Anomalous enhancement of the sheet carrier density beyond the classic limit on a SrTiO$_3$ surface

Neeraj Kumar, Ai Kitoh & Isao H. Inoue

Electrostatic carrier accumulation on an insulating (100) surface of SrTiO$_3$ by fabricating a field effect transistor with Parylene-C (6 nm)/HfO$_2$ (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, $V_G$ is the gate voltage, and $e$ is the elementary charge). The channel is so clean to exhibit small subthreshold swing of 170 mV/decade and large mobility of 11 cm$^2$/Vs for $n_{2D}$ of $1 \times 10^{14}$ cm$^{-2}$ at room temperature. Since $C_{2D}^{\text{ins}}$ does not depend on either $V_G$ nor time duration, $n_{2D}$ beyond $C_{2D}^{\text{ins}} V_G/e$ 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 $n_{2D}$ limit. However, the observed $n_{2D}$ 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 $en_{2D} = C_{2D}^{\text{ins}} V_G$, where $e$, $n_{2D}$, $C_{2D}^{\text{ins}}$, and $V_G$ are the elementary charge, sheet carrier density of the channel, sheet capacitance of the gate insulator, and gate voltage, respectively. 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 $\kappa \equiv (n_{2D}^2 dn_{2D}/dn_{2D})^{-1}$ ($\mu$ is the chemical potential). Meanwhile, for finite $\kappa$, $C_{2D}^{\text{ins}}$ is replaced by $(1/C_{2D}^{\text{ins}} + 1/C_{2D}^{\text{ch}})^{-1}$. $C_{2D}^{\text{ch}} \equiv e n_{2D}^2 \kappa$ is a matter capacitance. Total energy of the carriers corresponds to $1/C_{2D}^{\text{ch}}$, so in general, $C_{2D}^{\text{ch}}$ is positive and $n_{2D} < C_{2D}^{\text{ins}} V_G$. Nevertheless, negative $\kappa$, for which $e n_{2D} > C_{2D}^{\text{ins}} V_G$, is a long-standing target of research both experimentally$^{14-3}$ and theoretically$^{10,11}$, manifesting itself due to strong exchange interactions between carriers. Especially, in two-dimensional electron system (2DES), the exchange energy is negative and scales as $\kappa n_{2D}^2$, while the positive (e.g., kinetic) energy scales as $n_{2D}$; therefore, for sufficiently small $n_{2D}$, the total energy ($\propto 1/C_{2D}^{\text{ch}}$) 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 $C_{2D}^{\text{ins}} V_G/e$. 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 $V_G = e n_{2D}/C_{2D}$ is a sum of the voltage drop in the gate insulator $V_{\text{ins}} = e n_{2D}/C_{2D}^{\text{ins}}$ and the band-bending of the channel material $\varphi = e n_{2D}/C_{2D}^{\text{ch}}$. Therefore, $V_G = V_{\text{ins}} + \varphi$ means $1/C_{2D} = 1/C_{2D}^{\text{ins}} + 1/C_{2D}^{\text{ch}}$ (Fig. 1a). For the metallic channel, the chemical potential (Fermi energy) $\mu/e$ substitutes for $\varphi$, and $C_{2D}^{\text{ch}}$ is replaced by the quantum capacitance $C_{2D}^{\text{sto}} \equiv e^2 n_{2D}^2 \kappa$ (Fig. 1b). It is still possible to consider $C_{2D}^{\text{ch}}$ for the nonmetallic bulk part of the substrate, and $1/C_{2D} = 1/C_{2D}^{\text{ins}} + 1/C_{2D}^{\text{ch}} + 1/C_{2D}^{\text{sto}}$. But $1/C_{2D}^{\text{sto}} (\ll 1/C_{2D}^{\text{ch}})$ term is usually omitted. The channel material in this study is SrTiO$_3$. The FET changes from an insulator to metal by gating$^{12}$, so we use a notation $C_{2D}^{\text{sto}}$ in lieu of both $C_{2D}^{\text{ch}}$ and $C_{2D}^{\text{sto}}$. SrTiO$_3$ 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$^{3-11}$ or interface$^{16,17}$, as well as the large mobility of the confined 2D carriers without a freeze-out$^{18-21}$. Both the confinement and the large mobility are originated in or, if not more, influenced by the quantum paraelectricity$^{22}$ with a large and nonlinear dielectric response$^{23}$. Furthermore, at the surface and interface, where the inversion...
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 SrTiO3). By differentiating $V_{G1} = V_{\text{ins}} + \psi$ with respect to $n_{2D}$, and by using the Gauss’s law, we obtain $1/C_{2D} = 1/C_{2D}^{\text{ins}} + 1/C_{2D}^{\text{ch}}$. (b) For larger $V_{G1}$, the channel becomes metallic and $V_{G1} = V_{\text{ins}} + \mu/e$. Same as (a) the relationship $1/C_{2D} = 1/C_{2D}^{\text{ins}} + 1/C_{2D}^{\text{ch}}$ is obtained, where $C_{2D}$ is called a quantum capacitance (ref. 2).

