop is approximately centred (at variance with the Si3N4 case; Fig. 1c): this suggests the role of direct contact between the metal and the ferroelectric in reducing the depolarizing field at the interface, with a consequent stabilization of both polarization states. The result is consistent with the model of the ferroelectric Schottky diode. Indeed, since the work function of Ti is lower than the affinity of the semiconductor \((4.33 \text{ eV}\) (ref. 35) and \(4.80 \text{ eV}\) (ref. 36), respectively), a downward band bending is expected at the interface, resulting in an inward built-in electric field (Fig. 1a, inset). Thus, the lower (higher) junction resistance corresponds to inward (outward) ferroelectric polarization (Fig. 2a, inset). The presence of minor hysteresis loops (Supplementary Fig. 2b) further corroborates the ferroelectric origin of such effect, while other mechanisms connected to resistive switching in chalcogenides can be ruled out (Supplementary Section 3).

Figure 2c shows the cyclability of junctions checked by applying a sequence of negative and positive saturating pulses. To guarantee the full opening of the resistive window against possible inhomogeneities in coercivity or non-idealities in the hysteresis loop, we chose to employ pulses of 10.0 V for all the devices, while 4.5 V pulses already ensure 80% of such a resistive window. The maximum endurance obtained in these devices was of the order of \(10^6\) cycles. Figure 2d reports the modulation of junction conductance versus writing pulse width, with no major change down to 250 ns—the lowest pulse width accessible with our instrumentation. While the large capacitance in ferroelectric oxides requires miniaturization, the resistive behaviour of metal/GeTe junctions enables fast switching even for large electrodes.
Fig. 1 | Ferroelectric switching of GeTe by electrical gating and electric readout of the state. a, Sketch of the setup and the device under test (DUT) used for gating and ferroelectric imaging. Thin Au (5 nm)/Ti (5 nm) square gates (30 × 30 μm²) were evaporated on Si₃N₄ (10 nm)/GeTe (50 nm)/Si and connected to thicker Au (200 nm)/Cr (7 nm) stripes allowing for electrical contact with an SMU. The Si₃N₄ capping layer avoided the exposure of GeTe to chemicals during lithography. An optical image of the device is shown on the right. b, PFM maps measured at remanence on the surface of the gate (scan size, 0.7 × 0.2 μm²) for Vₜₚₑₑₑₑ from +8 to –8 V. The blue (red) state represents Pᵣ (Pₜₑₑₑₑ). The histograms with the percentage of outward (n₀) and inward (n₁) domains are reported below each map. c, PFM phase (circular dots) and RA product of the junction (black empty squares) versus the amplitude of the writing voltage pulse (Vₜₚₑₑₑₑ). The similarity of the two curves is a signature of ferroelectricity-driven resistive switching. Points b₁ (Vₜₚₑₑₑₑ = +8 V), b₂, b₃, b₄ (Vₜₚₑₑₑₑ = –2 V) and b₅ (Vₜₚₑₑₑₑ = –8 V) correspond to the mean value of the PFM phase over the images reported in the corresponding panels. d, Resistance-area product versus percentage of outward domains extracted from the PFM maps of b. The triangles refer to experimental data, while the dashed line is the trend expected from the parallel resistance model.


erroelectric control of SCC
The influence of ferroelectricity on SCC was studied by combining gating and SP in epitaxial Au (3 nm)/Fe (20 nm)/GeTe (15 nm)/Si samples (Methods). In an SP experiment (Fig. 3a), the magnetization M of the ferromagnetic layer is perpendicularly saturated to the slab (x axis; Fig. 3a) by direct current (d.c.) magnetic field H. The precession of M is excited by a microwave field bₑ oscilating along longitudinal axis y at a fixed frequency. The ferromagnetic resonance (FMR) condition is found by sweeping the amplitude of the external saturating field H. As a consequence of angular momentum conservation, the additional damping of M ascribed to GeTe corresponds to the injection of a d.c. pure-spin current jₑ along z into the GeTe layer, with spin polarization Pₑ parallel to equilibrium magnetization. SCC would result in the generation of jₑ at a fixed frequency. The ferromagnetic switching. Due to the voltage drop across the thick Si substrate, higher voltages (~50 V) are required for such switching. In this configuration, the overall resistance is determined by the silicon substrate, in series with two junctions, namely, Fe/GeTe and GeTe/Si. The latter dominates because of the larger difference in work functions/electron affinities (φₑGeTe = 4.80 eV, φₑSi(111) = 4.00 eV and φₑTi(111) ≈ 4.81 eV) (refs. 36,7) and the relatively low doping of Si, which determines a wider Schottky barrier. Therefore, the Si/GeTe interface provides an even more effective readout of the memory state, with a modulation of the resistance much larger (~4,000%) than that of Ti/GeTe.

