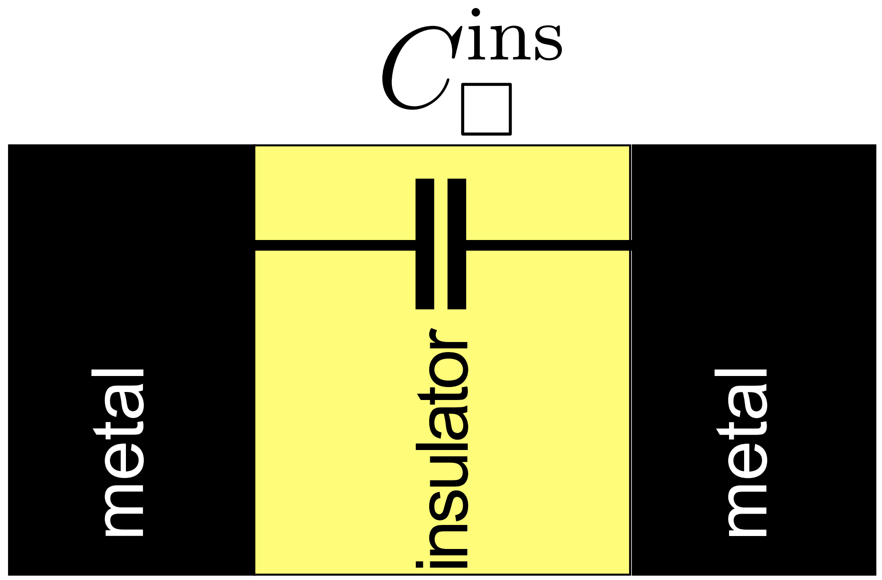
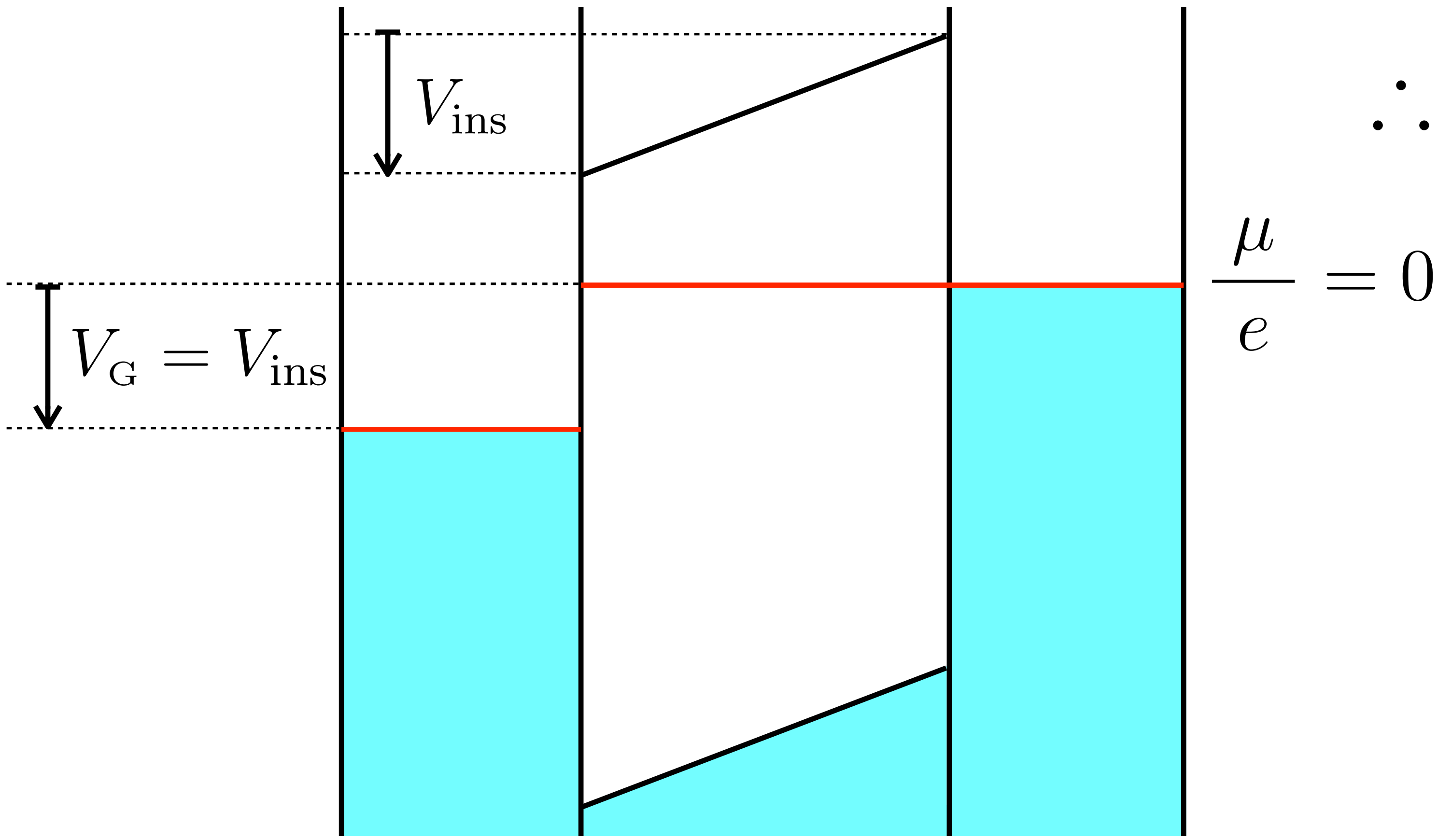
Enormous electrostatic carrier doping of $SrTiO_3$: negative capacitance?

National Institute of Advanced Industrial Science & Technology (AIST) (Tsukuba, Japan)

Isao H. Inoue Neeraj Kumar Ai Kitou

Ideal capacitor





$$V_{\mathrm{G}} = V_{\mathrm{ins}}$$

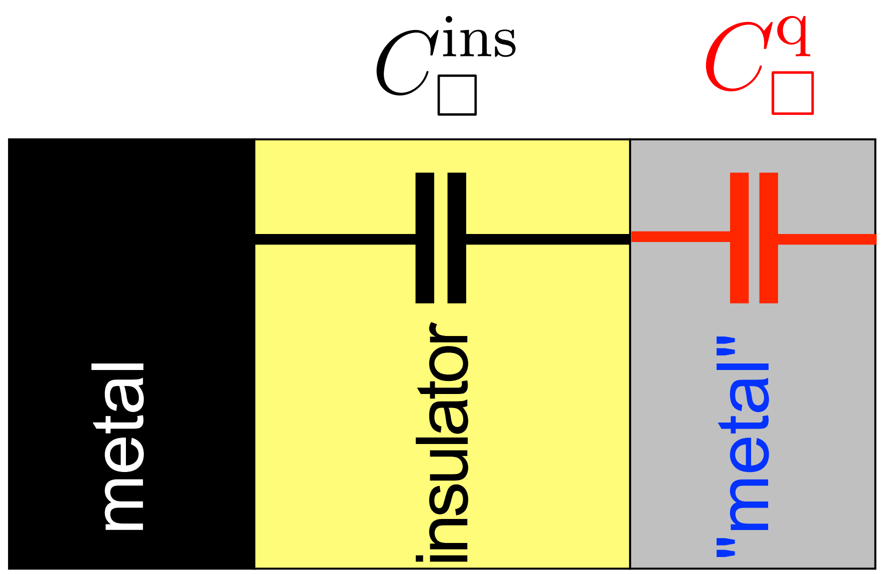
$$\frac{1}{e}\frac{dV_{\mathrm{G}}}{dn_\square} = \frac{1}{e}\frac{dV_{\mathrm{ins}}}{dn_\square}$$