symmetry is broken, the charge confinement induces some intriguing electronic properties; for example, the Rashba spin-orbit coupling at the surface of SrTiO3 discussed in refs 24–26. However, it is intensely difficult to fabricate such a high quality FET on SrTiO3 as to reveal the true nature of the exotic phenomena. The band gap of SrTiO3 is nearly 3.2 eV27,28, but it turns to be a good metal by orders of magnitude lower than the threshold of metallicity in Si (3.5 × 1018 cm−3) or Ge (3.5 × 1017 cm−3)29. Thus, the channel of SrTiO3 FET becomes conductive quite easily by the oxygen-defect formation. In other words, the channel current of some SrTiO3 FETs might be rather dominated by electrochemical reaction than purely electrostatic carrier-density modulation30. Therefore, in this paper, we propose an alternative gate insulator: an organic/inorganic bilayer consisting of 6 nm ultra-thin poly-xylylene (Parylene-C) and 20 nm HfO2, as schematically shown in Fig. 2a. The film of Parylene-C polymer is widely used for coating a variety of materials, 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 mK31. The bilayer gate insulator was deposited on the atomically-flat (100) surface (miscut-angle is less than about 0.03°) of non-doped SrTiO3 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 SrTiO3 crystals is noticeably insulating with the sheet resistance above our instrumental limit (~10 13 Ω) at room temperature, and this ability insulating with the sheet resistance above our instrumental limit (~10 13 Ω) at room temperature, and this

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ade. This is indeed in good coincidence with the values simply estimated from the $I_{D}\text{-}V_G$ plot, indicating that the contact resistance of our FET does not contribute to the $S$ value. Since the material-independent transport factor $m(T) = (k_B T/e) \ln 10$ is 60 mV/decade at 300 K, $S = 171$ mV/decade of this study is surprisingly small. (It was reported that the value of $S$ was ~100 mV/decade even for Si$^{34}$, ~250 mV/decade for SrTiO$_3$ $^{35}$, and ~1200 mV/decade for KTaO$_3$ $^{36}$). From $m = 2.8$, we deduced $C_{2D} = 0.50 \mu F/cm^2$. If we assume the dielectric constant of SrTiO$_3$ is 310 at room temperature, the effective thickness for $C_{2D}$ is 0.55 $\mu$m. This means in the subthreshold region the gate electric field can penetrate into deep bulk of SrTiO$_3$ (0.55 $\mu$m) without a large Thomas-Fermi screening of free carriers possibly originated in the defects of Parylene-C/SrTiO$_3$ interface. Put plainly, the Parylene-C passivation on the defect-prone SrTiO$_3$ surface $^{37,38}$ 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-$\kappa$ dielectric HfO$_2$ but also works as a good capacitive layer by itself. We fabricated Ti(10 nm)/Parylene-C (3 nm)/HfO$_2$ (20 nm)/Ti(5 nm)/Au(500 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 $C_{2D} = 0.28 \mu F/cm^2$ 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$_3$. This achievement, however, has given a new twist to the research of SrTiO$_3$. Figure 4a shows $n_{2D}$ 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, $n_{2D} = C_{2D} (V_G - 1.88)/e$, where $1/C_{2D} = 1/C_{2D}^{\text{ins}} + 1/C_{2D}^{\text{sto}}$ with $C_{2D}^{\text{ins}} = 0.28 \mu F/cm^2$ and $C_{2D}^{\text{sto}} = 0.50 \mu F/cm^2$. Thus, $n_{2D} = 1.1 \times 10^{12} (V_G - 1.88) \ cm^{-2}$. (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 $n_{2D}$ is much larger than this naive estimation; it reaches to around $1 \times 10^{14} \ cm^{-2}$ for $V_G = 6$ V. Even if this extra carriers are provided by the formation of oxygen/cation defects in the SrTiO$_3$ channel during the application of the large $V_G$, though the channel is
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$_3$ substrates (two results are shown in Fig. S3), and confirmed all of them showed qualitatively same $n_{2D}$ 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$_3$ ($C_{2D}^b = 0.50 \mu F/cm^2$), and a surface layer ($C_{2D}^s$). When $V_G$ is small, $C_{2D}^b$ is most dominant to $C_{2D}^s$, but as $V_G$ increased, accumulated carriers screen the gate voltage; i.e., for $V_G > V_{max}$, $C_{2D}^s$ becomes more dominant. Then, we introduced a tractable model:

$$\eta = \frac{C_{2D}^b}{C_{2D}^s} = \frac{1}{1 + \tanh \left[ \alpha (V_G - V_{min}) \right]}$$

where $\alpha = 0.68$ and $V_{min} = 2.8 V$ are non-essential parameters. This is an ad-hoc phenomenological model to express that $C_{2D}^b$ changes smoothly from $C_{2D}^s$-dominant to $C_{2D}^b$-dominant, thus the mathematical formula is not relevant. If $C_{2D}^s$ is a large positive number as that of a good metal, $C_{2D}^s$ and corresponding $n_{2D}$ behave as dash-dotted lines (purple) in Fig. 4a. Deviation is still large. Then, if we assume negative capacitance $C_{2D}^s = -0.31 \mu F/cm^2$, the calculated $n_{2D}$ coincides with the measured $n_{2D}$.