Figure 3c–f summarizes the investigation of SCC versus ferroelectric polarization. On application of voltage pulses, no major differences in shape and position of the FMR of the Fe layer were detected (Fig. 3c,d), which indicates that the magnetic layer was not affected by the process. The absolute value of the normalized current production Iₑ is higher in the two saturated states Pₑ and Pₑ with respect to the unpoled state. Remarkably, the sign of the SCC reverses with ferroelectric polarization (Fig. 3c,f), demonstrating the non-volatile ferroelectric control of the SCC in GeTe. Note as the top gate electrode, while the Si substrate was used as the bottom contact instead of GeTe (Fig. 3a). Such configuration favours uniform vertical switching of ferroelectric polarization and permits exploitation of the whole area of the sample for spin injection from the magnetic layer. Figure 3b shows the I–V curves at saturation, and the hysteresis loop of conductance versus Vₜₚₑₑₑₑ shows ferroelectric switching. Due to the voltage drop across the thick Si substrate, higher voltages (~50 V) are required for such switching. In this configuration, the overall resistance is determined by the silicon substrate, in series with two junctions, namely, Fe/GeTe and GeTe/Si. The latter dominates because of the larger difference in work functions/electron affinities (φₑGeTe = 4.80 eV, φₑSi(111) = 4.00 eV and φₑTi(111) ≈ 4.81 eV) (refs. 36,7) and the relatively low doping of Si, which determines a wider Schottky barrier. Therefore, the Si/GeTe interface provides an even more effective readout of the memory state, with a modulation of the resistance much larger (~4,000%) than that of Ti/GeTe.
that the current production is relatively large—between 10 and 20 mA mT \(^{-1}\) m\(^{-1}\). By repeating the poling several times to fully saturate the ferroelectric state, it eventually increases up to 66 mA mT \(^{-1}\) m\(^{-1}\), comparable to the value of 77 mA mT \(^{-1}\) m\(^{-1}\) observed with the same setup in platinum (ref. 41 and Supplementary Section 5), which is one of the reference materials for the generation of spin currents in fundamental studies and applications41. Figure 3g reveals that the amplitude of the SCC in GeTe remains constant from 100 to 300 K, demonstrating that GeTe is suitable for the tuneable and effective generation of pure spin currents at room temperature in a semiconducting platform compatible with CMOS. Contribution to the signal coming from thermoelectric effects in GeTe could be expected, but thermal gradients are not affected by ferroelectric polarization switching.

Finally, SP experiments were performed along the two inequivalent high-symmetry bulk (surface) directions ZA (FK) and ZU (FM) of the bulk (surface) Brillouin zone of GeTe (Fig. 3c,c and Fig. 3d,f, respectively), as defined in Supplementary Fig. 7 and ref. 11. The crystallographic orientation of the slabs was determined according to the diffraction pattern obtained during heterostructure growth (Methods). These measurements revealed charge production of different signs for the same ferroelectric polarization, in accordance with symmetries of the calculated SCC tensors (Supplementary Section 6).

**Mechanism of SCC and prototype device**

Two mechanisms could cause the observed conversion from spin to charge currents: the inverse Rashba–Edelstein effect (IREE) and the inverse spin Hall effect (ISHE). In IREE, when spin accumulation is produced by SP in the Rashba bands, the two Fermi contours are displaced, producing a net charge current perpendicular to both spin current and spin polarization. The switching of the chirality of spins achieved by reversing the ferroelectric polarization would lead to reversal of the charge current. We stress, however, that IREE is a surface/interface effect, unlikely here due to the possible suppression of the surface states of GeTe induced by the deposition of Fe (ref. 11); however, in our system, a spin current can propagate within the semiconducting GeTe film, suggesting a rather bulk-like origin of the observed SCC. Although we cannot completely rule out IREE, the quantitative arguments discussed below suggest a minor contribution from this phenomenon.