$$\therefore \quad \frac{1}{C_\square} = \frac{1}{C_\square^{\mathrm{ins}}}$$

because

$$en_\square = C_\square V_{\mathrm{G}}$$

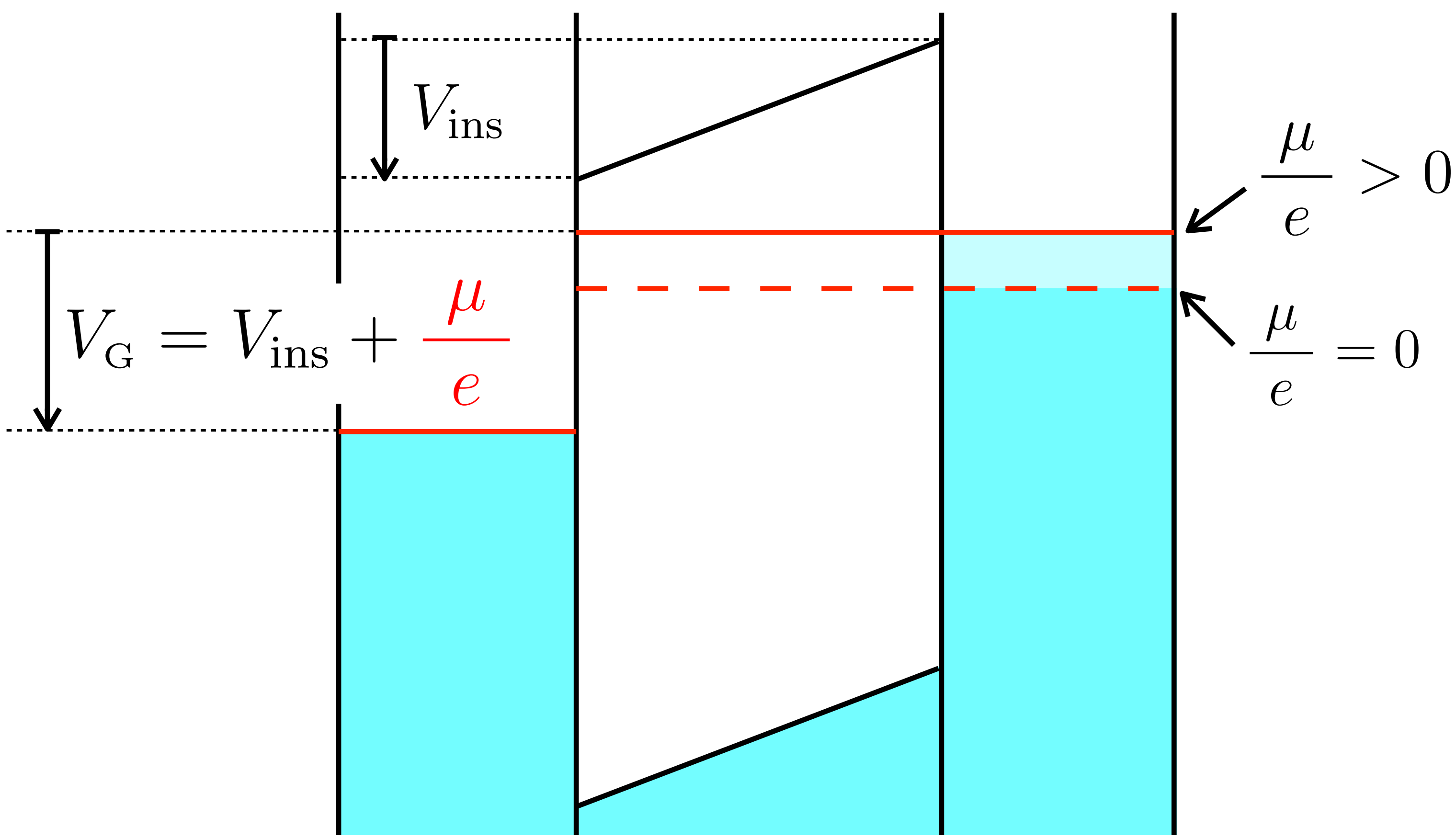
Non-ideal capacitor w/ a “metal” electrode



$$V_{\mathrm{G}} = V_{\mathrm{ins}} + \frac{\mu}{e}$$

$$\frac{1}{e}\frac{dV_{\mathrm{G}}}{dn_\square} = \frac{1}{e}\frac{dV_{\mathrm{ins}}}{dn_\square} + \frac{1}{e^2}\frac{d\mu}{dn_\square}$$

$$\therefore \quad \frac{1}{C_\square} = \frac{1}{C_\square^{\mathrm{ins}}} + \frac{1}{C_\square^{\mathrm{q}}}$$