We understand that $I_{SD}$, $C_{2D}^s$ and $n_{2D}$ should behave as shown schematically in Fig. 4b. Negative $C_{2D}^s = -0.31 \mu F/cm^2$, i.e., negative $\kappa$, is inevitable for explaining the large enhancement of $n_{2D}$. But a question arises. If this is ascribed to the exchange interaction of the quasi-2DES on SrTiO$_3$ as explained in literature, averaged distance between the electrons should be much larger than the Bohr radius $a_B$, i.e., $(\pi n_{2D} a_B^2)^{-1/2} \gg 1$, and the system may become like the Wigner crystal with negative chemical potential $\mu \approx -2.9 e^2 n_{2D}^{-1/2} / \varepsilon$, where $\varepsilon$ is a dielectric constant of SrTiO$_3$ (ref. 39). However, $n_{2D}$ in this study is in the order of $10^{14} cm^{-2}$, then the corresponding values $(\pi n_{2D} a_B^2)^{-1/2} \approx 11$ and $\mu \approx -53 eV$ are both unreasonable. It was suggested that negative $\kappa$ is also realised in electronic systems close to half filling, but this neither is applicable to our samples. Therefore, the significant enhancement of $n_{2D}$ cannot be explained solely by the negative $\kappa$ originating in the exchange interactions; we need an alternative idea.

Figure 3. Characteristics of SrTiO$_3$ FET with HfO$_2$ (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) $I_{SD} - V_{SD}$ plots for 3-terminal device with $L = 20 \mu m$ and $W = 80 \mu m$ for several $V_G$. (f) $WR_{exp} = W V_{SD}/I_{SD}$ 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 ($WR_{exp} = R_0 + LR_{2D}$) to deduce $R_{2D}$. (g) $R_{2D}$ vs. $V_{Geff}$. Solid line gives $S$ of 171 mV/decade.
Then, we consider the shift of μ further. In a rigid-band model, where the binding energy of each band shifts monotonously without changing the gaps, μ increases by the electron doping and decreases by the hole doping, always leading to positive dμ/dn_{2D} and thus positive κ 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, μ decreases effectively and dμ/dn_{2D} becomes negative 38 as shown in Fig. 4c (middle) more interesting is that the carrier confinement at the surface of SrTiO3 with perpendicular gate electric field gives rise to the Rashba effect 42. If the Rashba spin-orbit coupling is large, the band structure depends on the gate voltage, i.e., n_{2D}, leading to a non-rigid band structure as well. That is, the coupling lowers the band edge quadratically, and thus the negative dμ/dn_{2D} is realised 43,44 as depicted in Fig. 4c (bottom). However, the absolute value of our negative capacitance −0.31 μF/cm², which corresponds to dμ/dn_{2D} = −5.1 × 10^{−13} eV cm², is too large. For V_g between 4 V and 6 V, ∆n_{2D} is around 5 × 10^{13} cm⁻², then ∆μ ≈ −26 eV, which is difficult to be understood either by the Mott transition 41,43 or the Rashba effect 43–45.

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_{SD} while increasing V_g. This has already been observed in other SrTiO₃-FET, indicating a formation of conducting domains in the insulating matrix, which eventually forms a conducting filament by percolation 19. Inset shows the capacitance of the HfO₂/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 V.

In the metal region, C_{2D} → +∞, and comes back from −∞. However, 1/C_{2D} changes continuously, which explains the observed n_{2D}. Inset shows the capacitance of the HfO₂/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 V.
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$_3$ surface.

In summary, $n_{2D}$ of the channel of SrTiO$_3$ FET with Parylene-C (6 nm)/HfO$_2$ (20 nm) hybrid gate insulator showed anomalous enhancement ten times as large as the expected value $C_{2D}^{inv} V/\epsilon$, indicating negative $\kappa$, i.e., negative $\kappa_{2D}$. 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 $S=171$ mV/decade and large carrier mobility ~11 cm$^2$/V$s$. An intrinsic electronic inhomogeneity is a natural consequence of the negative $\kappa$, thus it can happen on the channel of our SrTiO$_3$ - FET. The missing link among the huge $n_{2D}$ 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.

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**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**

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