To understand the role of ISHE in the charge current production and its ferroelectric switching, we performed an analysis based on first-principles calculations. The intrinsic spin Hall conductivity (SHC) defined by the standard Kubo formula is invariant under the operation of inversion, which connects two ferroelectric ground states of the bulk crystal. Even though a sizeable SHE was predicted in GeTe (refs. 42,43), it should not be affected by simply reversing the spins in the Rashba bands, without additional modifications in the topology of the electronic states. Here we considered thin films of crystalline GeTe without standard periodic boundary conditions for bulk GeTe. We simulated a finite slab and revealed that the polarization charges at the surfaces of the film, either positive or negative depending on the ferroelectric polarization direction, affect the electric field inside the crystal. This induces non-trivial band reconstructions and eventually a difference in the SHC values calculated for opposite ferroelectric displacements (Supplementary Section 6). Figure 4a reports the calculated element of the SHC tensor (|σ\(_{zx}\)|) corresponding to the experimental configuration, with spin polarization along \(y\) and spin (charge) current along \(z\) (\(x\)) axis. It is evident that the electric field introduced by polarization charge can modulate the SCC, consistent with the experimental change in sign on the reversal of ferroelectric polarization (Fig. 3e,f).

The calculated SHC \(σ\(_{zx}\)\) permits the evaluation of the efficiency of SCC through the spin Hall angle, which is given by \(θ_{\text{SSH}} = |σ_{zx}|/|σ_{xx}|\). The experimental charge conductivity in our films is \(σ_{xx} = 3 \times 10^8 \Omega^{-1} \text{cm}^{-1}\) and \(σ_{zx}\) is of the order of 20\(\Omega^{-1} \text{cm}^{-1}\) for thin films (Fig. 4b, grey area). While the sign of \(θ_{\text{SSH}}\) depends on the polarization direction, its absolute value is around 1%, in agreement with similar SP curves obtained for both GeTe and Pt (refs. 44,45). This corroborates a dominant role of ISHE in SCC in Fe/GeTe heterostructures.

The ferroelectric control of spin–charge interconversion in FERSC on silicon could permit advances in beyond-CMOS computing. The sketch of the concept device (Fig. 4b) represents an alternative logic
solution with respect to the magnetoelectric spin–orbit element (MESO), recently proposed by Intel\(^\text{15}\). FERSC allows for both memory and spin transduction within the same material, thereby eliminating the need of complex magnetoelectric elements to control the ferromagnet, since information is stored in ferroelectric polarization rather than in magnetization. Nevertheless, the proposed device shares ferroelectric switching and spin–orbit readout with the MESO structure; therefore, the same favourable scaling laws delineated for the MESO device and demonstrated for CoFe/Pt apply\(^\text{46}\).

Further effort in terms of materials engineering would allow reduction in the switching voltage towards ultralow power consumption. Viable routes include the use of thinner films to
reduce the coercive voltage, miniaturization to reduce inhomogeneities and enhanced ferroelectric response of the unclamped ferroelectric. Lower switching voltage and energy for polarization reversal could also be achieved by doping and alloying GeTe with isovalent compounds.

**Conclusions**

We have shown that ferroelectric polarization in epitaxial films of GeTe can be switched by gating and used in an Fe/GeTe heterostructure to efficiently convert spin to positive or negative charge currents at room temperature. Ferroelectric switching is obtained with low voltages (<5 V), high robustness, switching times below 250 ns and endurance up to 10⁵ cycles. The readout of the state is non-destructive and the resistive windows for metal/GeTe and GeTe/Si interfaces are around 300% and 4,000%, respectively. By SP, we observed normalized charge current production in Fe/GeTe at room temperature, whose magnitude is comparable with that of platinum (the reference material), while the sign of the SCC coefficient can be reversed by ferroelectric polarization. Both Rashba–Edelstein and spin Hall effects have been suggested by theoretical arguments to account for the switchable SCC, but agreement between experimental data and calculated spin Hall angle indicates that ISHE has a dominant role in the Fe/GeTe system. Our results open a route to the non-volatile electric control of spin currents in semiconductor GeTe, a system that could potentially be monolithically integrated on silicon for beyond-CMOS devices such as reconfigurable spin-based in-memory computing devices.

