Out-of-plane Interface dipoles and anti-hysteresis in graphene-strontium titanate hybrid transistor
Sahoo, Anindita; Nafday, Dhani; Paul, Tathagata; Ruiter, Roald; Roy, Arunesh; Mostovoy, Maxim; Banerjee, Tamalika; Saha-Dasgupta, Tanusri; Ghosh, Anindam

Published in:
Npj 2d materials and applications

DOI:
10.1038/s41699-018-0055-5

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2018

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Sahoo, A., Nafday, D., Paul, T., Ruiter, R., Roy, A., Mostovoy, M., Banerjee, T., Saha-Dasgupta, T., & Ghosh, A. (2018). Out-of-plane interface dipoles and anti-hysteresis in graphene-strontium titanate hybrid transistor. Npj 2d materials and applications, 2, [9]. https://doi.org/10.1038/s41699-018-0055-5

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 18-11-2020
Out-of-plane interface dipoles and anti-hysteresis in graphene-strontium titanate hybrid transistor

Anindita Sahoo¹, Dhani Nafday², Tathagata Paul¹, Roald Ruiter³, Arunesh Roy³, Maxim Mostovoy³, Tamalika Banerjee⁴ and Arindam Ghosh¹,⁶

The out-of-plane electric polarization at the surface of SrTiO₃ (STO), an archetypal perovskite oxide, may stabilize new electronic states and/or host novel device functionality. This is particularly significant in proximity to atomically thin membranes, such as graphene, although a quantitative understanding of the polarization across graphene–STO interface remains experimentally elusive. Here, we report direct observation and measurement of a large intrinsic out-of-plane polarization at the interface of single-layer graphene and TiO₂-terminated STO (100) crystal. Using a unique temperature dependence of anti-hysteretic gate-transfer characteristics in dual-gated graphene-on-STO field-effect transistors, we estimate the polarization to be as large as ≈12 μC cm⁻², which is also supported by the density functional theory calculations and low-frequency noise measurements. The anti-hysteretic transfer characteristics is quantitatively shown to arise from an interplay of band bending at the STO surface and electrostatic potential due to interface polarization, which may be a generic feature in hybrid electronic devices from two-dimensional materials and perovskite oxides.

INTRODUCTION

The rich and diverse phenomenology of perovskite oxides,¹⁻⁴ which includes electronic and structural phase transitions, colossal magnetoresistance to ferroelectricity and superconductivity, holds great promise for new concepts in device technology and material engineering. The crystal structure of SrTiO₃ (STO), a crucial member of the perovskite oxide family that forms the building block of complex oxide heterostructures,⁵⁻⁶ is centrosymmetric and hence a paraelectric in the bulk. STO approaches an incipient ferroelectric state at low temperatures, but quantum fluctuations prohibit a long-range ferroelectric order to develop.⁷ The quest for stabilizing ferroelectricity in STO has a long history, and it is now known that chemical doping,⁸ nanostructuring,¹⁰ manipulation of oxygen stoichiometry¹¹⁻¹₂ or application of inhomogeneous deformation (flexoelectricity)¹³ can cause spontaneous electric polarization in the bulk. However, the surface of a STO (100) crystal, in both TiO₂ and SrO terminations, can intrinsically host out-of-plane dipole moments due to inversion symmetry breaking at surface, which the Ti or the Sr ions are vertically displaced away from the corresponding oxygen planes. Although surface reconstruction in STO has been established with multiple spectroscopic¹⁴⁻¹⁶ and surface topography¹⁷¹⁸ probes, a direct evaluation of the resulting electric polarization has been difficult. Experiments with piezoresponse force microscopy¹⁷,¹⁸ and flexoelectric response¹⁹ yield surface polarization of ~0.5–10 μC cm⁻², which is strongly influenced by local oxygen stoichiometry,¹⁹,²⁰ grain boundaries²⁰,²¹ or surface strain.²⁰ Apart from the natural relevance to in-built ferroelectricity, the importance of surface electrostatics in STO is paramount because it can directly impact charge transfer superconductivity,⁵ oxide heterostructures⁵,²²,²³ and two-dimensional (2D) electronics as active substrates.²⁴⁻²⁶

