

Received: 06 January 2016 Accepted: 22 April 2016 Published: 12 May 2016

# **OPEN** Anomalous enhancement of the sheet carrier density beyond the classic limit on a SrTiO<sub>3</sub> surface

Neeraj Kumar, Ai Kitoh & Isao H. Inoue

Electrostatic carrier accumulation on an insulating (100) surface of SrTiO₃ by fabricating a field effect transistor with Parylene-C (6 nm)/HfO<sub>2</sub> (20 nm) bilayer gate insulator has revealed a mystifying phenomenon: sheet carrier density  $n_{2D}$  is about 10 times as large as  $C_{2D}^{\text{ins}} V_G / e$  ( $C_{2D}^{\text{ins}}$  is the sheet capacitance of the gate insulator,  $V_{\rm G}$  is the gate voltage, and e is the elementary charge). The channel is so clean to exhibit small subthreshod swing of 170 mV/decade and large mobility of 11 cm<sup>2</sup>/Vs for n<sub>2D</sub> of  $1 \times 10^{14}$  cm $^{-2}$  at room temperature. Since  $C_{\rm 2D}^{\rm ins}$  does not depend on either  $V_{\rm G}$  nor time duration,  $n_{\rm 2D}$ beyond  $C_{2D}^{ins} V_G/e$  is solely ascribed to negative charge compressibility of the carriers, which was in general considered as due to exchange interactions among electrons in the small  $n_{\rm 2D}$  limit. However, the observed n<sub>2D</sub> is too large to be naively understood by the framework. Alternative ideas are proposed in this work.

The Gauss's law Q = CV in a field effect transistor (FET) is generally believed to be  $en_{2D} = C_{2D}^{ins} V_G$ , where,  $e, n_{2D}$ ,  $C_{2D}^{ins}$ , and  $V_{G}$  are the elementary charge, sheet carrier density of the channel, sheet capacitance of the gate insulator, and gate voltage, respectively<sup>1</sup>. The equation is valid, but only when the channel is an ideal metal, where the gate electric field is completely screened (zero screening length) at the channel surface due to the infinite charge compressibility  $\kappa \equiv (n_{\rm 2D}^2 d\mu/dn_{\rm 2D})^{-1}$  ( $\mu$  is the chemical potential). Meanwhile, for finite  $\kappa$ ,  $C_{\rm 2D}^{\rm ins}$  is replaced by  $(1/C_{\rm 2D}^{\rm ins} + 1/C_{\rm 2D}^{\rm q})^{-1}$ .  $C_{\rm 2D}^{\rm q} \equiv e^2 n_{\rm 2D}^2 \kappa$  is called a quantum capacitance<sup>2</sup>. Total energy of the carriers corresponds to  $1/C_{\rm 2D}^{\rm q}$ , thus, in general,  $C_{\rm 2D}^{\rm q}$  is positive and  $en_{\rm 2D} < C_{\rm 2D}^{\rm ins} V_{\rm G}$ . Nevertheless, negative  $\kappa$ , for which  $en_{\rm 2D} > C_{\rm 2D}^{\rm ins} V_{\rm G}$ , is a long-standing target of research both experimentally<sup>3-9</sup> and theoretically<sup>10,11</sup>, manifesting itself due to strong exchange interactions between carriers. Especially, in two-dimensional electron system (2DES), the exchange energy is negative and scales as  $\sqrt{n_{2D}}$ , while the positive (e.g., kinetic) energy scales as  $n_{2D}$ ; therefore, for sufficiently small  $n_{2D}$ , the total energy  $(\propto 1/C_{2D}^q)$  can be negative. What we demonstrate here is, however, far beyond the classic examples. A quasi-2DES at the channel of  $SrTiO_3$  FET shows anomalous enhancement of  $n_{2D}$ : ten times as large as  $C_{\rm 2D}^{\rm ins}V_{\rm G}/e$ . The enhancement cannot be explained only by the exchange interaction, suggesting another mechanism of inducing negative  $\kappa$ .

A schematic cross-section of a standard FET is shown in Fig. 1 with the band diagrams and the relationships between the capacitances following a widely-accepted concept of the accumulation-type metal-oxide-semiconductor FET; thick substrate (channel) of the FET is implicitly grounded in the far distance, which gives zero of the chemical potential. The gate voltage  $V_G = e n_{\rm 2D}/C_{\rm 2D}$  is a sum of the voltage drop in the gate insulator  $V_{\rm ins} = e n_{\rm 2D}/C_{\rm 2D}^{\rm ins}$  and the band-bending of the channel material  $\varphi = e n_{\rm 2D}/C_{\rm 2D}^{\rm ch}$ . Therefore,  $V_G = V_{\rm ins} + \varphi$  means  $1/C_{\rm 2D} = 1/C_{\rm 2D}^{\rm ins} + 1/C_{\rm 2D}^{\rm ch}$  (Fig. 1a). For the metallic channel, the chemical potential (Fermi energy)  $\mu/e$  substitutes for  $\varphi$ , and  $C_{\rm 2D}^{\rm ch}$  is replaced by the quantum capacitance  $C_{\rm 2D}^{\rm q} = e^2 n_{\rm 2D}^2 \kappa$  (Fig. 1b). It is still possible to consider  $C_{\rm 2D}^{\rm ch}$  for the nonmetallic bulk part of the substrate, and  $1/C_{\rm 2D} = 1/C_{\rm 2D}^{\rm ins} + 1/C_{\rm 2D}^{\rm ch}$ . But  $1/C_{\rm 2D}^{\rm ch}$  ( $\ll 1/C_{\rm 2D}^{\rm q}$ ) term is usually omitted. The channel material in this study is SrTiO<sub>3</sub>. It changes from an insulator to metal by gating <sup>12</sup>, so we use a potation  $C_{\rm 2D}^{\rm sto}$  in a classic material for solid state  $C_{\rm 2D}^{\rm th}$  and  $C_{\rm 2D}^{\rm ch}$  and  $C_{\rm 2D}^{\rm ch}$  is a classic material for solid state  $C_{\rm 2D}^{\rm ch}$  and  $C_{\rm 2D}^{\rm ch}$  is a classic material for solid state  $C_{\rm 2D}^{\rm ch}$ so we use a notation  $C_{2D}^{\text{sto}}$  in lieu of both  $C_{2D}^{\text{ch}}$  and  $C_{2D}^{\text{q}}$ . SrTiO<sub>3</sub> is a classic material for solid-state physics but is a cynosure of modern oxide-electronics researches because of the formation of quasi 2DES at the surface<sup>13–15</sup> or interface<sup>16,17</sup>, as well as the large mobility of the confined 2D carriers without a freeze-out<sup>18–21</sup>. Both the confinement and the large mobility are originated in or, if not more, influenced by the quantum paraelectricity<sup>22</sup> with a large and nonlinear dielectric response<sup>23</sup>. Furthermore, at the surface and interface, where the inversion