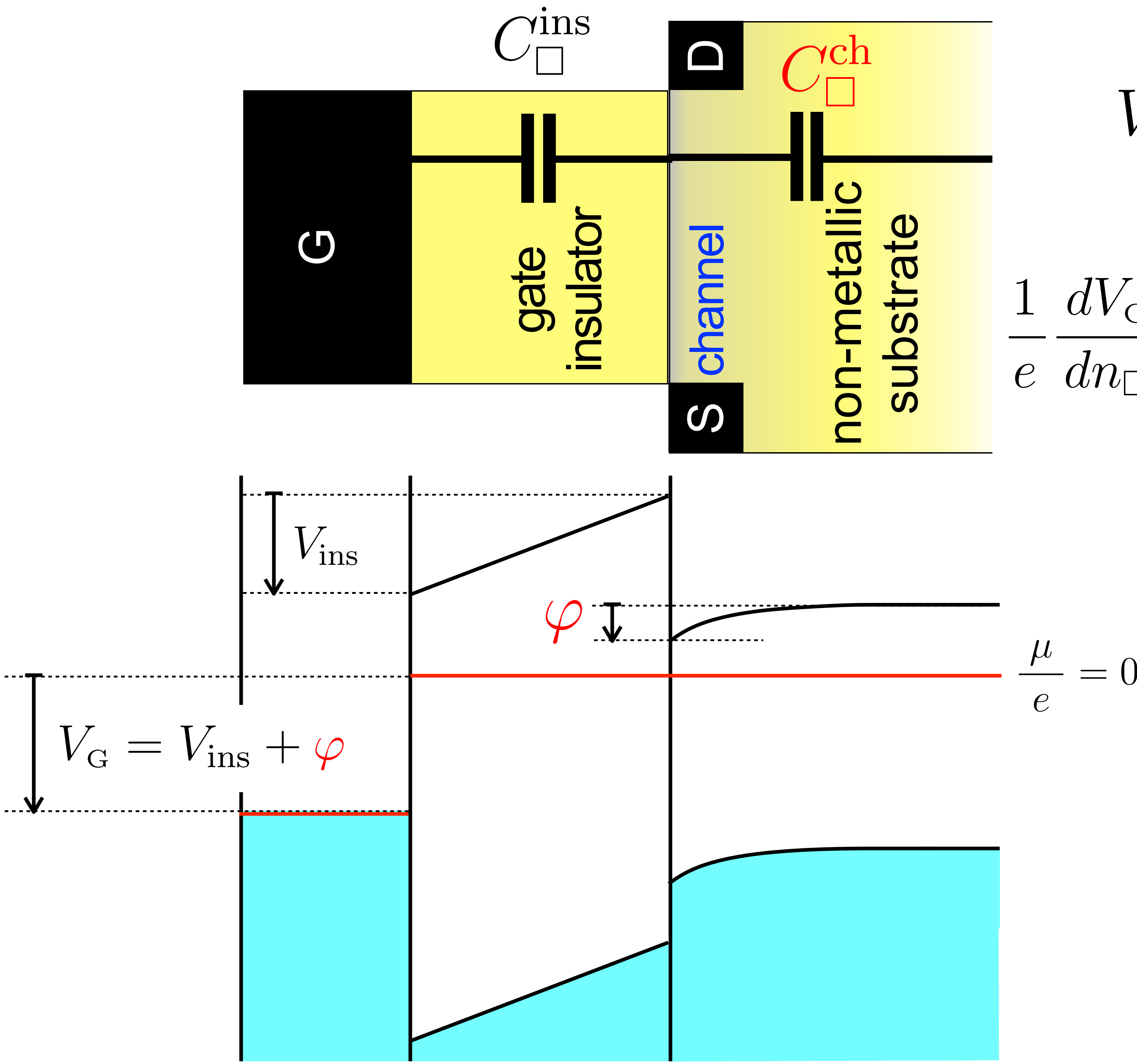


$$C_\square^{\mathrm{q}} = e^2 \frac{dn_\square}{d\mu}$$

quantum capacitance

$$\frac{dn_\square}{d\mu}$$ ~ charge compressibility

Normal FET w/ semi-conductor channel

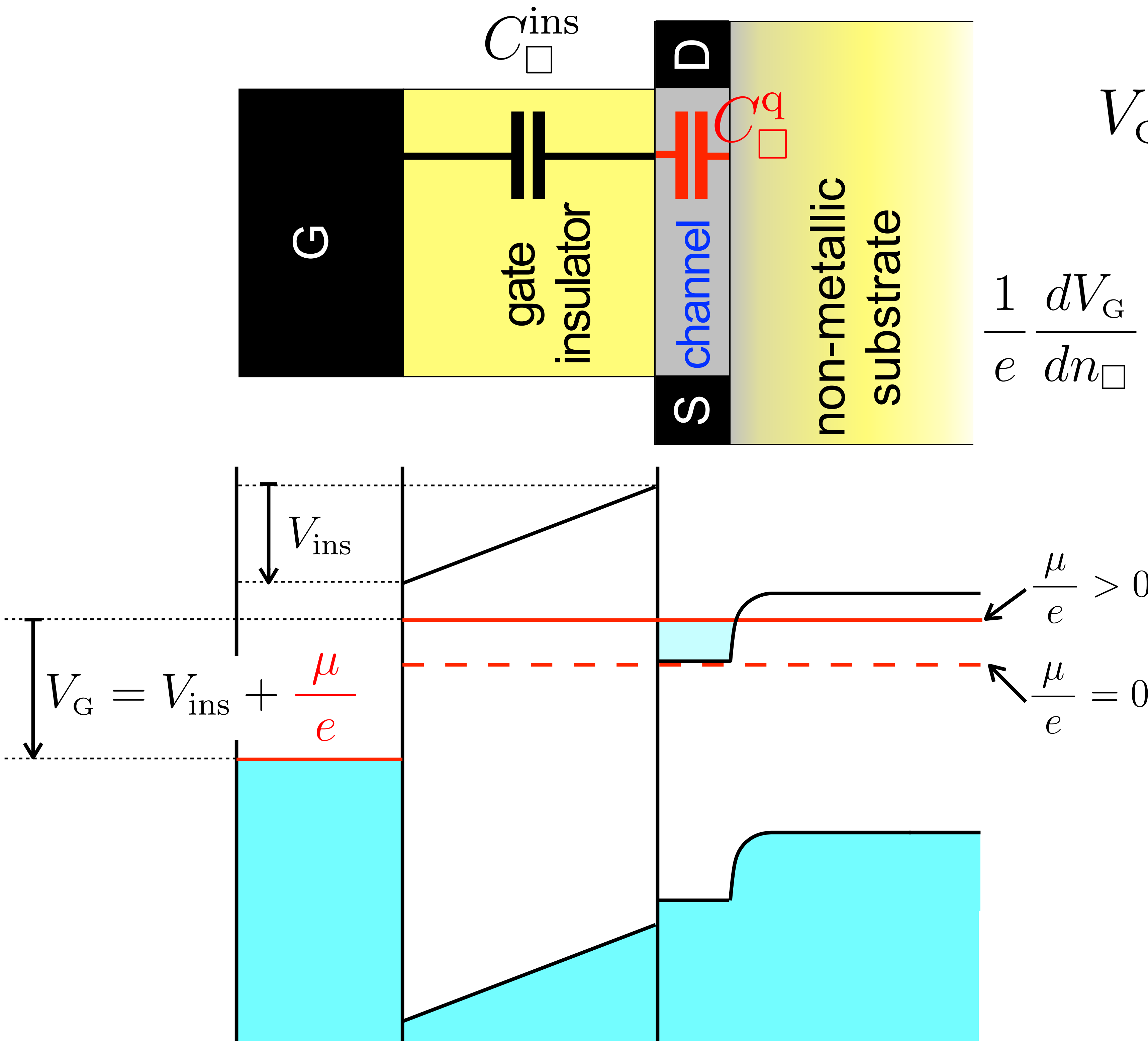


$$V_{\text{G}} = V_{\text{ins}} + \varphi$$

$$\frac{1}{e}\frac{dV_{\text{G}}}{dn_\square} = \frac{1}{e}\frac{dV_{\text{ins}}}{dn_\square} + \frac{1}{e}\frac{d\varphi}{dn_\square}$$

$$\therefore \quad \frac{1}{C_\square} = \frac{1}{C_\square^{\text{ins}}} + \frac{1}{C_\square^{\text{ch}}}$$

Field effect transistor w/ a "metal" channel



$$V_{\mathrm{G}} = V_{\mathrm{ins}} + \frac{\mu}{e}$$

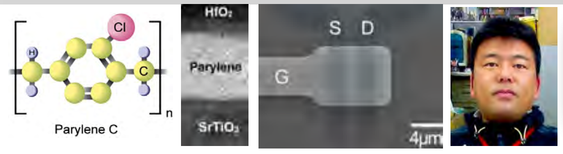
$$\frac{1}{e}\frac{dV_{\mathrm{G}}}{dn_\square} = \frac{1}{e}\frac{dV_{\mathrm{ins}}}{dn_\square} + \frac{1}{e^2}\frac{d\mu}{dn_\square}$$

$$\therefore \quad \frac{1}{C_\square} = \frac{1}{C_\square^{\mathrm{ins}}} + \frac{1}{C_\square^{\mathrm{q}}}$$