Hybrid field-effect transistors (FETs) from layered solids such as graphene and molybdenum disulfide (MoS₂) on STO substrate aim to combine the high crystallinity and atomically clean interface to spectacular bulk dielectric properties of STO (dielectric constant >10⁶ at low temperatures). It is however unclear if the out-of-plane polarization at the STO surface is stable in the presence of graphene, for example, against possible atomic reorganization and screening. Recent observations of (anti-)hysteretic gate-transfer characteristics at slow sweep rates in graphene FETs fabricated on STO(100) substrate²⁵,²⁶ are attributed to “ferroelectric-like” electric polarization at the STO surface, which indeed bear close resemblance to transfer characteristics of graphene FET on ferroelectric substrates.²⁷⁻³¹ While this has been described as the effect of gate voltage-dependent dynamic trapping and detrapping of charge at the channel–substrate interface, identifying the microscopic origin of such interface states, and its connection to electric polarization at the surface, remains an outstanding experimental challenge.

Here we have probed the interface of graphene and STO by constructing dual-gated graphene-on-STO FETs, which allow direct calibration of the graphene–STO interface against the interface between graphene and hexagonal boron nitride (hBN), a conventional trap-free³² well-characterized dielectric for graphene devices. While the transfer characteristics using hBN top gate shows no hysteresis, that using STO back gate becomes strongly anti-hysteretic at low temperature (≤200 K), which is quantitatively associated with in-built electric polarization at the graphene–STO interface.
RESULTS AND DISCUSSION

Device fabrication and electrical measurement

The transport and 1/f noise measurements were carried out in a dual-gated single-layer graphene (SLG) field-effect transistor with hBN as the back gate and STO as the back gate dielectric. The schematic of a typical dual-gated SLG transistor with the electrical layout is shown in Fig. 1a. The TiO2 surface termination of the 0.5 mm thick STO (100) substrate (from CrysTec GmbH) was achieved through chemical processes and annealing (Fig. S1 in Supplementary Information). The SLG and hBN flakes were exfoliated on SiO2/Si1−x++ substrates, and subsequently transferred onto the TiO2−terminated surface of STO through van der Waals epitaxy13,34 (see Methods for more details). The layer number of graphene was verified by Raman spectroscopy as shown in Fig. 1d. The absence of D peak at 1350 cm−1 in the Raman spectrum confirms a defect-free graphene channel. The metal contacts were patterned by e-beam lithography followed by thermal deposition of S/50 nm of chromium/gold. The optical microscope image of the SLG/hBN heterostructure before transferring onto STO, and the dual-gated transistor after depositing contact pads, are shown in Fig. 1b, c, respectively. All measurements of resistance and noise were carried out using low-frequency AC technique34−40 in four probe geometry under high vacuum condition (~10−5 torr). The carrier mobility of the graphene channel, similar for both electrons and holes, was found to be ~2000 cm²Vs−1 at ~140 K, which increases to ~7300 cm²Vs−1 at ~140 K and increases to ~7300 cm²Vs−1 at ~140 K, in agreement with recent experimental report33 (Fig. S2 in the Supplementary Information). The resistance of the graphene channel increases with increasing temperature up to ~60 K beyond which it either saturates or decreases marginally (Fig. S3 in the Supplementary Information).

Measurement of dielectric constant of STO

The resistance of the dual-gated SLG transistor with varying top gate voltage (V_{TG}) shows conventional bell curve with a charge neutrality point (CNP) or Dirac point at V_{TG} ≈ −1.6 V (Fig. 1e). The hysteresis in the top gate sweep is nearly negligible, as expected from trap-free interface of SLG and hBN.35,36 The dual-gated geometry allows a direct measurement of the dielectric constant of STO (ε_r^{STO}) from the locus of the CNP in the (V_{TG}, V_{BG}) space, which balances the STO back gate capacitance with the known capacitance of hBN top gate. In Fig. 1f, the resistance at T = 100 K of the dual-gated SLG transistor is shown while sweeping V_{BG} at different fixed back gate voltages (V_{BG}). The CNP (V_{CNP}) shifts expectedly to the left with increasing V_{BG}42,43 (Fig. 1g) gives a straight line which can be fitted with the equation,

\[ V_{CNP} = -\frac{C_B}{C_T} V_{BG} - \frac{n_0 e}{C_T} \]