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan. Correspondence and requests for materials should be addressed to I.H.I. (email: isaocaius@gmail.com)

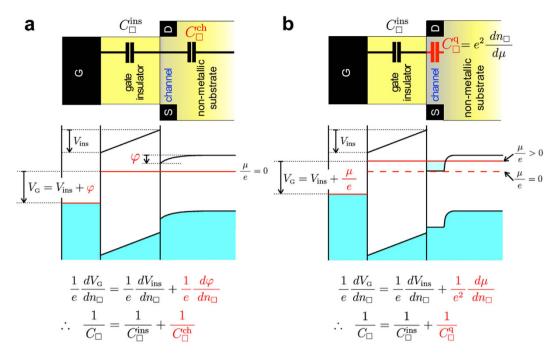


Figure 1. Schematic pictures of the cross section and the band diagram of FET. Neither distance nor energy of the picture scales to that of the real device. (a) The channel is an n-type non-metallic material (e.g., non-doped SrTiO<sub>3</sub>). By differentiating  $V_{\rm G} = V_{\rm ins} + \varphi$  with respect to  $n_{\rm 2D}$ , and by using the Gauss's law, we obtain  $1/C_{\rm 2D} = 1/C_{\rm 2D}^{\rm ins} + 1/C_{\rm 2D}^{\rm ch}$ . (b) For larger  $V_{\rm G}$ , the channel becomes metallic and  $V_{\rm G} = V_{\rm ins} + \mu/e$ . Same as (a) the relationship  $1/C_{\rm 2D} = 1/C_{\rm 2D}^{\rm ins} + 1/C_{\rm 2D}^{\rm q}$  is obtained, where  $C_{\rm 2D}^{\rm q}$  is called a quantum capacitance (ref. 2).  $n_{\rm 2D} = C_{\rm 2D} V_{\rm G}$  becomes larger than  $C_{\rm 2D}^{\rm ins} V_{\rm G}$  only when  $C_{\rm 2D}^{\rm q}$  is negative.

symmetry is broken, the charge confinement induces some intriguing electronic properties; for example, the Rashba spin-orbit coupling at the surface of  $SrTiO_3$  discussed in refs 24–26.

However, it is intensely difficult to fabricate such a high quality FET on SrTiO $_3$  as to reveal the true nature of the exotic phenomena. The band gap of SrTiO $_3$  is nearly  $3.2\,{\rm eV^{27.28}}$ , but it turns to be a good metal by *a very tiny electron doping* of  $8.5\times10^{15}\,{\rm cm^{-3}}$  (corresponding to the removal of a few oxygen atoms out of  $10^7$ ), which is orders of magnitude lower than the threshold of metallicity in Si  $(3.5\times10^{18}\,{\rm cm^{-3}})$  or Ge  $(3.5\times10^{17}\,{\rm cm^{-3}})^{29}$ . Thus, the channel of SrTiO $_3$  FET becomes conductive quite easily by the oxygen-defect formation. In other words, the channel current of some SrTiO $_3$  FETs might be rather dominated by electrochemical reaction than purely electrostatic carrier-density modulation $^{30}$ . Therefore, in this paper, we propose an alternative gate insulator: an organic/inorganic bilayer consisting of 6 nm ultra-thin poly-monochloro-*para*-xylylene (Parylene-C) and 20 nm HfO $_2$ , as schematically shown in Fig. 2a. The film of Parylene-C polymer is widely used for coating a variety of material surfaces, because it is highly conformal, pin-hole free, quite inert to any gases and chemicals, and sufficiently stable from around 200 °C down to at least 60 mK $^{31}$ . The bilayer gate insulator was deposited on the atomically-flat (100) surface (miscut-angle is less than about 0.03°) of non-doped SrTiO $_3$  single crystals provided by Shinkosha Co., Ltd. The photos of our FETs are shown in Fig. 2, and the cross-section images obtained by the transmission electron microscopy (TEM) are shown in Fig. 3a–d. The step and terrace surface of our SrTiO $_3$  crystals is noticeably insulating with the sheet resistance above our instrumental limit (~ $10^{13}\,\Omega$ ) at room temperature, and this surface is kept sufficiently insulating after the fabrication process of FET.