$$C_\square^{\mathrm{q}} = e^2 \frac{dn_\square}{d\mu}$$

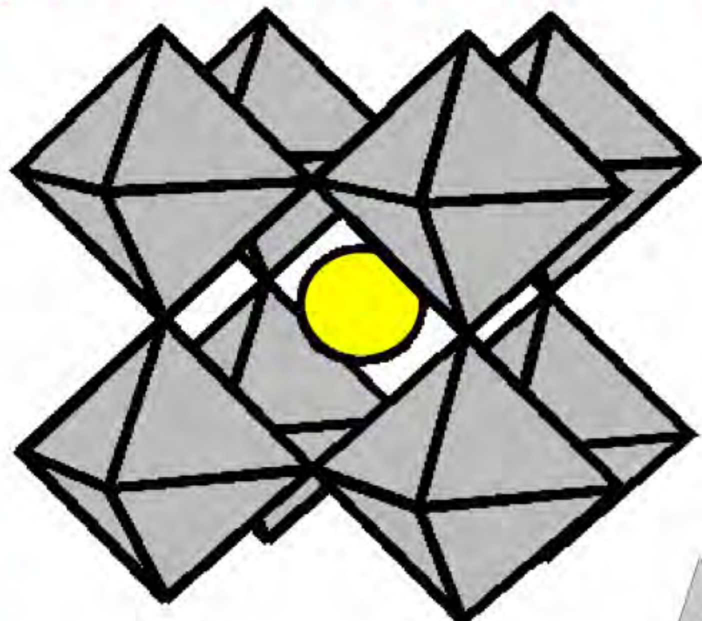
quantum capacitance

$$\frac{dn_\square}{d\mu}$$ ~ charge compressibility



Insulating $SrTiO_3$ single crystal

perovskite structure

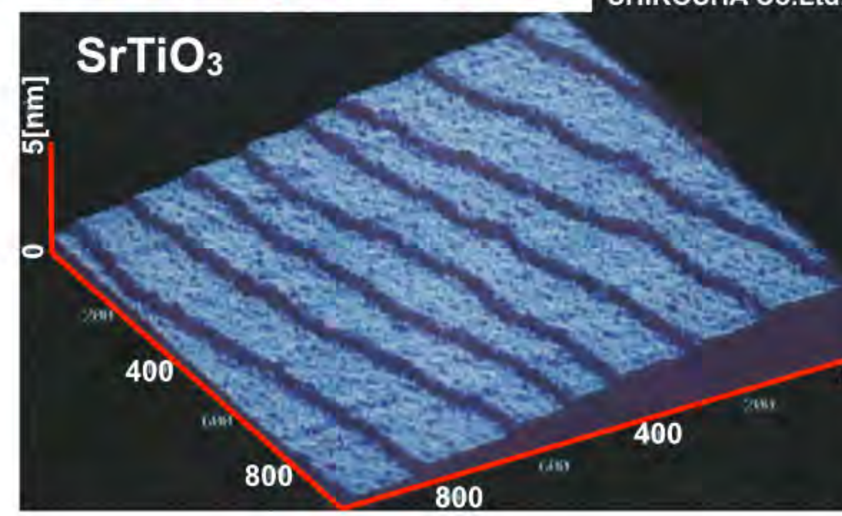


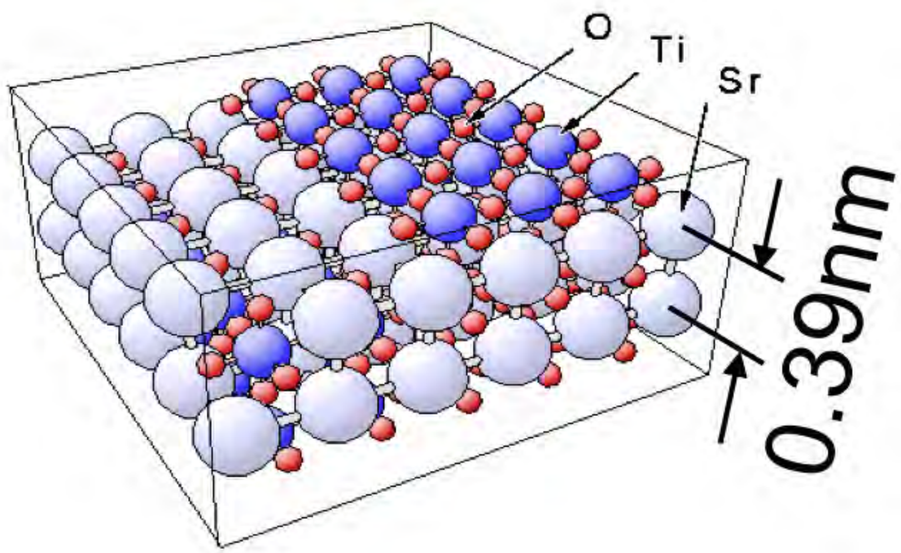
Insulator with ~3.3eV band gap

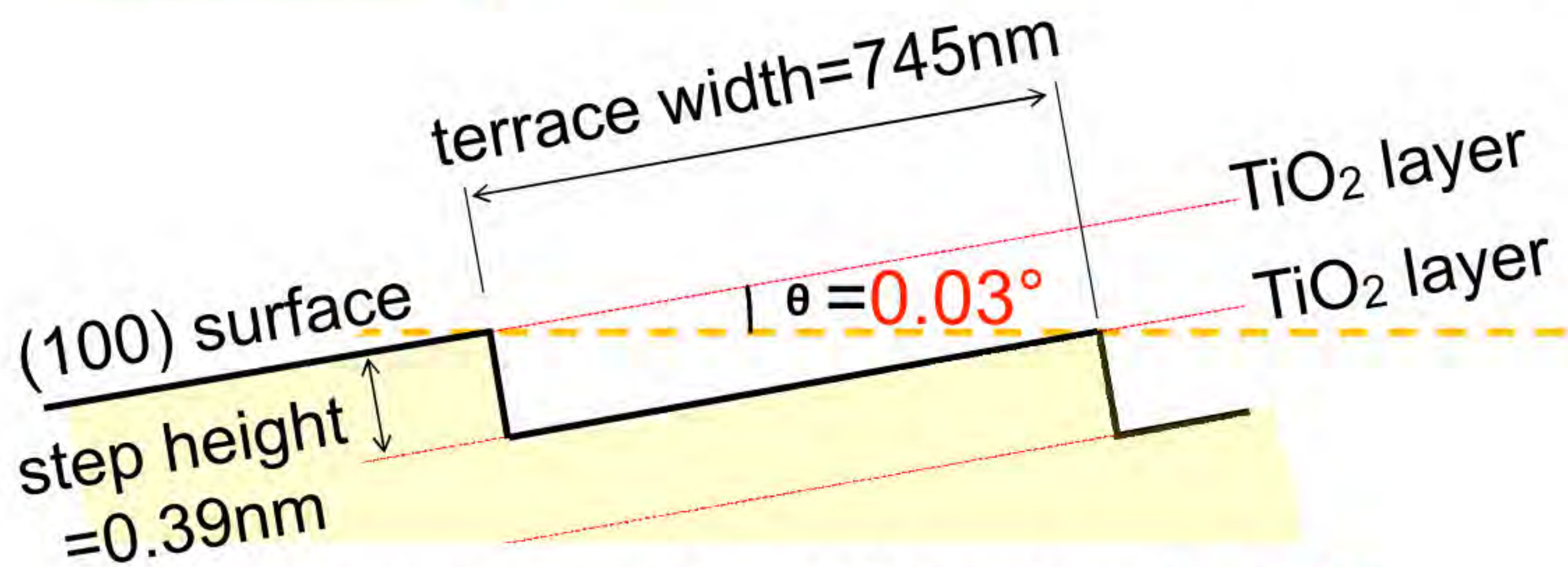
highly transparent

Step-and-terrace surface is easily obtained

From a catalog of SHIKOSHA Co.Ltd.

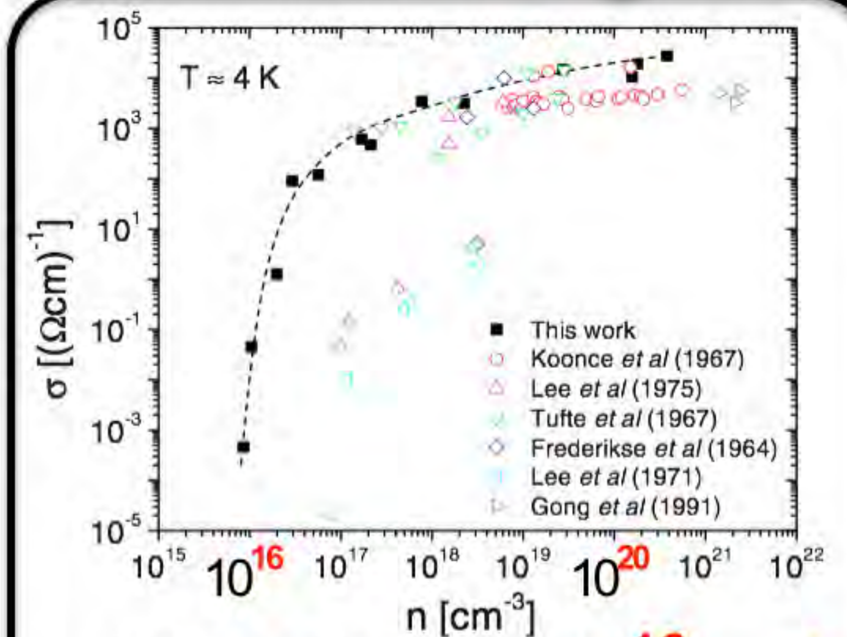






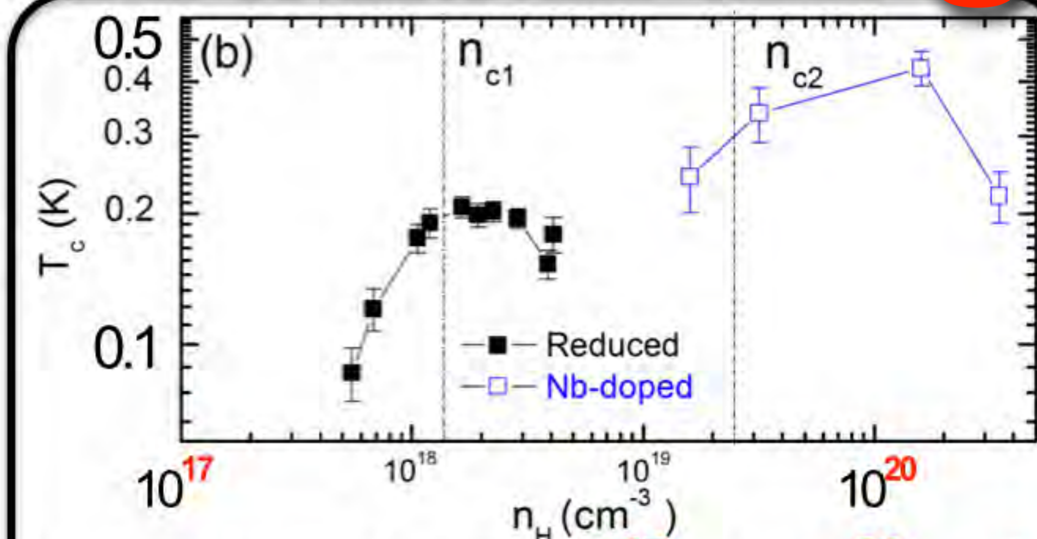
terrace width=0.39nm/tan(0.03°)

$SrTiO_3$ is an interesting material



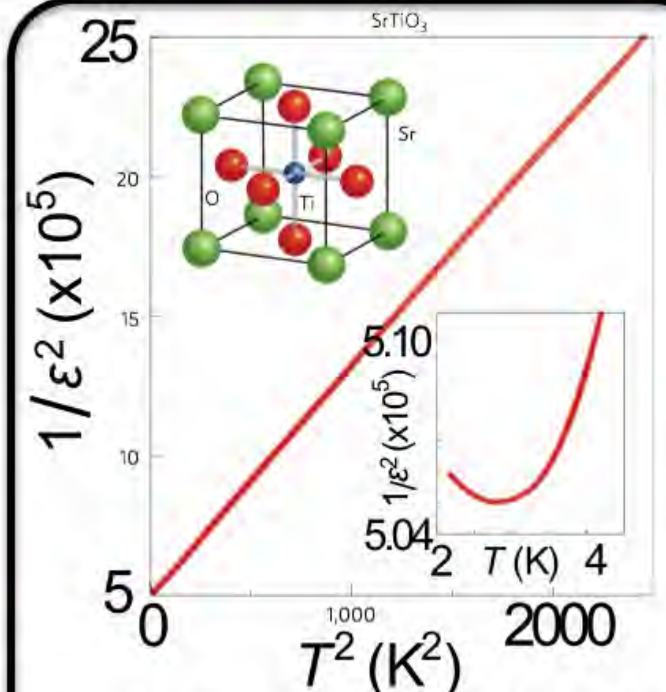
MI transition at 10^{16} cm^{-3}

X. Lin *et al.*, PRL **112**, 207002 (2014)



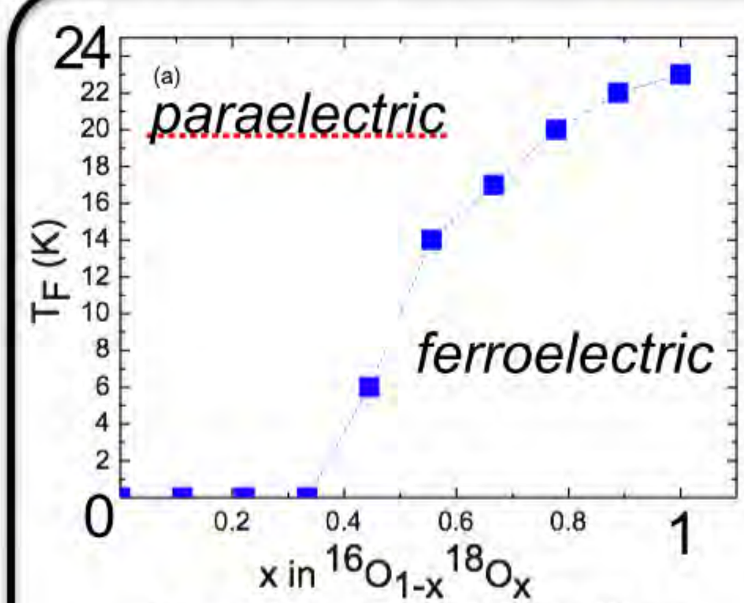
superconductivity 5×10^{17} — 4×10^{20} cm^{-3}