where C_B and C_T are the capacitances of the back gate with STO as dielectric and the top gate with hBN as dielectric, respectively, n_0 is the intrinsic carrier density in graphene and e is the electronic charge. Since C_T (≈2.7×10⁻³ F m⁻²) is known from the thickness of hBN (=13 nm, measured from atomic force microscopy), we obtain the dielectric constant \( \varepsilon_r^{STO} = C_B d_{STO} / \varepsilon_0 (d_{STO} being the
thickness of STO and \( \varepsilon_0 \) the vacuum permittivity) (also see Fig. S4 in the Supplementary Information). The magnitude of \( \varepsilon_{\text{STO}} \), measured at different temperatures, as shown in Fig. 1h, are in agreement with previous reports\(^7,44–47\) and matches well with the value of \( \varepsilon_{\text{STO}} \) estimated from Hall measurement at low temperatures. This agreement confirms that both graphene–hBN and graphene–STO interfaces in our device are atomically clean, and free of undesired adsorbates and chemical species.

Anti-hysteretic transfer characteristics
Unlike the top gate, sweeping of the back gate voltage \( V_{BG} \) in forward and reverse directions led to strong anti-hysteresis in the transfer characteristics. The extent of anti-hysteresis depends on both temperature and sweep range of \( V_{BG} \). As shown in Fig. 2a, the anti-hysteresis decreases with increasing temperature and vanishes at the temperature range of 150–180 K whereas, it decreases with decreasing sweep range (Fig. 2b). See Fig. S5 in the Supplementary Information for results from different devices. Hysteretic transfer characteristics in graphene FET\(^{26,50}\) on SiO\(_2\) and other substrates\(^{49–51}\) are commonly attributed to slow charge transfer in the presence of impurity states and absorbed water molecules. Although our experiment was performed under high vacuum condition, and the collapse of the anti-hysteretic transfer characteristics is observed at significantly low temperature (~180 K), the possibility of physi/chemisorption of OH\(^-\) and H\(^+\) on individual atomic site\(^53\) cannot be ruled out. However, the independence of the anti-hysteretic behaviour to the ramp rate in \( V_{BG} \) (Fig. S6 in the Supplementary Information) suggests a fundamentally different physical mechanism in our case.

The similarity of the transfer characteristics to that observed in the earlier studies of graphene transistors on STO substrate\(^{25,26}\) and also in the single/multilayer graphene on ferroelectric substrates\(^{27–31}\) strongly suggests that electric polarization at the surface gives rise to quantum confined states that trap, store and release charge from graphene periodically as \( V_{BG} \) is swept back and forth. The temperature and sweep range dependence provide crucial insight into the energy and confinement scale of these states. Figure 2c shows the CNPs (\( V_{\text{CNP}} \)) for varying sweep range \( \Delta V_{BG} \) of the back gate. The symmetric positions of the CNPs about \( V_{BG} = 0 \) for the forward and reverse sweep directions eliminate oxygen vacancy-mediated anti-hysteretic transfer characteristics.\(^53\) In all devices, the (anti-)hysteresis becomes undetectable for \( \Delta V_{BG} \ll 20 \) V, i.e., maximum \( |V_{BG}| = 10 \) V, which is insensitive to temperature (for \( T \leq 200 \) K). This indicates the energy of the localized trapping state (measured from the Dirac point), \( E_t \sim E_F = h\nu_F \pi C_0 (V_{BG} - V_{\text{CNP}})/e \sim 0.15 \) eV, where \( \nu_F \) is the Fermi velocity. The inset of Fig. 2c confirms similar behaviour in a different device (D1).