The high quality of our FET manifested itself in the subthreshold behaviour. Figure 3e shows  $I_{\rm SD} - V_{\rm SD}$  plot for fixed  $V_{\rm G}$  for the three-terminal device (See Fig. 2c).  $I_{\rm SD} \propto V_{\rm SD}$  for small  $V_{\rm G}$ , but it shows upward convex for  $V_{\rm G} \gtrsim 1.6\,\rm V$ , which is called the threshold voltage  $V_{\rm th}$  and the region  $V_{\rm SD} < V_{\rm th}$  is dubbed as the subthreshold region. As shown in the  $I_{\rm SD} - V_{\rm G}$  curves in Fig. S1 of the Supplementary Materials, it is seen in the subthreshold region that  $\log_{10}I_{\rm SD} \propto V_{\rm G}$ . Indeed, with  $\varphi$  in Fig. 1a,  $I_{\rm SD} \propto \exp(e\varphi/k_{\rm B}T)$ , where T is the temperature and  $k_{\rm B}$  is the Boltzmann constant, because only the thermally activated carriers of the valence band can contribute to the transport. Since  $\varphi = n_{\rm 2D}/C_{\rm 2D}^{\rm sto} = (1 + C_{\rm 2D}^{\rm sto}/C_{\rm 2D}^{\rm ins})^{-1}V_{\rm G}$ , the subthreshold swing defined as  $S \equiv \Delta V_{\rm G}/\Delta(\log_{10}I_{\rm SD})$  can be expressed as  $S = (k_{\rm B}T/e)\ln 10 \times (1 + C_{\rm 2D}^{\rm sto}/C_{\rm 2D}^{\rm ins}) \equiv n(T) \times m$ . n(T) is denoted as transport factor, and m as body factor 32,33. By measuring S, we can obtain  $C_{\rm 2D}^{\rm sto}/C_{\rm 2D}^{\rm cins}$  ratio.

S is in general estimated from the  $I_{\rm SD}-V_{\rm G}$  plot, but it might include a significant contribution of the contact resistance. Therefore, we deduced S in a more comprehensive manner. We carried out  $I_{\rm SD}-V_{\rm G}$  measurements in the subthreshold region with fixed  $V_{\rm SD}=1$  V for the devices with L=2, 4 and 9  $\mu$ m and W=4L. Then,  $WR_{exp}$  was plotted against L (Fig. 3f). Here,  $R_{exp}=V_{\rm SD}/I_{\rm SD}$  at  $V_{\rm G}^{\rm eff}\equiv V_{\rm G}-V_{\rm G}^{\rm O}=0.5$  V.  $V_{\rm G}^{\rm O}$  is the cut-off gate voltage, below which  $I_{\rm SD}$  is smaller than the noise level of 100 fA (see Supplementary Materials for details). By comparing  $WR_{exp}$  with  $R_{\rm O}+LR_{\rm 2D}$ , the sheet resistance  $R_{\rm 2D}$  is obtained. We applied this method for dozens of  $V_{\rm G}^{\rm eff}$ , and all the  $R_{\rm 2D}$  values were plotted in Fig. 3g. We can see  $\log_{10}R_{\rm 2D}$  is clearly proportional to  $V_{\rm G}^{\rm eff}$ , and deduced S=171 mV/dec-

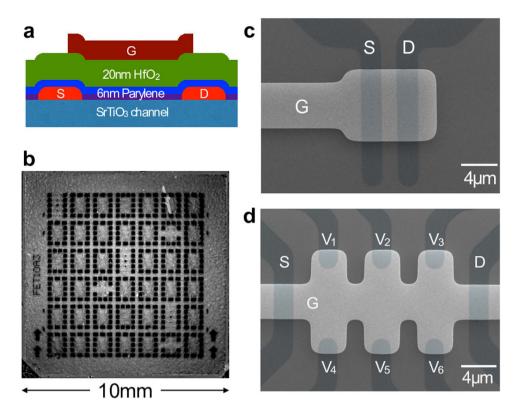


Figure 2. FET with HfO<sub>2</sub> (20 nm)/Parylene-C (6 nm) solid-state bilayer gate insulator studied in this work. (a) Schematic cross-section image of our three-terminal FET device. (b) Photograph of a  $10 \text{ mm} \times 10 \text{ mm}$  (100) SrTiO<sub>3</sub> substrate with the FET devices fabricated on it. Scanning electron microscopy images of (c) a three-terminal FET device, and (d) multi-terminal one. G, S and D stand for gate, source, and drain electrodes, respectively.  $V_1 - V_6$  are potential probes.

ade. This is indeed in good coincidence with the values simply estimated from the  $I_{\rm SD}-V_{\rm G}$  plot, indicating that the contact resistance of our FET does not contribute to the S value. Since the material-independent transport factor  $n(T)=(k_{\rm B}\,T/e)\ln 10$  is  $60\,{\rm mV/decade}$  at  $300\,{\rm K}$ ,  $S=171\,{\rm mV/decade}$  of this study is surprisingly small. (It was reported that the value of S was ~ $100\,{\rm mV/decade}$  even for Si<sup>34</sup>, ~ $250\,{\rm mV/decade}$  for SrTiO<sub>3</sub><sup>35</sup>, and ~ $1200\,{\rm mV/decade}$  for KTaO<sub>3</sub><sup>36</sup>). From m=2.8, we deduced  $C_{\rm 2D}^{\rm sto}=0.50\,\mu{\rm F/cm^2}$ . If we assume the dielectric constant of SrTiO<sub>3</sub> is  $310\,{\rm at}$  room temperature, the effective thickness for  $C_{\rm 2D}^{\rm sto}$  is  $0.55\,\mu{\rm m}$ . This means in the subthreshold region the gate electric field can penetrate into deep bulk of SrTiO<sub>3</sub> ( $0.55\,\mu{\rm m}$ ) without a large Thomas-Fermi screening of free carriers possibly originated in the defects of Parylene-C/SrTiO<sub>3</sub> interface. Put plainly, the Parylene-C passivation on the defect-prone SrTiO<sub>3</sub> surface<sup>37,38</sup> works fairly well. This is one of the two important premisses of this study.