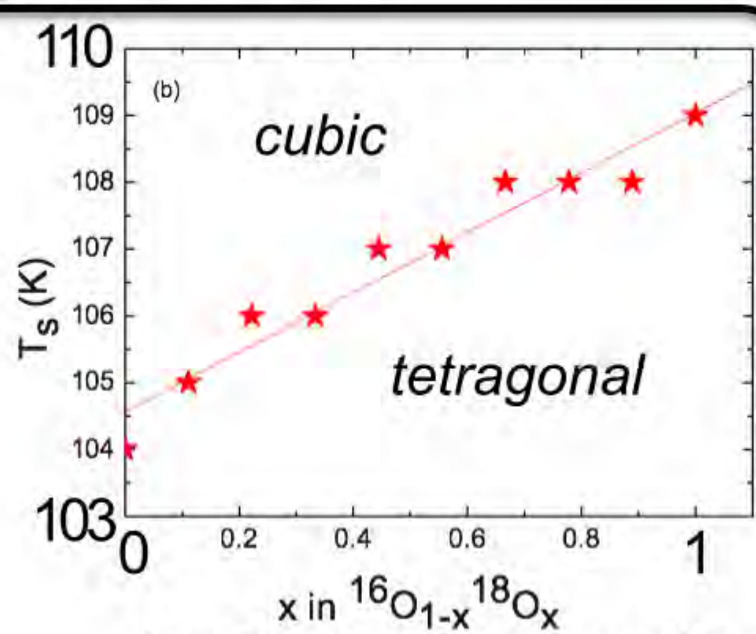
A. Spinelli *et al.*, PRB **81**, 155110 (2010)



quantum paraelectric

S. E. Rowley *et al.*,
Nat. Phys. **10**, 367 (2014)





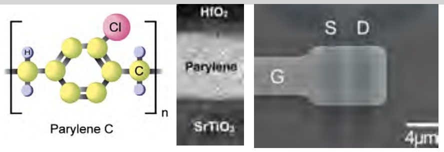
ferroelectric transition
by oxygen isotope exchange

structural phase transition

A. Bussmann-Holder & A. R. Bishop, PRB **78**, 104117 (2008)

strong Rashba spin-orbit coupling

D. Bucheli *et al.*, PRB **89**, 195448 (2014)



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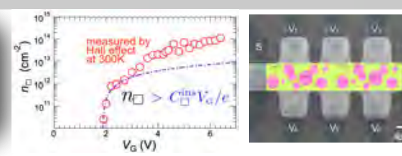
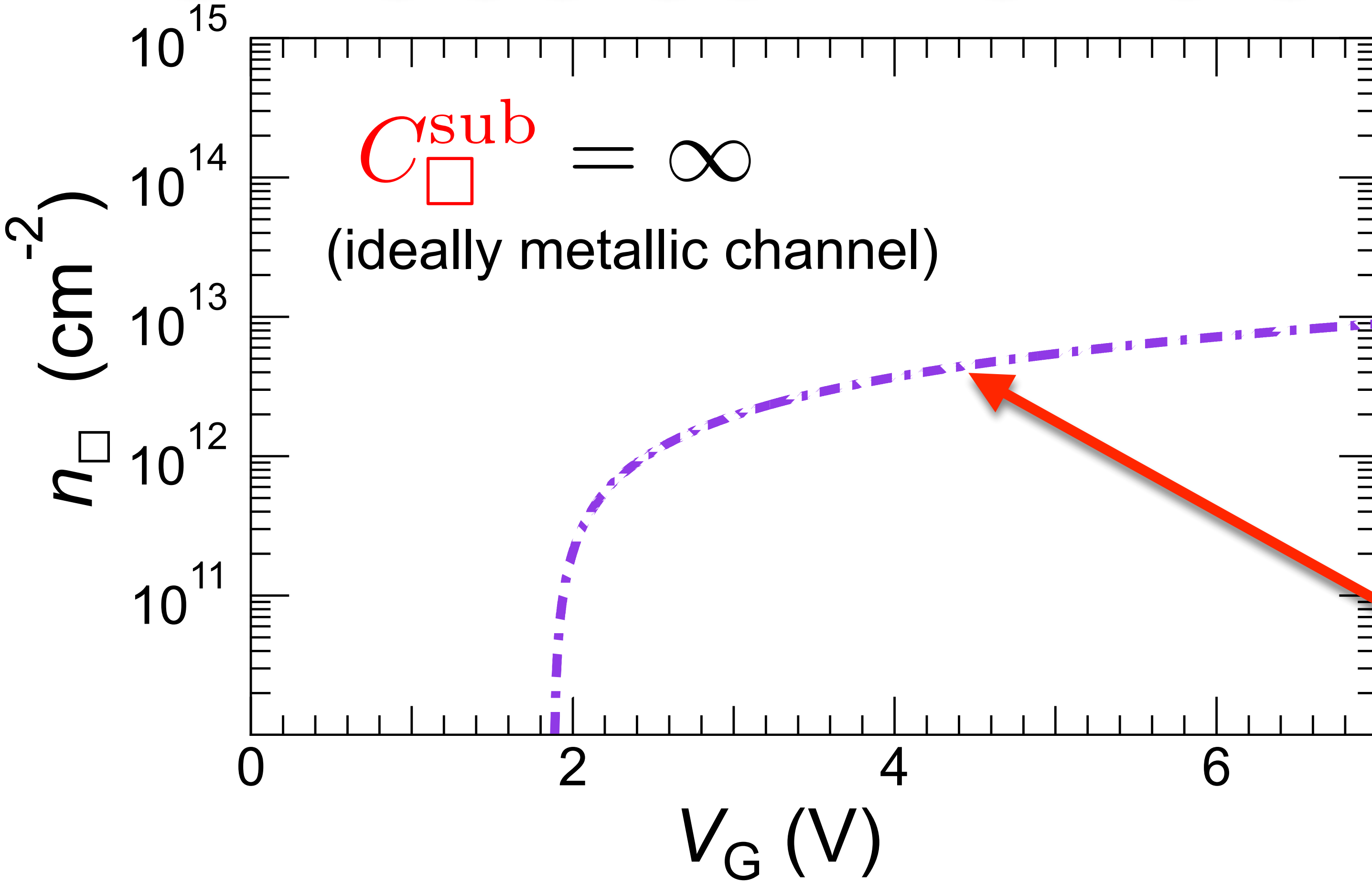
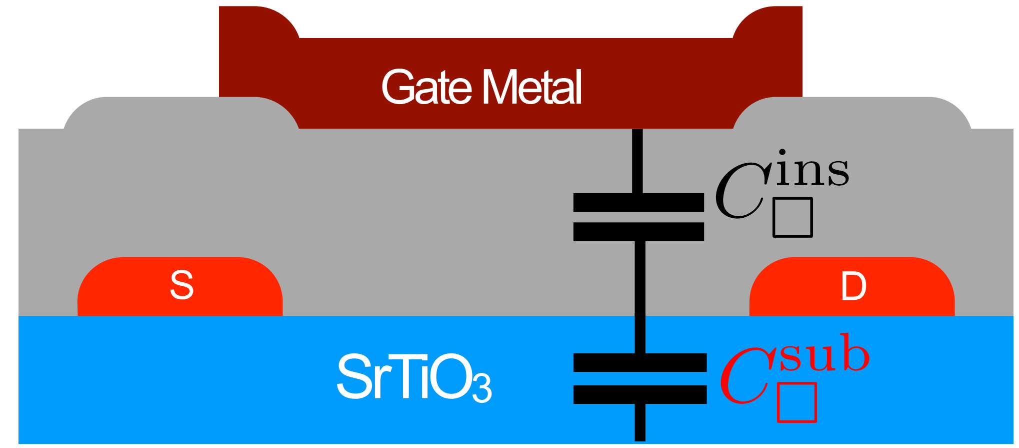
Isao H. Inoue, Invited Talk @ SPICE Workshop, *Mainz, Germany* 2 July 2015