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** Temperature and gate voltage range-dependent transfer characteristics. a Anti-hysteresis in transfer characteristics with respect to back gate voltage (\( V_{BG} \)) at different temperatures showing the decrease in anti-hysteresis with increasing temperature. b Anti-hysteresis in transfer characteristics with respect to \( V_{BG} \) at 70 K showing the decrease in anti-hysteresis with decreasing sweep range of \( V_{BG} \). The arrows indicate the direction of \( V_{BG} \) sweep in (a, b). c The CNP of forward and reverse sweep directions as a function of overall sweep range of \( V_{BG} (\Delta V_{BG}) \) at different temperatures for devices D2 and D1 (inset). d The difference in CNP of forward and reverse sweep directions of \( V_{BG} \) as a function of temperature at different sweep ranges for devices D2 and D1 (inset).
The temperature dependence of the hysteresis (Fig. 2a) provides an estimate of the energy barrier to charge exchange between the substrate (STO) and graphene. To quantify this, we have plotted the difference in CNP (ΔV_{CNP}) for the forward and the reverse sweep directions in Fig. 2d as a function of temperature. For large sweep range ΔV_{BG} ≥ 100 V, the anti-hysteresis in both D1 (inset) and D2 vanishes at ≈ 150 – 200 K, suggesting a confinement energy scale Φ_c ≈ 0.02 eV. At lower ΔV_{BG}, the hysteretic behaviour vanishes at lower T, possibly due to lower magnitude of effective polarization due to remnant domains.

The temperature-dependent anti-hysteretic behaviour can arise from two possible mechanisms. First, the structural transition to the tetragonal phase at low temperatures is known to form domains in the near-surface region, causing rumpling of the surface. This may potentially cause trap states of possibly both structural (domain) and electrostatic (dipole moments) origin. Although the tetragonal domains have been observed to persist up to ∼105 K, the temperature dependence of resistance in our case seems to indicate the structural transition to be limited below ~60 K (Fig. S3 in supplementary information). The structural origin is further unlikely because the temperature scale of disappearance of the anti-hysteresis is found to be strongly sweep range dependent, being ∼30 K and >200 K (extrapolated) for sweep ranges of ±10 and ±40 V, respectively, in the same device (D2, Fig. 2d). Second, an alternative origin of the hysteretic behaviour can be traced to electrostatically confined trap states arising due to formation of surface dipoles. Our DFT calculations at the graphene–STO interface indicate a possible origin of such surface dipole moments which can be attributed to the movement of Ti and Sr atoms at the surface of STO (Fig. 3a–d). The DFT calculation was performed to estimate the surface polarization, following the formalism adopted by Vanderbilt et al. 54 considering slab geometries of paraelectric/ferroelectric bulk compounds.

Two key aspects of the DFT calculations can be summarized as below (see Fig. S8 and associated discussions in the Supplementary Information for more details). First, the vertical displacement (Δz, shown in Fig. 3d) of Ti atoms in TiO₂ layer and Sr atoms in SrO layer result in a formation of out-of-plane dipole moment on the surface of STO. The surface dipole moment of bare STO (P_{STO} = −13.89 μC cm⁻², in agreement with ref. 54) is significantly enhanced to P_{STO+SLG} = −34.90 μC cm⁻² in the presence of graphene. This result is obtained by assuming an epitaxial registration between graphene and STO (model-1). Calculations were also carried out considering model-2, where the lattice parameters of graphene were kept intact. See Supplementary Information section for details. The polarization (P_{STO+SLG}) calculated for model-1 and model-2 turned out to be −34.9 and −24 μC cm⁻², respectively. Thus, the polarization computed from model-2 geometry gives better agreement to experimental value and that obtained from simple phenomenological model. Such enhancement is presumably caused by the rumpling of the surface TiO₂ layer in the presence of graphene, as observed in DFT optimized structure. Second, the band gap at the STO surface ΔE_{gap} ≈ 0.21 eV is considerably smaller than the band gap of bulk STO ΔE_{gap} ≈ 1.84 eV (Fig. 3e). Notwithstanding the intrinsic underestimation of band gap in DFT due to over-screening problem, 55 this indicates a gradual bending of the bulk bands to surface, 56 as shown in the schematic of Fig. 3f. The competing effects of band bending and electrostatic energy due to polarization at the surface can be combined to
develop a phenomenological model for the observed anti-hysteretic behavior (Fig. 3f–h). A quantum well may be formed by the decrease in the band gap and the increase in the electrostatic potential $\Delta E_{\text{gap}} \approx \Delta E_{\text{eff}} A_{\text{cell}} / 2\epsilon_0 \epsilon_r$, at the surface due to the dipolar field, where $A_{\text{cell}}$ is the area of the TiO$_2$ unit cell. Equating the latter to the confinement scale $\Phi_0 \approx 0.02 \text{ eV}$, and assuming air gap between Ti and O atoms ($\epsilon_r \approx 1$) at the surface, we get $P \approx 13 \mu\text{C cm}^{-2}$, which is similar to that obtained from DFT for bare STO, but smaller than expected from graphene–STO hybrid. DFT is well known to overestimate the polarization value even as much as by an order of magnitude, as observed in bulk materials. In the presence of out-of-plane polarization $P$ at STO surface, the interfacial potential barrier that determines the trapping–detrapping rate of charge across the interface, and hence the $1/f$ noise, is modified by the local effective electric field $E_{\text{eff}}$. The typical time dependence of resistance fluctuations of the graphene channel is shown in Fig. 4d for two representative $V_{\text{BG}}$, with a $1/f$-like power spectral density $S_f(R^2)$ (Fig. 4e). The details of the noise measurement techniques are discussed in the Methods section and Supplementary Information. Figure 4c, f correlates the variation in noise magnitude with $V_{\text{BG}}$ (Fig. 4f) with the anti-hysteretic behavior in the channel resistance $R$ (Fig. 4c). We find that $\langle (\Delta R)^2 \rangle / R^2$ (obtained by integrating $S_f(R^2)$ over the experimental frequency range) displays a strong (anti-)hysteretic two-state behaviour as a function of $V_{\text{BG}}$. The top gate dependence of noise in the same graphene channel is non-hysteretic and exhibits conventional V-shaped behavior (Fig. 57 in the Supplementary Information section), confirming that the anti-hysteretic behaviour is due to surface electrical polarization on STO. Remarkably, the $V_{\text{BG}}$ dependence of $\langle (\Delta R)^2 \rangle / R^2$ collapses on a single trace as function of density $n$, irrespective of the sweep directions or temperature (Fig. 4g). Since $n = |E_{\text{eff}}|/|E_0|$, the monotonic change in noise across the Dirac point ($E_{\text{eff}} = 0$) indicates an unconventional microscopic origin that depends on the direction of $E_{\text{eff}}$, rather than just its magnitude.