The other premise is that the ultra-thin Parylene-C film works not only as a passivation layer protecting  $SrTiO_3$  channel from the high-k dielectric  $HfO_2$  but also works as a good capacitive layer by itself. We fabricated  $Ti(10\,\mathrm{nm})/\mathrm{Parylene-C}$  (3 nm)/ $HfO_2$  (20 nm)/ $Ti(5\,\mathrm{nm})/\mathrm{Au}(500\,\mathrm{nm})$  parallel plate capacitors, and scrutinised the capacitance by both quasi-static and ac measurement. Details are given in the Supplementary Materials. The deduced sheet capacitance of the gate insulator of our FET, Parylene-C (6 nm)/ $HfO_2$  (20 nm), is  $C_{2D}^{\mathrm{ins}} = 0.28\,\mu\mathrm{F/cm}^2$  as well as the dielectric constants of 21.5 and 2.70 for the  $HfO_2$  layer and the Parylene-C layer, respectively, consistent to the values of 20 and 3.15 reported in literature. Alternatively, we may also assume the dielectric constants of 20 and 3.15 for  $HfO_2$  and Parylene-C, respectively. Then, the film thickness becomes 18.6 nm and 3.5 nm for  $HfO_2$  and Parylene-C, respectively, both of which are almost equivalent to the results of TEM.

By using this bilayer gate insulator, we have finally obtained both the fairly clean channel and the continuous electrostatic control of the carrier density on SrTiO<sub>3</sub>. This achievement, however, has given a new twist to the research of SrTiO<sub>3</sub>. Figure 4a shows  $n_{\rm 2D}$  obtained by the Hall effect measurement for the multi-terminal FET device (Fig. 2d: details of the experiments are described in the Supplementary Materials). As mentioned above,  $n_{\rm 2D} = C_{\rm 2D} (V_{\rm G} - 1.88)/e$ , where  $1/C_{\rm 2D} = 1/C_{\rm 2D}^{\rm ins} + 1/C_{\rm 2D}^{\rm sto}$  with  $C_{\rm 2D}^{\rm ins} = 0.28\,\mu\text{F/cm}^2$  and  $C_{\rm 2D}^{\rm sto} = 0.50\,\mu\text{F/cm}^2$ . Thus,  $n_{\rm 2D} = 1.1 \times 10^{12} (V_{\rm G} - 1.88)\,\text{cm}^{-2}$ . (It should be noted here that the 1.88 V offset, above which the accumulation of the carriers in the channel becomes observable by the Hall effect measurements, may be due to the relatively larger contact resistance of the multi-terminal FET device used for the measurements; however, the origin of this offset does not affect to the following discussion). To our surprise, the measured  $n_{\rm 2D}$  is *much larger than this naive estimation*; it reaches to around  $1 \times 10^{14}\,\text{cm}^{-2}$  for  $V_{\rm G} = 6\,\text{V}$ . Even if this extra carriers are provided by the formation of oxygen/cation defects in the SrTiO<sub>3</sub> channel during the application of the large  $V_{\rm G}$  (though the channel is

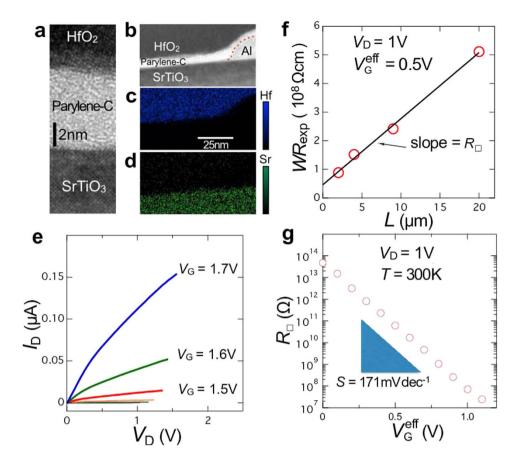


Figure 3. Characteristics of SrTiO<sub>3</sub> FET with HfO<sub>2</sub> (20 nm)/Parylene-C (6 nm) bilayer gate insulator. (a) Cross sectional TEM image of the channel. (b) Cross sectional scanning TEM (STEM) image near the Al electrode (dotted line is a guide to eyes separating Parylene-C and Al). (c) Energy-dispersive x-ray spectroscopy mapping for Hf atom and (d) that for Sr atom. (e)  $I_{\rm SD}-V_{\rm SD}$  plots for 3-terminal device with  $L=20~\mu{\rm m}$  and  $W=80~\mu{\rm m}$  for several  $V_{\rm G}$ . (f)  $WR_{\rm exp}\equiv WV_{\rm SD}/I_{\rm SD}$  for four FETs with different sizes but fixed W/L ratio plotted as a function of L (open circles). Solid line is the least-square fit ( $WR_{\rm exp}=R_{\rm O}+LR_{\rm 2D}$ ) to deduce  $R_{\rm 2D}$ . (g)  $R_{\rm 2D}$  vs.  $V_{\rm G}^{\rm eff}$  plot gives S of 171 mV/decade.

fairly protected by Parylene-C layer and is actually clean), it should be noted that  $n_{2D}$  cannot be modulated without a change of  $C_{2D}$ , independent of sources of the carriers.