Sheet carrier density of $SrTiO_3$

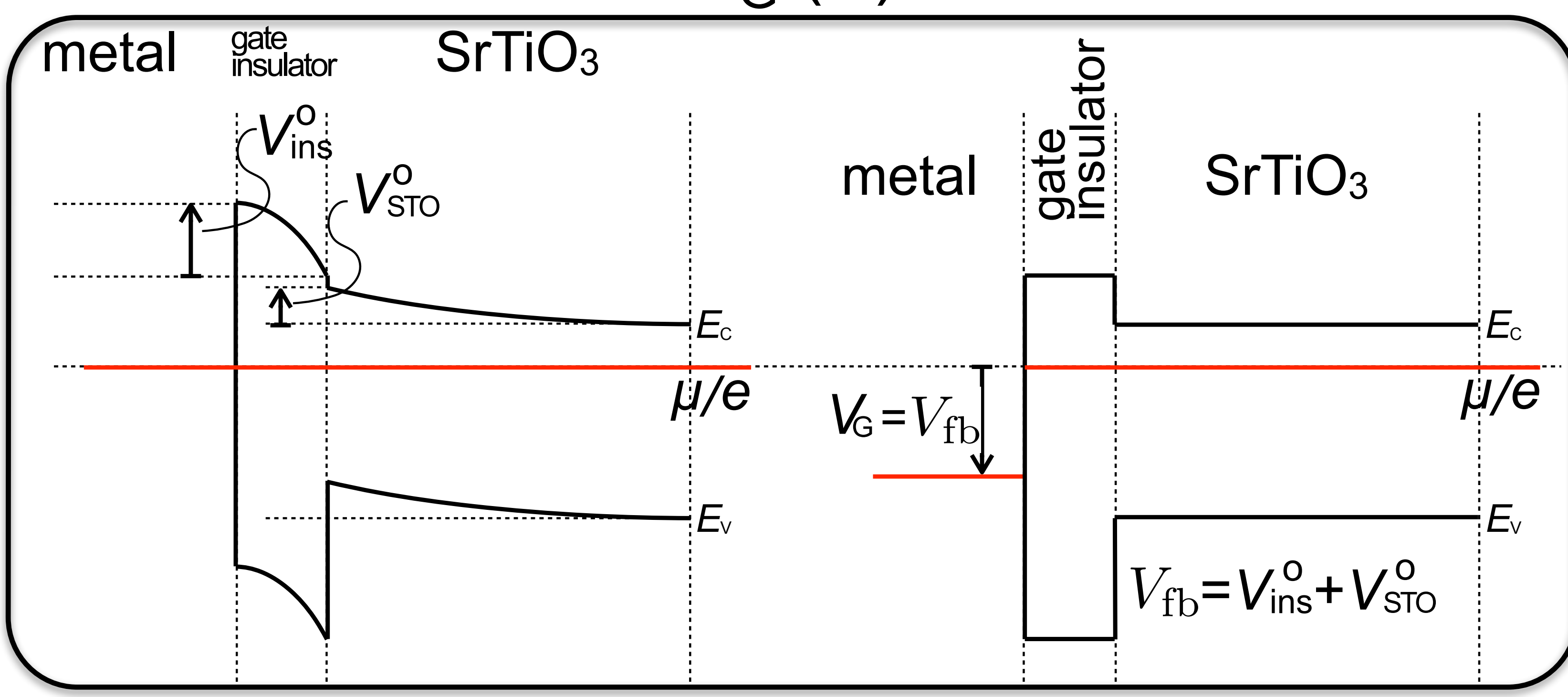




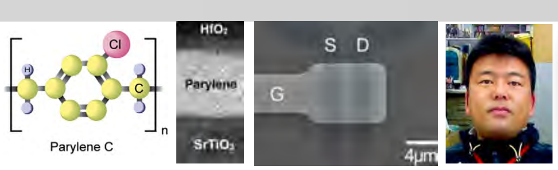
$$e n_{\square} = C^{\mathrm{ins}}_{\square}(V_G - V_{\mathrm{fb}})$$

$$= \left(\frac{1}{C^{\mathrm{ins}}_{\square}}\right)^{-1}(V_G - V_{\mathrm{fb}})$$

if $C^{\mathrm{sub}}_{\square} = \infty$
(ideally metallic channel)



$$V_{\mathrm{fb}} = 1.88\ \mathrm{V}$$
$$C^{\mathrm{ins}}_{\square} = 0.28\ \mu\mathrm{F/cm^2}$$



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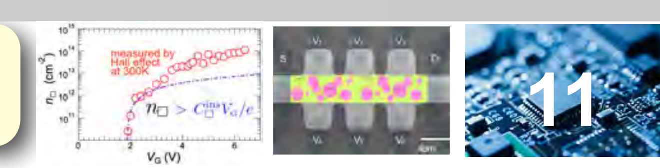
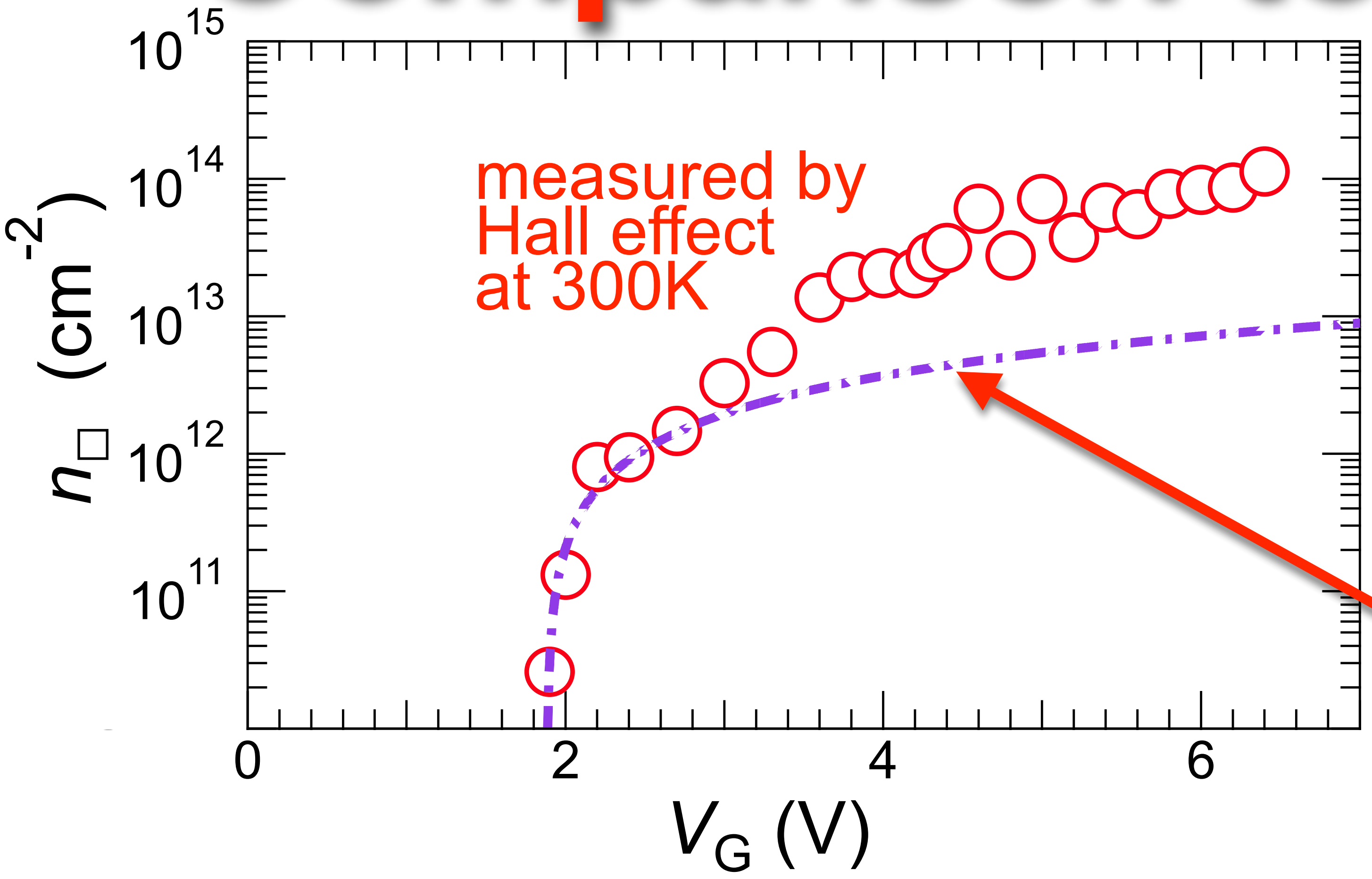
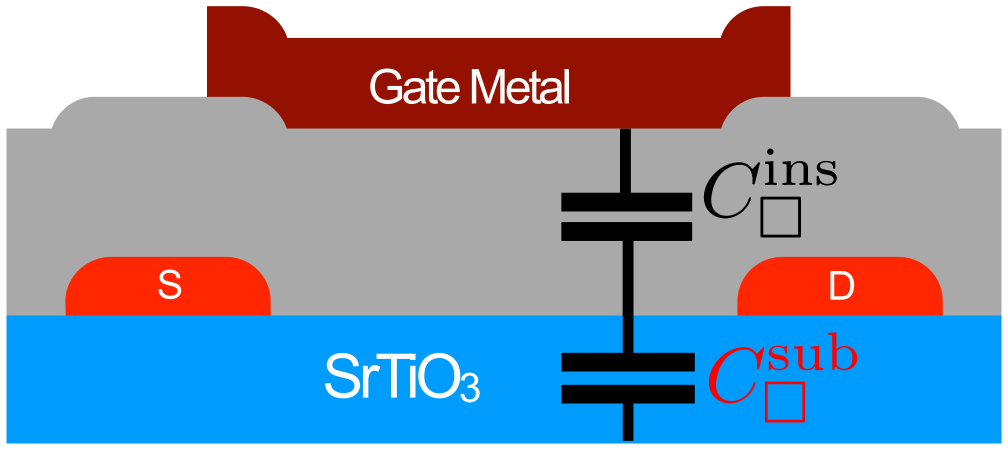


Comparison to Hall effects





$$\boxed{en_\square = C^{\rm ins}_\square (V_{\rm G} - V_{\rm fb})}$$

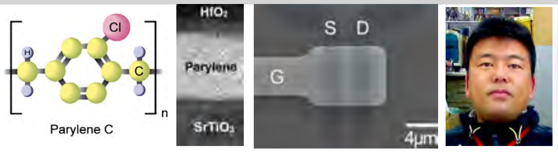
$$= \left(\frac{1}{C^{\rm ins}_\square}\right)^{-1} (V_{\rm G} - V_{\rm fb})$$

Large deviation!!