When the STO surface is spontaneously polarized, the interface potential barrier $V_s \approx E_t - \Phi_0$ naturally leads to correlated

---

**Fig. 4** Low-frequency $1/f$ noise. Schematics of the potential energy barrier of STO surface, a $V_{b1}$ at electron-doped region with positive effective electric field ($E_{\text{eff}}$) and b $V_{b2}$ at hole-doped region with negative $E_{\text{eff}}$ showing $V_{b2} > V_{b1}$, where $\Phi_0$ represents the interface dipole moment. c The anti-hysteresis in the transfer characteristics of device D1 at 30 K. d The time series of resistance fluctuations at $V_{\text{BG}} = 90$ V and $-30$ V, showing higher noise for $V_{\text{BG}} > 90$ V. e Power spectral density ($S_f(R^2)$) of the resistance fluctuations showing $1/f$ noise characteristics. f Normalized $1/f$ noise ($\langle (\Delta R)^2 \rangle / R^2$) of SLG on STO with forward sweep (FS) and reverse sweep (RS) of $V_{\text{BG}}$ at 30 K, showing a very large magnitude on the right side of the charge neutrality point (CNP) and almost two order of magnitude lower value on the left side of CNP for both FS and RS directions of $V_{\text{BG}}$. g Normalized $1/f$ noise ($\langle (\Delta R)^2 \rangle / R^2$) vs. carrier density ($n$) of the SLG channel at different temperatures from 7 K to 150 K showing a bistable feature in the electron-doped (red background) and hole-doped (blue background) regions for both FS and RS directions of $V_{\text{BG}}$. h The exponential fitting (blue line) of the noise magnitude near CNP which provides the magnitude of interfacial polarization.
number-mobility fluctuation noise in the graphene channel that is sensitive to the direction of $E_{\text{eff}}$ with respect to the dipole moment $\mathbf{p}$ at the surface. Here, $E_i (\approx \Delta E_{\text{gap}} / 2 \approx 0.1 \text{ eV})$ is the zero-field surface barrier for electron exchange. When the characteristic trapping time scale $\tau = \tau_0 \exp[2ad]$ is distributed as $\sim 1/\tau_0$, estimation of surface polarization through slab calculation yields $P \approx 10 \mu \text{C m}^{-2}$, which is in good agreement to that obtained from the $T$ dependence of anti-hysteresis (Fig. 2a).