We have measured the Hall effect for more than ten FET devices on three different SrTiO<sub>3</sub> substrates (two results are shown in Fig. S3), and confirmed all of them showed qualitatively same  $n_{\rm 2D}$  enhancement. In order to explain this large discrepancy, we have assumed a naive model that the channel is a *serial* connection of a bulk SrTiO<sub>3</sub> ( $C_{\rm 2D}^b = 0.50\,\mu\text{F/cm}^2$ ), and a surface layer ( $C_{\rm 2D}^s$ ). When  $V_{\rm G}$  is small,  $C_{\rm 2D}^b$  is most dominant to  $C_{\rm 2D}^{\rm sto}$ , but as  $V_{\rm G}$  increased, accumulated carriers screen the gate voltage; *i.e.*, for  $V_{\rm G} > V_{\rm min}$ ,  $C_{\rm 2D}^s$  becomes more dominant. Then, we introduced a tractable model:  $1/C_{\rm 2D}^{\rm sto} = (1-\eta) \times (1/C_{\rm 2D}^b) + \eta \times (1/C_{\rm 2D}^s)$ , where  $\eta \equiv 1/2 + \tanh \left[\alpha(V_{\rm G} - V_{\rm min})\right]$ . ( $\alpha = 0.68$  and  $V_{\rm min} = 2.8$  V are non-essential parameters). This is an ad-hoc phenomenological model to express that  $C_{\rm 2D}^b$  changes smoothly from  $C_{\rm 2D}^{\rm sto}$ -dominant to  $C_{\rm 2D}^s$ -dominant, thus the mathematical formula is not relevant. If  $C_{\rm 2D}^s$  is a large positive number as that of a good metal,  $1/C_{\rm 2D}^{\rm sto}$  and corresponding  $n_{\rm 2D}$  behave as dash-dotted lines (purple) in Fig. 4a. Deviation is still large. Then, if we assume negative capacitance  $C_{\rm 2D}^s = -0.31\,\mu\text{F/cm}^2$ , the calculated  $n_{\rm 2D}$  coincides with the measured  $n_{\rm 2D}$ . We understand that  $I_{\rm SD}$ ,  $C_{\rm 2D}^{\rm sto}$  and  $n_{\rm 2D}$  should behave as shown schematically in Fig. 4b. Negative

We understand that  $I_{\text{SD}}$ ,  $C_{\text{2D}}^{\text{2d}}$  and  $n_{\text{2D}}$  should behave as shown schematically in Fig. 4b. Negative  $C_{\text{2D}}^{\text{sto}} = -0.31 \,\mu\text{F/cm}^2$ , i.e., negative  $\kappa$ , is inevitable for explaining the large enhancement of  $n_{\text{2D}}$ . But a question arises. If this is ascribed to the exchange interaction of the quasi-2DES on SrTiO<sub>3</sub> as explained in literature<sup>3-5</sup>, averaged distance between the electrons should be much larger than the Bohr radius  $a_{\text{B}}$ , i.e.,  $(\pi n_{\text{2D}} a_{\text{B}}^2)^{-1/2} \gg 1$ , and the system may become like the Wigner crystal with negative chemical potential  $\mu \simeq -2.9 \, e^2 n_{\text{2D}}^{1/2} / \varepsilon$ , where  $\varepsilon$  is a direlectric constant of SrTiO<sub>3</sub> (ref. 39). However,  $n_{\text{2D}}$  in this study is in the order of  $10^{14} \, \text{cm}^{-2}$ , then the corresponding values  $(\pi n_{\text{2D}} a_{\text{B}}^2)^{-1/2} \simeq 11$  and  $\mu \simeq -53 \, \text{eV}$  are both unreasonable. It was suggested that negative  $\kappa$  is also realised in electronic systems close to half filling<sup>40</sup>, but this neither is applicable to our samples. Therefore, the significant enhancement of  $n_{\text{2D}}$  cannot be explained solely by the negative  $\kappa$  originating in the exchange interactions; we need an alternative idea.

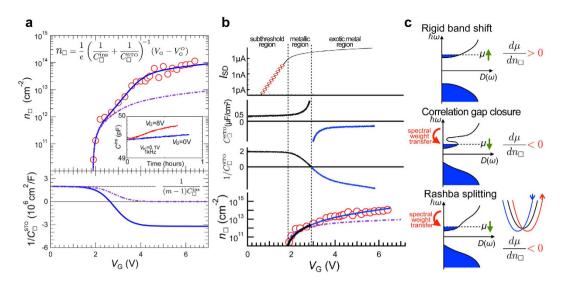


Figure 4. Interpretation of  $n_{\rm 2D}$  enhancement by a negative  $\kappa$  model. (a) Top: sheet carrier density  $n_{\rm 2D}$  (open circles) obtained by the Hall effect measurement for the multi-terminal FET device. Solid line (blue) is a least-square fit of the data to  $n_{\rm 2D} = C_{\rm 2D}(V_{\rm G} - V_{\rm G}^0)/e$ , where  $1/C_{\rm 2D} = 1/C_{\rm 2D}^{\rm ins} + 1/C_{\rm 2D}^{\rm sto}$ ,  $c_{\rm 2D}^{\rm ins}$  is  $0.28\,\mu\rm F/cm^2$ , and  $V_{\rm G}^0$  is  $1.88\,\rm V$ . For  $C_{\rm 2D}^{\rm sto}$ , we used a model shown in the bottom panel (See main text for details). Bottom: the dash-dotted line (purple) represents a case that  $C_{\rm 2D}^{\rm sto} = (m-1)C_{\rm 2D}^{\rm ins}$  in the subthreshold region with the body factor m of  $2.8\,\rm c$  changes to  $C_{\rm 2D}^{\rm sto} = \infty$  of the ideal metal. The solid line (blue) becomes negative which explains the enhancement of  $n_{\rm 2D}$ . Inset shows the capacitance of the HfO<sub>2</sub>/Parylene-C gate insulator as a function of time measured while continuously applying the voltage. The variation is less than 2% for one hour even for the application of  $8\,\rm V$  which is close to the breakdown voltage. (b) Schematic picture of  $I_{\rm SD}$ ,  $C_{\rm 2D}^{\rm sto}$  and  $n_{\rm 2D}$  with respect to  $V_{\rm G}$ . In the metal region,  $C_{\rm 2D}^{\rm sto} \to +\infty$ , and comes back from  $-\infty$ . However,  $1/C_{\rm 2D}^{\rm sto}$  changes continuously, which explains the observed  $n_{\rm 2D}$ . (c) Negative capacitance means the charge compressibility  $\kappa \equiv (n_{\rm 2D}^2 d\mu/dn_{\rm 2D})^{-1}$  is negative, i.e.,  $d\mu/dn_{\rm 2D}$  is negative. In the general rigid-band model,  $d\mu/dn_{\rm 2D} > 0$ . If the density of states  $D(\omega)$  is changed by the carrier doping,  $d\mu/dn_{\rm 2D} < 0$  can be realised. Closure of the correlation gap such as the Mott transition, and a band-splitting such as the Rashba effect are the typical examples.