**Methods**

**Growth of GeTe films.** GeTe films were epitaxially grown by molecular beam epitaxy (MBE) on Si(111) substrates (p-type boron doping; thickness, 500 μm; resistivity, 1–10 2Ω·cm; miscut, <0.1°; thermal oxide capping layer, 100 nm). The substrates were cleaned by wet etching before they were loaded into the MBE system to remove the oxide. Thermal desorption of water was induced in the growth chamber by annealing. A proper thermal treatment allowed obtaining a Si(111)−⟨1 3 5 3⟩R30°−Sb surface before cooling down to the deposition temperature (250°C), as described elsewhere. This deposition was done by co-evaporating Ge and Te with dual-filament effusion cells and a Te/Ge flux ratio of about 1.6. Then, a thick capping layer of either amorphous Te deposited by MBE or in situ sputtered Si₃N₄ (5 nm) (x = 5; y = 4) was grown on each sample to protect the film from exposure to atmosphere. The choice of capping layer depends on the final application of the sample. Hall measurements revealed that GeTe films are intrinsically p-type doped (p ≈ 2 × 10¹⁰ cm⁻³) − a typical concentration for this material due to the presence of about 10% Ge vacancies. The mobility at room temperature is ≈ 95 cm² V⁻¹ s⁻¹.

**Decapping procedure.** To recover a clean and well-ordered GeTe(111) surface from samples capped with protective amorphous Te, we employed an established procedure described in detail elsewhere: a sputter etch by argon ions permits to remove the first few nanometres of oxidized Te, while the remaining capping layer is thermally desorbed in an ultrahigh vacuum by annealing at 250°C. Ordered GeTe(111) surfaces were obtained, with their typical six-fold symmetry verified by in situ low-energy electron diffraction, which also permits to distinguish the high-symmetry ZA and ZU directions of the samples.

**Electrical characterization.** Measurements of resistivity versus writing pulse (Fig. 3) were performed at room temperature on decapped GeTe samples. Square contacts (40×40 μm) of Ti were directly deposited by electron-beam evaporation using a shadow mask. Top-bottom geometry was employed for electrical characterization. Electrical poling was realized between a metallic probe connected to a Ti contact and another contact on one edge of the sample realized by silver paint. Square voltage pulses with a minimum duration of 300 μs were generated by a Keithley 2611B SMU. In case of shorter pulses (down to 250 ns), a TF 2000 analyser (aixACCT) was used. In both cases, pulses were sent and afterwards the I–V curves at relatively low voltages (<1 V) were measured by employing the same instrument.

**Piezoresponse force microscopy.** Devices for imaging the ferroelectric domains under a gate electrode were fabricated by standard optical lithography on GeTe (50 nm)/p-Si samples capped with Si₃N₄ (10 nm). The capping layer avoided the exposure of GeTe to chemicals during lithography, since standard solvents used for resist development are etchants of chalcogenides. Si₃N₄ is particularly suitable as a capping layer: it can be sputtered on GeTe in situ and its relatively small bandgap limits the impact on I–V curves as compared with direct metal/semiconductor junctions. As sketched in Fig. 1a, a thin metallic contact made of Fe (5 nm)/Ti (5 nm) defined a mesa (30 × 30 μm), which is then connected to an external poling circuit by a thicker sputtered electrode made of Au (200 nm)/Cr (7 nm), isolated from GeTe by 120 nm SiO₂. The second electrode was constituted by a grounded lateral contact on one side of the sample.

**Spin pumping.** Heterostructures for SP experiments were obtained by depositing the remaining part of the stack in situ by MBE, after decapping. The epitaxial Fe (20 nm) layer was grown on GeTe(111) at room temperature. A protective Au (3 nm) layer was then deposited on top to avoid oxidation of the ferromagnet. The samples were cut in the form of elongated rectangular slabs (2.4 × 0.4 μm) by means of a dicing saw, with the longer side of the slabs corresponding to either ZA or ZU in-plane crystallographic directions of GeTe, to measure different components of SHC tensors.

SP experiments were carried out using a Bruker ESP300E X-band CW spectrometer at a fixed frequency of 9.68 GHz and microwave power of 200 mW, with a loop-gap Bruker ER 4118X-MSS cavity. Measurements were carried out in a range of 100–300 K in a He-saturated cryostat, to avoid oxidation of the Fe layer. Voltage pulses for ferroelectric poling were applied using a Keithley 2400 source meter. The transverse d.c. voltage generated was measured by a Keithley 2182 A nanovoltmeter.