In conclusion, we have shown that the dipole field at the surface of STO, created due to the off-centric movement of atoms at the TiO$_2$-terminated surface, strongly impacts both transfer characteristics and low-frequency noise in the graphene-STO hybrid FETs. The key observation of temperature and back gate voltage sweep range-dependent anti-hysteretic transfer characteristics in both resistance and noise suggest formation of trap states at the STO surface due to band renormalization and electrostatic confinement. We quantitatively estimate surface polarization $P \sim 12 \mu \text{C m}^{-2}$, which is in good agreement with DFT calculated polarization at graphene/STO interface. Our experiment will be useful in characterizing and exploiting interfaces of graphene and polarizable materials.

METHODS

TiO$_2$ surface termination of STO

The STO substrates were held with a teflon holder and ultrasonicated in ethanol, deionized (DI) water, buffered hydrofluoric acid and then again in DI water for 30 min in each of them. After cleaning, the STO substrates were placed in a tube furnace and annealed for 2.5 h in an oxygen atmosphere of 300 cc min$^{-1}$ at 960 °C. Then, the substrates were cooled down to room temperature naturally which generates TiO$_2$ terminated surface on STO.

Device fabrication and measurements

Graphene and hBN layers were first exfoliated on SiO$_2$ substrate by conventional micromechanical exfoliation. We used a drop of EL9 (baked at 80 °C for 2 h) placed on a transparent plastic sheet to lift suitable layers attached to the EL9 was transferred on to STO surface at ~60 °C. For this, we have used a custom-made transfer of graphene and hBN with appropriate orientation and sequence from DI water for 30 min in each of them. After cleaning, the STO substrates were placed in a tube furnace and annealed for 2.5 h in an oxygen flow of 300 cc min$^{-1}$ at 960 °C. Then, the substrates were cooled down to room temperature naturally which generates TiO$_2$ terminated surface on STO. Device fabrication and measurements

Graphene and hBN layers were first exfoliated on SiO$_2$ substrate by conventional micromechanical exfoliation. We used a drop of EL9 (baked at 80 °C for 2 h) placed on a transparent plastic sheet to lift suitable layers of graphene and hBN with appropriate orientation and sequence from SiO$_2$ substrate at ~60 °C. For this, we have used a custom-made transfer set-up consisting of an optical microscope-based high-precision mechanical manipulator. Subsequently, the stack of 2D heterostructure attached to the EL9 was transferred on to STO surface at $T \approx 100$ °C and the EL9 was dissolved away with acetone to obtain the required heterostructure. Since the EL9 does not come into contact with the graphene/STO or graphene/hBN interfaces at any stage of the fabrication process, the method leads to highly clean van der Waals interfaces.

Transport and noise measurements were performed using a lock-in amplifier while biasing the device in the ohmic regime. The 1/f noise in the graphene channel on STO was measured by calculating the Fourier transform of the auto-correlation function of resistance fluctuations, $\Delta R(t) = R(t) - \langle R \rangle$, where $\langle R \rangle$ is the resistance averaged over the experimental time period. We simultaneously measured the time series data for both in-phase and out-of-phase component of the channel resistance, which give total noise and background noise respectively. By subtracting the background noise from the total noise, we get the sample noise. See the Supplementary Information section for details.

DFT calculations

DFT calculations were performed within the framework of plane-wave basis set as implemented in VASP with projector augmented-wave potential. For details please see Supplementary Information section.

Data availability

The data regarding experimental and theoretical matter that support the findings of this study are available from A.S. (email: aninditas@isic.ac.in) and T.S.D. (email: tanusri@boson.bose.res.in), respectively, upon reasonable request.

ACKNOWLEDGEMENTS

The authors thank the Department of Science and Technology (DST) and The Netherlands Organisation for Scientific Research (NWO) for a funded project. A.S., T.P. and A.G. thank the Centre for Nano Science and Engineering (CeNSE), Indian Institute of Science for providing National Nanofabrication (NNIC) and Micro and Nano Characterization Facility (MNCF).