Then, we consider the shift of  $\mu$  further. In a rigid-band model, where the binding energy of each band shifts monotonously without changing the gaps,  $\mu$  increases by the electron doping and decreases by the hole doping, always leading to positive  $d\mu/dn_{\rm 2D}$  and thus positive  $\kappa$  as shown in Fig. 4c (top). On the contrary, in strongly correlated electron systems, the carrier doping drives the spectral weight transfer (naively a change of the density of states) from the higher energy incoherent states to the lower energy quasiparticle band to fill the Mott-Hubbard gap. Since the band gap decreases,  $\mu$  decreases effectively and  $d\mu/dn_{\rm 2D}$  becomes negative as shown in Fig. 4c (middle) more interesting is that the carrier confinement at the surface of  ${\rm SrTiO_3}$  with perpendicular gate electric field gives rise to the Rashba effect 1. If the Rashba spin-orbit coupling is large, the band structure depends on the gate voltage, i.e.,  $n_{\rm 2D}$ , leading to a non-rigid band structure as well. That is, the coupling lowers the band edge quadratically, and thus the negative  $d\mu/dn_{\rm 2D}$  is realised 13.44 as depicted in Fig. 4c (bottom). However, the absolute value of our negative capacitance  $-0.31\,\mu{\rm F/cm^2}$ , which corresponds to  $d\mu/dn_{\rm 2D} = -5.1\times 10^{-13}\,{\rm eV}\,{\rm cm^2}$ , is too large. For  $V_{\rm G}$  between 4 V and 6 V,  $\Delta n_{\rm 2D}$  is around 5 × 10<sup>13</sup> cm<sup>-2</sup>, then  $\Delta \mu \simeq -26\,{\rm eV}$ , which is difficult to be understood either by the Mott transition 10.41 or the Rashba effect 13.45.

We think a clue to approach this problem is an inhomogeneity of the channel. As shown in Fig. S7c in the Supplementary Materials, we have observed a sudden decrease of the internal voltage distribution in the channel along  $I_{\rm SD}$  while increasing  $V_{\rm G}$ . This has already been observed in other SrTiO $_3$ -FET, indicating a formation of conducting domains in the insulating matrix, which eventually forms a conducting filament by percolation<sup>19</sup>. Here we assume that the channel consists of two regions, *i.e.*, the metallic domains with the negative sheet capacitance  $C_{\rm 2D}^{+}$ , and the non-metallic matrix with the normal positive sheet capacitance  $C_{\rm 2D}^{+}$ . Then, the channel sheet capacitance  $C_{\rm 2D}^{+}$ , which is given by  $C_{\rm 2D}^{+} = (1-\xi)C_{\rm 2D}^{+} + \xi C_{\rm 2D}^{-}$  with the volume fraction  $\xi$  can be  $-0.31\,\mu{\rm F/cm^2}$ , even if  $C_{\rm 2D}^{-}$  is the value which gives a reasonably small  $\Delta\mu$ . Details are given in the Supplementary Materials.

Inhomogeneity of Parylene-C thickness in our gate insulator (~30% at most), and other features such as the one dimensional metallic state at the step edge of SrTiO<sub>3</sub> (ref. 46) would be the origins of charge inhomogeneity. Moreover, the large positive  $\kappa$ , which the insulating SrTiO<sub>3</sub> substrate holds due to the quantum paraelectricity, can augment the inhomogeneities further. Nevertheless, those "extrinsic inhomogeneities" cannot explain the 1000% enhancement of  $n_{\rm 2D}$  as observed in this study. Therefore, we made an inference that an electronic phase separation with the spinodal instability may be induced by  $\kappa \to 0$ , i.e.,  $C_{\rm 2D}^{\rm sto} \to \infty$  in our case<sup>47</sup>. In fact, the phase separation and the charge segregation are natural consequences of the negative capacitance even in ideally homogeneous 2DES<sup>43</sup>. The charge segregation may cause a local charge imbalance at finite length scales. The frustration between the electrostatic cost and the energy gain due to the phase separation is a possible mechanism of charge inhomogeneous (stripe) states<sup>48</sup>. However, in our FET, the local charge on the SrTiO<sub>3</sub> surface is balanced by the

charge on the gate, thus the frustration may be weaken and the typical size of inhomogeneous regions can be microscopic. We hope that this insight motivate further investigation and brings us better understanding of the intriguing physics still hidden in the SrTiO<sub>3</sub> surface.

In summary,  $n_{\rm 2D}$  of the channel of SrTiO<sub>3</sub> FET with Parylene-C (6 nm)/HfO<sub>2</sub> (20 nm) hybrid gate insulator showed anomalous enhancement: ten times as large as the expected value  $C_{\rm 2D}^{\rm sins}V_{\rm G}/e$ , indicating negative  $\kappa$ , *i.e.*, negative  $C_{\rm 2D}^{\rm sto}$ . However, if the whole channel is a single metallic state with the negative  $\kappa$ , the chemical potential shift becomes too large. On the other hand, transport behaviour suggests the inhomogeneous carrier distribution of the channel, though the channel is fairly clean as evidenced by the small subthreshold swing  $S=171\,{\rm mV/decade}$  and large carrier mobility ~11 cm²/Vs. An intrinsic electronic inhomogeneity is a natural consequence of the negative  $\kappa$ , thus it can happen on the channel of our SrTiO<sub>3</sub> -FET. The missing link among the huge  $n_{\rm 2D}$  enhancement, the negative  $\kappa$ , and the intrinsic inhomogeneity will be elucidated by detailed studies.