**First-principles calculations.** Our calculations based on density functional theory were performed using the QUANTUM ESPRESSO package interfaced with the PAOFLOW code. We treated the exchange and correlation interaction within the generalized gradient approximation, further improved by a novel pseudohybrid Hubbard self-consistent approach AGBN0 (ref. 36). The ion–electron interaction was taken into account with the projector augmented-wave (PAW) fully relativistic pseudopotentials from the database. The electronic wave functions were expanded in a plane-wave basis set with cutoff of 50 Ry. Spin–orbit coupling was included self-consistently. In bulk calculations, we used the optimized hexagonal unit cell (a = 4.22 Å; c = 10.89 Å) containing six atoms. The surfaces with polarization outwards (P₁₀) and inwards (P₋₁₀) were modelled in a slab approach by stacking 3–4 bulk unit cells along the [0001] direction followed by a large vacuum region of at least 20 Å. We added dipole corrections to the local potential to reduce the spurious interaction resulting from the periodic boundary conditions. Brillouin zone sampling at the density functional theory level was performed following the Monkhorst–Pack scheme using grids of 16 × 16 × 3 and 16 × 16 × 1 for bulk and surface calculations, respectively.

Electronic structures and SHC values were calculated with the help of tight-binding Hamiltonians. The latter were constructed from the projections of wave functions on pseudatomic orbitals following implementation in the PAOFLOW code. In the case of standard bulk calculations (Supplementary Fig. 5), we interpolated the Hamiltonians to a denser Κ-point grid (48 × 48 × 12) and calculated the spin polarization of each eigenstate |k⟩ represented as S(Δk) = [Sₓ(Δk), Sᵧ(Δk), Sₜ(Δk)], where Sₓ(Δk) = (ψ(Δk)|σₓ|ψ(Δk)) and σₓ, σᵧ denote the Pauli matrices. The intrinsic SHC computations were based on the Kubo formula following the details given elsewhere. To model a bulk which includes the effects of finite asymmetric interfaces realized in the experiments, we used real-space Hamiltonians obtained from the surface calculations. After extracting the matrix elements corresponding to the central part of the slab, we constructed the Hamiltonians of the retrieved bulks, which correspond to the surface slabs with polarizations P₁₀ and P₋₁₀. Finally, we calculated the spin-dependent electronic structures as well as SHC values based on the interpolated Hamiltonians, by following the standard procedure described above. We emphasize that such an approach allowed us to calculate the spin currents perpendicular to the interface, which cannot be evaluated from simple surface calculations.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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References