AUTHOR CONTRIBUTIONS

A.S., D.N., T.P., R.R., A.R., M.M., T.B., T.S.-D. and A.G. designed the experiments. R.R. prepared the TiO$_2$ terminated STO substrate. A.S. and T.P. fabricated the devices and performed the measurements. D.N. and T.S.-D. performed the DFT calculations. A.S., D.N., T.S.-D. and A.G. analysed the data and discussed the results.

ADDITIONAL INFORMATION

Supplementary information accompanies the paper on the npj 2D Materials and Applications website [https://doi.org/10.1038/s41469-018-0055-5].

Competing interests: The authors declare no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

REFERENCES

1. Zubko, P., Gariglio, S., Gabay, M., Ghosez, P. & Triscone, J. M. Interface physics in complex oxide heterostructures. Annu. Rev.Condens. Matter Phys. 2, 141–165 (2011).
2. Catalan, G. Progress in perovskite nickelate research. Phase Transit. 81, 729–749 (2008).
3. Cohen, R. E. Origin of ferroelectricity in perovskite oxides. Nature 358, 136–138 (1992).
4. Bednorz, J. G. & Müller, K. A. Perovskite-type oxides—the new approach to high- $T_c$ superconductivity. Rev. Mod. Phys. 60, 585 (1988).
5. Ohtomo, A. & Hwang, H. Y. A high-mobility electron gas at the LaAlO$_3$/SrTiO$_3$ heterointerface. Nature 427, 423–426 (2004).
6. Reyren, N. et al. Superconducting interfaces between insulating oxides. Science 317, 1196–1199 (2007).
7. Müller, K. A. & Burkard, H. SrTiO$_3$: An intrinsic quantum paraelectric below 4 k. Phys. Rev. B 19, 3593–3602 (1979).
8. Durán, A., Martínez, D., Díaz, J. A. & Siqueiros, J. M. Ferroelectricity at room temperature in pr-doped SrTiO$_3$. J. Appl. Phys. 97, 104109 (2005).
9. Kumar, A. S. et al. Magnetic and ferroelectric properties of Fe doped SrTiO$_3$–x films. J. Phys. Conf. Ser. 200, 092010 (2010).
10. Lee, D. et al. Emergence of room-temperature ferroelectricity at reduced dimensions. Science 349, 1314–1317 (2015).
11. Kim, Y. S. et al. Localized electronic states induced by defects and possible origin of ferroelectricity in strontium titanate thin films. Appl. Phys. Lett. 94, 202906 (2009).
12. Jang, H. W. et al. Ferroelectricity in strain-free SrTiO$_3$ thin films. Phys. Rev. Lett. 104, 197601 (2010).
13. Zubko, P., Catalan, G., Buckley, A., Welche, P. R. L. & Scott, J. F. Strain-gradient-induced polarization in SrTiO$_3$ single crystals. Phys. Rev. Lett. 99, 167601 (2007).
14. Bickel, N., Schmidt, G., Heinz, K. & Müller, K. Ferroelectrelaxation of the SrTiO$_3$ (100) surface. Phys. Rev. Lett. 62, 2009 (1989).
15. Herger, R. et al. Surface of strontium titanate. Phys. Rev. Lett. 98, 076102 (2007).
16. Dadgireviren, O. E. et al. Surface phase, morphology, and charge distribution transitions on vacuum and ambient annealed SrTiO$_3$ (100). Phys. Rev. B 83, 195303 (2016).
17. Kholkin, A., Bidkin, I., O斯塔chuk, T. & Petzet, J. Room temperature surface piezoelectricity in SrTiO3 ceramics via piezoresponse force microscopy. Appl. Phys. Lett. 93, 222905 (2008).
18. Khanbabae, B. et al. Large piezoelectricity in electric-field modified single crystals of SrTiO3. Appl. Phys. Lett. 109, 222901 (2016).
19. Petzet, J. et al. Dielectric, infrared, and raman response of undoped SrTiO3 ceramics: evidence of polar grain boundaries. Phys. Rev. B 64, 184111 (2001).
20. Kim, M. et al. Nonstochiometry and the electrical activity of grain boundaries in SrTiO3. Phys. Rev. Lett. 86, 4506 (2001).
21. Rupprecht, G. & Bell, R. O. Microwave losses in strontium titanate above the phase transition. Phys. Rev. 125, 1915 (1962).
22. Boussquet, E. et al. Improper ferroelectricity in perovskite oxide artificial superlattices. Nature 452, 732–736 (2008).