# **Methods Summary**

Experimental and data analysis methods with associated references are available in the Supplementary Materials.

#### References

- 1. Ahn, C. H. et al. Electrostatic modification of novel materials. Rev. Mod. Phys. 78, 1185-1212 (2006).
- 2. Luryi, S. Quantum capacitance devices. Appl. Phys. Lett. 52, 501-503 (1988).
- 3. Kravchenko, S. V., Pudalov, V. M. & Semenchinsky, S. G. Negative density of states of 2d electrons in a strong magnetic field. *Phys. Lett. A* 141, 71–74 (1989).
- 4. Eisenstein, J. P., Pfeiffer, L. N. & West, K. W. Negative compressibility of interacting two-dimensional electron and quasiparticle gases. *Phys. Rev. Lett.* **68**, 674–677 (1992).
- 5. Eisenstein, J. P., Pfeiffer, L. N. & West, K. W. Compressibility of the two-dimensional electron gas: Measurements of the zero-field exchange energy and fractional quantum Hall gap. *Phys. Rev. B* **50**, 1760–1778 (1994).
- 6. Dultz, S. C. & Jiang, H. Thermodynamic signature of a two-dimensional metal-insulator transition. *Phys. Rev. Lett.* **84**, 4689–4692 (2000).
- 7. Ilani, S. et al. Measurement of the quantum capacitance of interacting electrons in carbon nanotubes. Nat. Phys. 2, 687-691 (2006).
- 8. Li, L. et al. Very large capacitance enhancement in a two-dimensional electron system. Science 332, 825-828 (2011).
- Tinkl, V. et al. Large negative electronic compressibility of LaAlO<sub>3</sub>-SrTiO<sub>3</sub> interfaces with ultrathin LaAlO<sub>3</sub> layers. Phys. Rev. B 86, 075116 (2012).
- Kopp, T. & Mannhart, J. Calculation of the capacitances of conductors: perspectives for the optimization of electronic devices. J. Appl. Phys. 106, 064504 (2009).
- 11. Li, Q., Hwang, E. H. & Das Sarma, S. Temperature-dependent compressibility in graphene and two-dimensional systems. *Phys. Rev. B* **84**, 235407 (2011).
- 12. Nakamura, H. et al. Low temperature metallic state induced by electrostatic carrier doping of SrTiO<sub>3</sub>. Appl. Phys. Lett. 89, 133504 (2006)
- 13. Santander-Syro, A. F. et al. Two-dimensional electron gas with universal subbands at the surface of SrTiO<sub>3</sub>. Nature **469**, 189–193 (2011).
- Meevasana, W. et al. Creation and control of a two-dimensional electron liquid at the bare SrTiO<sub>3</sub> surface. Nat. Mater. 10, 114–118 (2011).
- Delugas, P., Fiorentini, V., Mattoni, A. & Filippetti, A Intrinsic origin of two-dimensional electron gas at the (001) surface of SrTiO<sub>3</sub>.
   Phys. Rev. B 91, 115315 (2015).
- 16. Ohtomo, A. & Hwang, H. Y. A high-mobility electron gas at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> heterointerface. Nature 427, 423-426 (2004).
- 17. Stemmer, S. & Allen, S. J. Two-dimensional electron gases at complex oxide interfaces. Ann. Rev. Mater. Sci. 44, 151–171 (2014).
- 18. Spinelli, A., Torija, M. A., Liu, C., Jan, C. & Leighton, C. Electronic transport in doped SrTiO<sub>3</sub>: Conduction mechanisms and potential applications. *Phys. Rev. B* 81, 155110 (2010).
- 19. Eyvazov, A. B., Inoue, I. H., Stoliar, P., Rozenberg, M. J. & Panagopoulos, C. Enhanced and continuous electrostatic carrier doping on the SrTiO<sub>3</sub> surface. *Sci. Rep.* **3**, 1721 (2013).
- 20. Chen, Y. G. et al. Extreme mobility enhancement of two-dimensional electron gases at oxide interfaces by charge-transfer-induced modulation doping. *Nat. Mater.* **14**, 801–806 (2015).
- 21. Gallagher, P. et al. A high-mobility electronic system at an electrolyte-gated oxide surface. Nat. Comm. 6, 6437 (2015).
- 22. Hemberger, J., Lunkenheimer, P., Viana, R., Böhmer, R. & Loidl, A. Electric-field-dependent dielectric constant and nonlinear susceptibility in SrTiO<sub>3</sub>. *Phys. Rev. B* **52**, 13159 (1995).
- 23. Reich, K. V., Schecter, M. & Shklovskii, B. I. Accumulation, inversion, and depletion layers in SrTiO<sub>3</sub>. Phys. Rev. B 91, 115303 (2015).
- 24. Nakamura, H., Koga, T. & Kimura, T. Experimental evidence of cubic Rashba effect in an inversion-symmetric oxide. *Phys. Rev. Lett.* **108**, 206601 (2012).
- 25. King, P. D. C. et al. Quasiparticle dynamics and spin-orbital texture of the SrTiO<sub>3</sub> two-dimensional electron gas. Nat. Comm. 5, 3414 (2014).
- Santander-Syro, A. F. et al. Giant spin splitting of the two-dimensional electron gas at the surface of SrTiO<sub>3</sub>. Nat. Mater. 13, 1085–1090 (2014).
- 27. Noland, J. A. Optical Absorption of Single-Crystal Strontium Titanate. Phys. Rev. 94, 724 (1954).
- 28. van Benthem, K., Elsässer, C. & French, R. H. Bulk electronic structure of SrTiO<sub>3</sub>: Experiment and theory. *J. Appl. Phys.* **90**, 6156–6164 (2001).
- 29. Lin, X. et al. Critical doping for the onset of a two-band superconducting ground state in SrTiO<sub>3- $\delta$ </sub>. Phys. Rev. Lett. **112**, 207002 (2014).
- 30. Jeong, J. et al. Suppression of metal-insulator transition in VO<sub>2</sub> by electric fieldinduced oxygen vacancy formation. Science 339, 1402–1405 (2013).
- 31. Nakamura, H. et al. Tuning of metal-insulator transition of quasi-two-dimensional electrons at Parylene/SrTiO<sub>3</sub> interface by electric field. J. Phys. Soc. Jpn. 78, 083713 (2009).
- 32. Salahuddin, S. & Datta, S. Use of negative capacitance to provide voltage amplification for low power nanoscale devices. *Nano Lett.* **8**, 405–410 (2008).
- 33. Jain, A. & Alam, M. A. Proposal of a hysteresis-free zero subthreshold swing field-effect transistor. *IEEE Trans. Electr. Dev.* **61**, 3546–3552 (2014).
- 34. del Alamo, J. A. Nanometre-scale electronics with III-V compound semiconductors. Nature 479, 317-323 (2011).
- Shibuya, K., Ohnishi, T., Sato, T. & Lippmaa, M. Metal-insulator transition in SrTiO<sub>3</sub> induced by field effect. J. Appl. Phys. 102, 083713 (2007).
- Yoshikawa, A. et al. Electric-field modulation of thermopower for the KTaO<sub>3</sub> field-effect transistors. Appl. Phys. Express 2, 121103 (2009).