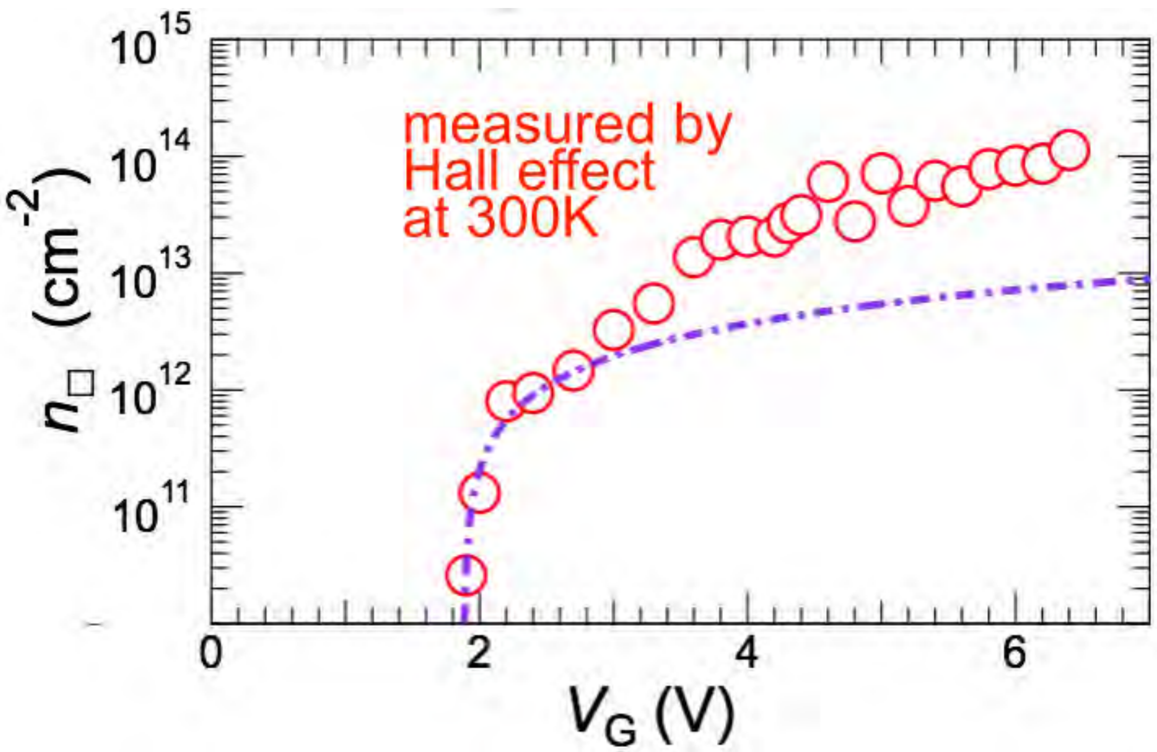
$$\text{if } \quad C^{\rm sub}_\square = \infty$$

(ideally metallic channel)

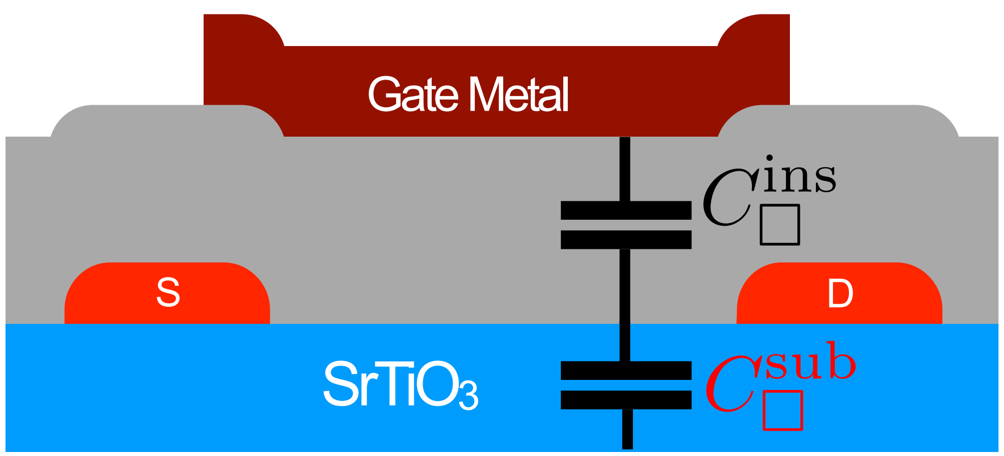
$$V_{\rm fb} = 1.88\,{\rm V}$$
$$C^{\rm ins}_\square = 0.28\,\mu{\rm F/cm}^2$$



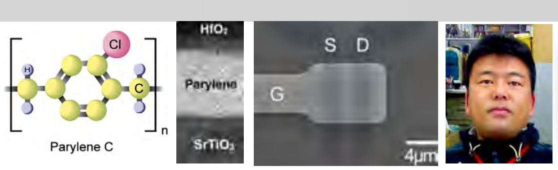
$n_\square$ cannot be larger than $C_\square^{\rm ins} V_{\rm G}/e$?

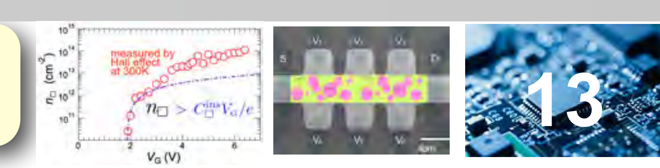


$$e n_\square = C_\square V_{\rm G} = \left(\frac{1}{C_\square^{\rm ins}} + \frac{1}{C_\square^{\rm sub}} \right)^{-1} V_{\rm G}$$

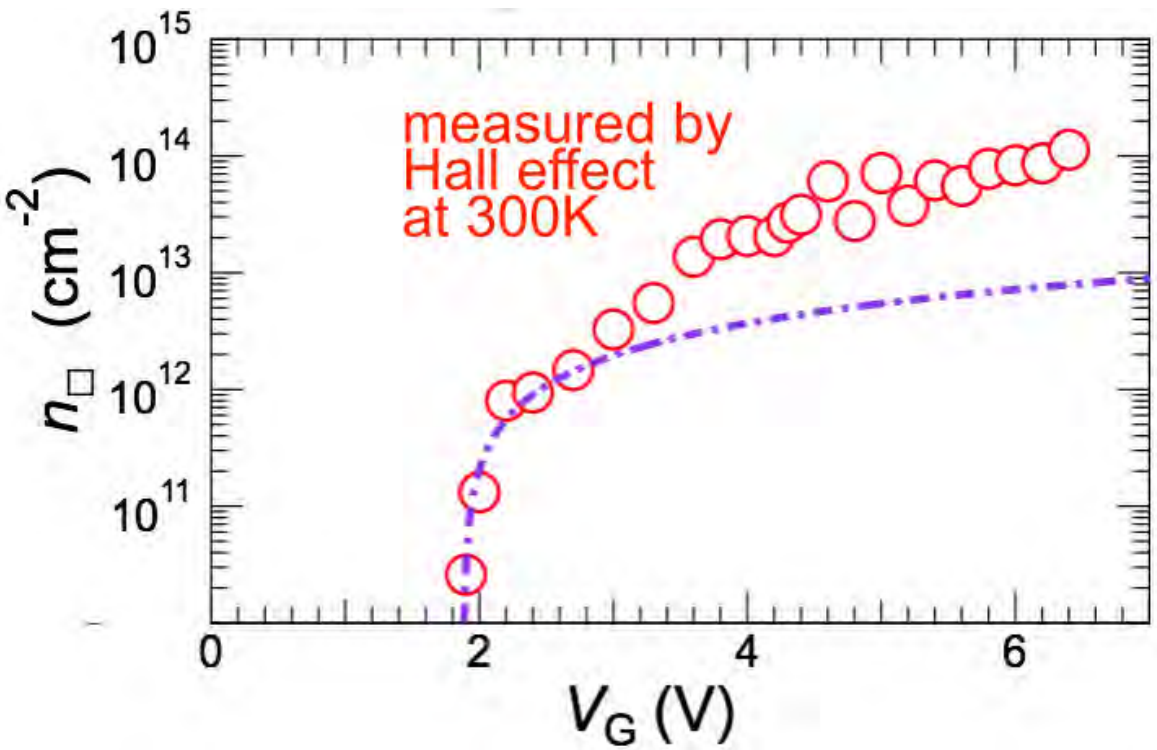


	ideal **insulator** no screening
$C_\square^{\rm sub}$	0 $\because \ \frac{\varepsilon}{d} \to 0$ for $d \to \infty$
$n_\square$	0

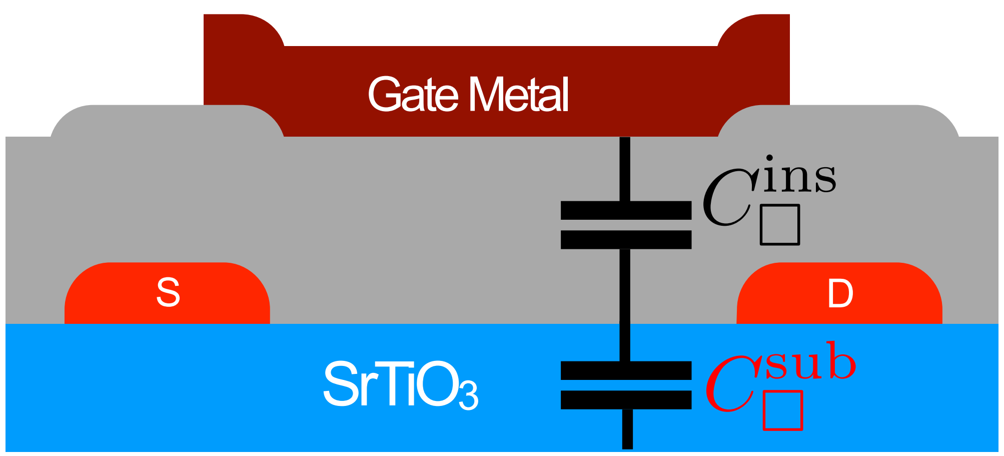




$n_\square$ cannot be larger than $C_\square^{\rm ins} V_{\rm G}/e$?