23. Li, Y. et al. Superlattice films. Appl. Phys. Lett. 91, 252904 (2007).
24. Couto, N. J. G., Sacépé, B. & Morpurgo, A. F. Transport through graphene on SrTiO3. Phys. Rev. Lett. 107, 225501 (2011).
25. Saha, S. et al. Unconventional transport through graphene on SrTiO3: a plausible effect of SrTiO3 phase transitions. Sci. Rep. 4, 6173 (2014).
26. Sachs, R., Lin, Z. & Shi, J. Ferroelectric-like SrTiO3 surface dipoles probed by graphene. Sci. Rep. 4, 3657 (2014).
27. Song, E. B. et al. Robust bi-stable memory operation in single-layer graphene ferroelectric memory. Appl. Phys. Lett. 99, 042109 (2011).
28. Hong, X. et al. Unusual resistance hysteresis in n-layer graphene field effect transistors fabricated on ferroelectric Pb(Zr0.2Ti0.8)O3. Appl. Phys. Lett. 97, 033114 (2010).
29. Yusuf, M. H., Nielsen, B., Dawber, M. & Du, X. Intrinsinc and intrinsic charge trapping at the graphene/ferroelectric interface. Nano Lett. 14, 5437–5444 (2014).
30. Hong, X. Emerging ferroelectric transistors with nanoscale channel materials: the possibilities, the limitations. J. Phys. Condens. Matter 28, 103003 (2016).
31. Kurchak, A. I. & Strikha, M. V. Antihysteresis of the electrical resistivity of graphene field effect sensors for ferroelectric thin film studies. Nano Lett. 13, 4374–4379 (2013).
32. Henderson, M. A. The interaction of water with solid surfaces: fundamental aspects revisited. Surf. Sci. Rep. 46, 1–308 (2002).
33. Roy, K. et al. Graphene-MoS 2 hybrid structures for multifunctional photoresponsive memory devices. Adv. Mater. 29, 1700071 (2017).
34. Perdue, J. P. & Levy, M. Physical content of the exact Kohn-Sham orbital energies: band gaps and derivative discontinuities. Phys. Rev. Lett. 51, 1884 (1983).
35. Shen, J., Lee, H., Valentí, R. & Jeschke, H. O. Ab initio study of the two-dimensional metallic state at the surface of SrTiO3: importance of oxygen vacancies. Phys. Rev. B 86, 195119 (2012).
36. Picozzi, S., Yamauchi, K., Sanyal, B., Sergienko, I. A. & Dagotto, E. Dual nature of improper ferroelectricity in a magnetoelectric multiferroic. Phys. Rev. Lett. 99, 227201 (2007).
37. Sahoo, A. Ha, D. S., Ramanathan, S. & Ghosh, A. Conductivity noise study of the insulator-metal transition and phase coexistence in epitaxial samarium nickelate thin films. Phys. Rev. B 90, 085116 (2014).
38. Chandini, U. & Ghosh, A. Simple kinetic sensor to structural transitions. Phys. Rev. B 81, 134105 (2010).
39. Zhang, Y., Mednez, E. E. & Du, X. Mobility-dependent low-frequency noise in graphene field-effect transistors. ACS Nano 5, 8124–8130 (2011).
40. Jayaraman, R. & Sodini, C. G. A 1/f noise technique to extract the oxide trap density near the conduction band edge of silicon. IEEE Trans. Electron Devices 36, 1773–1782 (1989).
41. Wunderlich, W., Ohta, H. & Koumoto, K. Enhanced effective mass in doped SrTiO3 and related perovskites. Phys. B Condens. Matter 404, 2202–2212 (2009).
42. Koster, G., Kropman, B. L., Rijnders, G. J. H. M., Blank, D. H. A. & Rogalla, H. Quasi-ideal strontium titanate crystal surfaces through formation of strontium hydroxide. Appl. Phys. Lett. 73, 2920–2922 (1998).
43. Kawasaki, M. et al. Atomic control of the SrTiO3 crystal surface. Science 266, 1540–1542 (1994).
44. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 47, 558 (1993).
45. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169 (1996).
46. Blochl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953 (1994).
47. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758 (1999).