- 37. Gentils, A. et al. Point defect distribution in high-mobility conductive SrTiO3 crystals. Phys. Rev. B 81, 144109 (2010).
- 38. Zhuang, H. L., Ganesh, P., Cooper, V. R., Xu, H. & Kent, P. R. C. Understanding the interactions between oxygen vacancies at SrTiO<sub>3</sub> (001) surfaces. *Phys. Rev. B* **90**, 064106 (2014).
- Skinner, B. & Shklovskii, B. I. Anomalously large capacitance of a plane capacitor with a two-dimensional electron gas. Phys. Rev. B 82, 155111 (2010).
- 40. Hale, S. T. F. & Freericks, J. K. Many-body effects on the capacitance of multilayers made from strongly correlated materials. *Phys. Rev. B* 85, 205444 (2012).
- 41. He, J. *et al.* Spectroscopic evidence for negative electronic compressibility in a quasi-three-dimensional spin-orbit correlated metal. *Nat. Mater.* **14**, 577–582 (2015).
- 42. Bychkov, Y. A. & Rashba, E. I. Properties of a 2D electron gas with lifted spectral degeneracy. JETP Lett. 39, 78-81 (1984).
- 43. Caprara, S., Peronaci, F. & Grilli, M. Intrinsic instability of electronic interfaces with strong Rashba coupling. *Phys. Rev. Lett.* **109**, 196401 (2012).
- 44. Bucheli, D., Grilli, M., Peronaci, F., Seibold, G. & Caprara, S. Phase diagrams of voltage-gated oxide interfaces with strong Rashba coupling. *Phys. Rev. B* 89, 195448 (2014).
- 45. Steffen, K., Loder, F. & Kopp, T. Spin-orbit controlled quantum capacitance of a polar heterostructure. *Phys. Rev. B* **91**, 075415 (2015).
- 46. Bristowe, N. C., Fix, T., Blamire, M. G., Littlewood, P. B. & Artacho, E. Proposal of a One-Dimensional Electron Gas in the Steps at the LaAlO<sub>3</sub>-SrTiO<sub>3</sub> Interface. *Phys. Rev. Lett.* **108**, 166802 (2012).
- 47. Seibold, G., Bucheli, D. & Caprara, S. Grilli Phase separation and long wave-length charge instabilities in spin-orbit coupled systems. *Euro. Phys. Lett.* **109**, 17006 (2015).
- 48. Emery, V. J. & Kivelson, S. Frustrated electronic phase separation and high-temperature superconductors *Physica C* **209**, 597–621 (1993).

# **Acknowledgements**

We are grateful to S. Fratini, D. Jiménez, E. A. Miranda, T. Oka, M. J. Rozenberg, D. D. Sarma, A. Sawa, B. I. Shklovskii, P. Stoliar, and J. Zaanen for valuable discussions and suggestions, A. Matsuo, Y. Nakayama, and F. Uesugi for TEM measurements, and H. Oosato for the help of HfO<sub>2</sub> deposition. N. K was an International Research Fellow of Japan Society for the Promotion of Science (JSPS). This study was supported by Grants-in-Aid for Scientific Research (category A, grant number 242444062 and 15H02113), Grants-in-Aid for JSPS Fellows (grant number 25-03502), and Nanotechnology Platform Project sponsored by Ministry of Education, Culture, Sports, Science and Technology (MEXT) Japan.

#### **Author Contributions**

N.K. and A.K. fabricated the devices, and N.K. performed all the measurements. I.H.I. conceived and supervised the project. All the authors discussed the results, and N.K. and I.H.I. cowrote the manuscript.

### **Additional Information**

**Supplementary information** accompanies this paper at http://www.nature.com/srep

**Competing financial interests:** The authors declare no competing financial interests.

How to cite this article: Kumar, N. et al. Anomalous enhancement of the sheet carrier density beyond the classic limit on a SrTiO<sub>3</sub> surface. Sci. Rep. 6, 25789; doi: 10.1038/srep25789 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/