1. Zutic, I., Fabian, J. & Sarma, D. Spintronics: fundamentals and applications. Rev. Mod. Phys. 76, 323–410 (2004).
2. Awschalom, D. D. & Flatté, M. E. Challenges for semiconductor spintronics. Nat. Phys. 3, 153–159 (2007).
3. Schmidt, G., Ferrand, D., Molenkamp, L. W., Filip, A. T. & van Wees, B. J. Fundamental obstacle for electrical spin injection from a ferromagnetic metal into a diffuse semiconductor. Phys. Rev. B 62, R4790 (2000).
4. Dietl, T. A ten-year perspective on dilute magnetic semiconductors and oxide spintronics. Nat. Mater. 9, 965–974 (2010).
5. Tu, N. T., Hai, P. N., Anh, L. D. & Tanaka, M. High-temperature ferromagnetism in new n-type Fe-doped ferromagnetic semiconductor (In,Fe)Sb. Appl. Phys. Express 11, 063005 (2018).
6. Kato, Y. K., Myers, R. C., Gossard, A. C. & Awschalom, D. D. Observation of spin Hall effect in semiconductors. Science 306, 1910–1913 (2004).
7. Galperov, S. D. et al. Spin-galvanic effect. Nature 417, 153–156 (2002).
8. Awschalom, D. & Samarth, N. Spintronics without magnetism. Physics 2, 50 (2009).
9. Benítez, L. A. et al. Tunable room-temperature spin galvanic and spin Hall effects in van der Waals heterostructures. Nat. Mater. 19, 170–175 (2020).
10. Noé, P. et al. Non-volatile electric control of spin–charge conversion in a SrTiO₃ Rashba system. Nature 580, 483–486 (2020).
11. Picozzi, S. Ferroelectric Rashba semiconductors as a novel class of multifunctional materials. Front. Phys. 2, 10 (2014).
12. Di Sante, D., Barone, P., Bertacco, R. & Picozzi, S. Electric control of the giant Rashba effect in bulk Ge. Adv. Mater. 25, 509–513 (2013).
13. Liebmann, M. et al. Giant Rashba-type spin splitting in ferroelectric GeTe(111). Adv. Mater. 28, 560–565 (2016).
14. Rinaldi, C. et al. Ferroelectric control of the spin texture in GeTe. Nano Lett. 18, 2751–2758 (2018).
15. Manipatruni, S. et al. Tunable high-purity epitaxial (Ge,Sn)Te/SnTe(111) using molecular beam epitaxy. J. Appl. Phys. 119, 075306 (2016).
16. Krellner, D. et.al. Ferroelectric switching in epitaxial GeTe films. AIP. Mater. 2, 066101 (2014).
17. Polking, M. J. et al. Ferroelectric order in individual nanometre-scale crystals. Nat. Mater. 11, 700–709 (2012).
18. Nakala, P. et al. Inverting polar domains via electrical pulsing in metallic germanium telluride. Nat. Commun. 8, 15033 (2017).
19. Krellner, D. et al. Ferroelectric self-poling in GeTe films and crystals. Crystals 9, 335 (2019).
20. Wang, Y., Liu, X., Burton, J. D., Jaswal, S. S. & Tymbal, E. Y. Ferroelectric instability under screened Coulomb interactions. Phys. Rev. Lett. 109, 247404 (2012).
21. Lei, Z. et al. Ferroelectric switching of multiferroic CoFeB/BaTiO3. Nano Lett. 18, 4532–4539 (2018).
22. Li, G. et al. Surface reconstruction-induced coincidence lattice instability under screened Coulomb interactions. Phys. Rev. B 89, 075306 (2016).
23. Hery, D., Song, Y., Li, P. & Zutic, I. Silicon spin communication. Appl. Phys. Lett. 99, 082502 (2011).
24. Kolobov, A. V. et al. Ferroelectric switching in epitaxial GeTe films. Appl. Mater. 2, 066101 (2014).
25. Polking, M. J. et al. Ferroelectric order in individual nanometre-scale crystals. Nat. Mater. 11, 700–709 (2012).
26. Nakala, P. et al. Inverting polar domains via electrical pulsing in metallic germanium telluride. Nat. Commun. 8, 15033 (2017).
27. Krellner, D. et al. Ferroelectric self-poling in GeTe films and crystals. Crystals 9, 335 (2019).
28. Wang, Y., Liu, X., Burton, J. D., Jaswal, S. S. & Tymbal, E. Y. Ferroelectric instability under screened Coulomb interactions. Phys. Rev. Lett. 109, 247404 (2012).
29. Fei, Z. et al. Ferroelectric switching of a two-dimensional metal. Nature 560, 336–339 (2018).
30. Sharma, P. et al. Room-temperature ferroelectric semimetal. Sci. Adv. 5, eaax5080 (2019).
31. Rabe, K. M., Ahn, C. H. & Triscone, J.-M. Physics of Ferroelectrics: A Modern Perspective (Springer, 2007).
32. Baldrati, L. et al. Electrical switching of magnetization in the artificial multiferroic CoFe/BaTiO3. Adv. Electron. Mater. 2, 1600085 (2016).
33. Park, J.-W. et al. Optical properties of pseudobinary GeTe, Ge₅Sb₅Te₈, Ge₆Sb₆Te₉, Ge₇Sb₇Te₁₀, and SnTe from ellipsometry and density functional theory. Phys. Rev. B 80, 115209 (2009).
34. Yamada, H. et al. Giant electroresistance of super-tetragonal BiFeO₃-based ferroelectric tunnel junctions. ACS Nano 7, 5385–5390 (2013).
35. Rinaldi, C. et al. Evidence for spin to charge conversion in GeTe(111). Appl. Mater. 4, 032501 (2016).
36. Chantaraoula, A. et al. A Ferroelectric memristor. Nat. Mater. 11, 860–864 (2012).
37. Blom, P. W. M., Wolf, R. M., Cillesen, J. F. M. & Krijn, M. P. C. M. Ferroelectric Schottky diode. Phys. Rev. Lett. 73, 2107–2110 (1994).
38. Cantoni, M., Petri, D., Rinaldi, C. & Bertacco, R. Bandstructure line-up of epitaxial Fe/MgO/Ga heterostructures: a combined X-ray photoemission and low-temperature transport study. Appl. Phys. Lett. 98, 32103–32104 (2011).
39. Edwards, A. H. et al. Electronic structure of intrinsic defects in crystalline germanium telluride. Phys. Rev. B 73, 45201 (2006).
40. Michaelsson, H. B. The work function of the elements and its periodicity. J. Appl. Phys. 48, 4729–4733 (1977).
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**Competing interests**
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