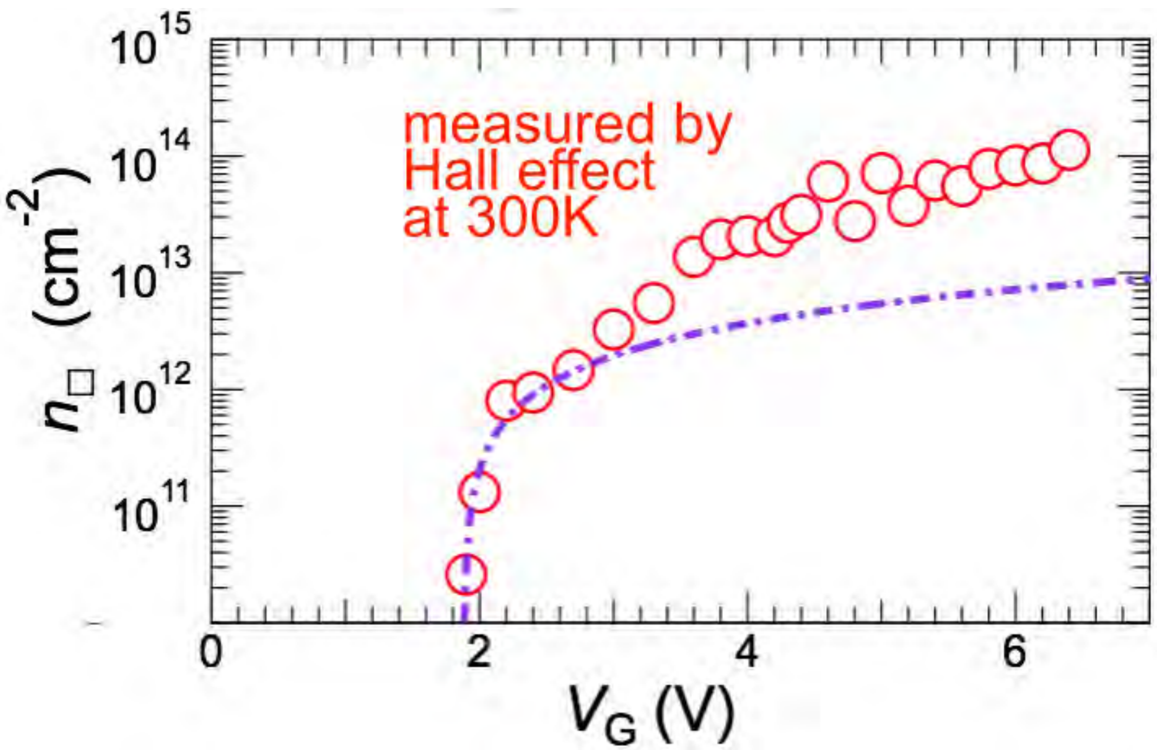


$$en_\square = C_\square V_{\rm G}$$
$$= \left(\frac{1}{C_\square^{\rm ins}} + \frac{1}{C_\square^{\rm sub}}\right)^{-1} V_{\rm G}$$

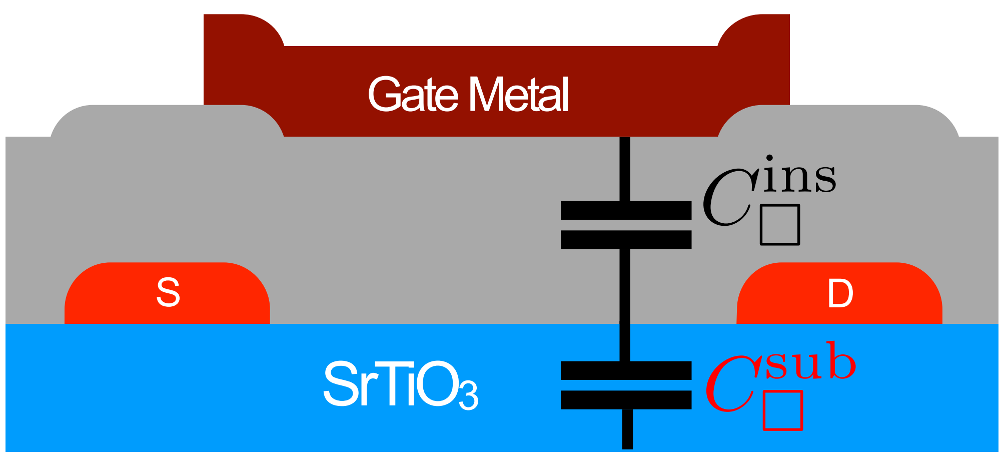


	ideal **metal** perfect screening	$\cdots$	ideal **insulator** no screening
$C_\square^{\rm sub}$	∞	$\cdots$	0 $\because \frac{\varepsilon}{d} \to 0$ for $d \to \infty$
$n_\square$	$C_\square^{\rm ins} V_{\rm G}/e$	$\cdots$	0

$n_\square$ cannot be larger than $C^{\mathrm{ins}}_\square V_\mathrm{G}/e$?

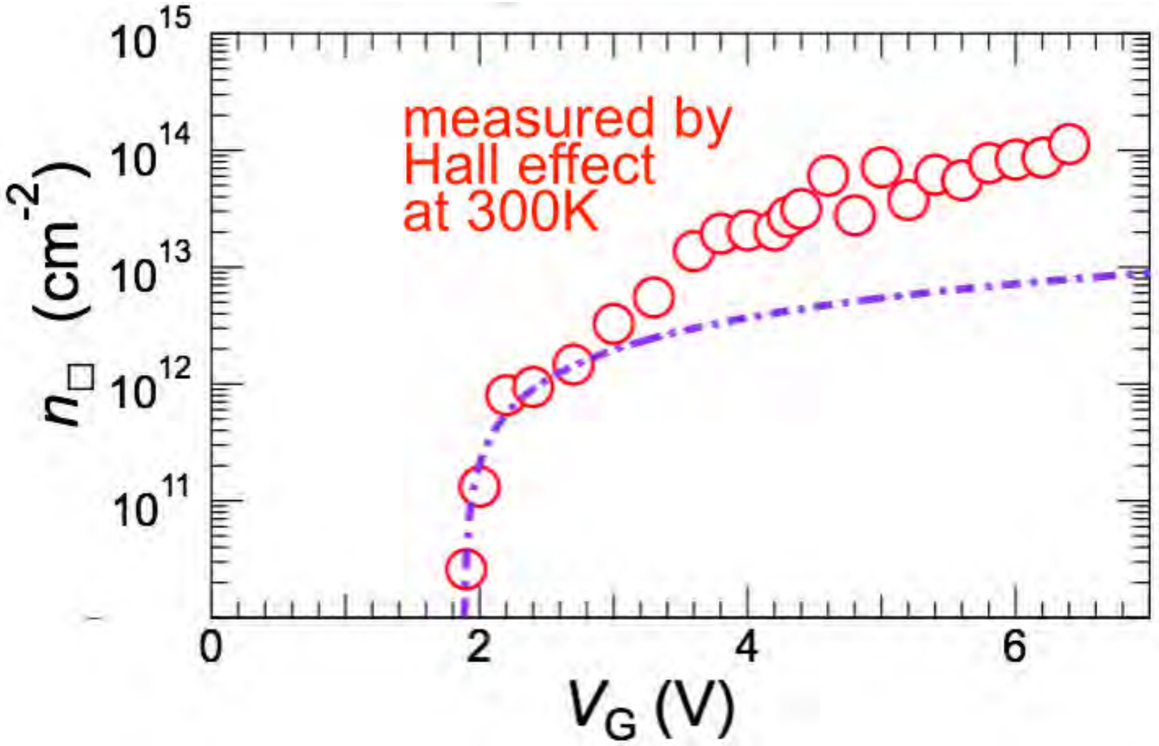


$$en_\square = C_\square V_\mathrm{G}$$
$$= \left(\frac{1}{C^{\mathrm{ins}}_\square} + \frac{1}{C^{\mathrm{sub}}_\square}\right)^{-1} V_\mathrm{G}$$



	ideal **metal** perfect screening	$\cdots$	ideal **insulator** no screening
$C^{\mathrm{sub}}_\square$	∞	$\cdots$	0 $\because \frac{\varepsilon}{d} \to 0$ for $d \to \infty$
$n_\square$	**maximum!?** $\boxed{C^{\mathrm{ins}}_\square V_\mathrm{G}/e}$	$\cdots$	0

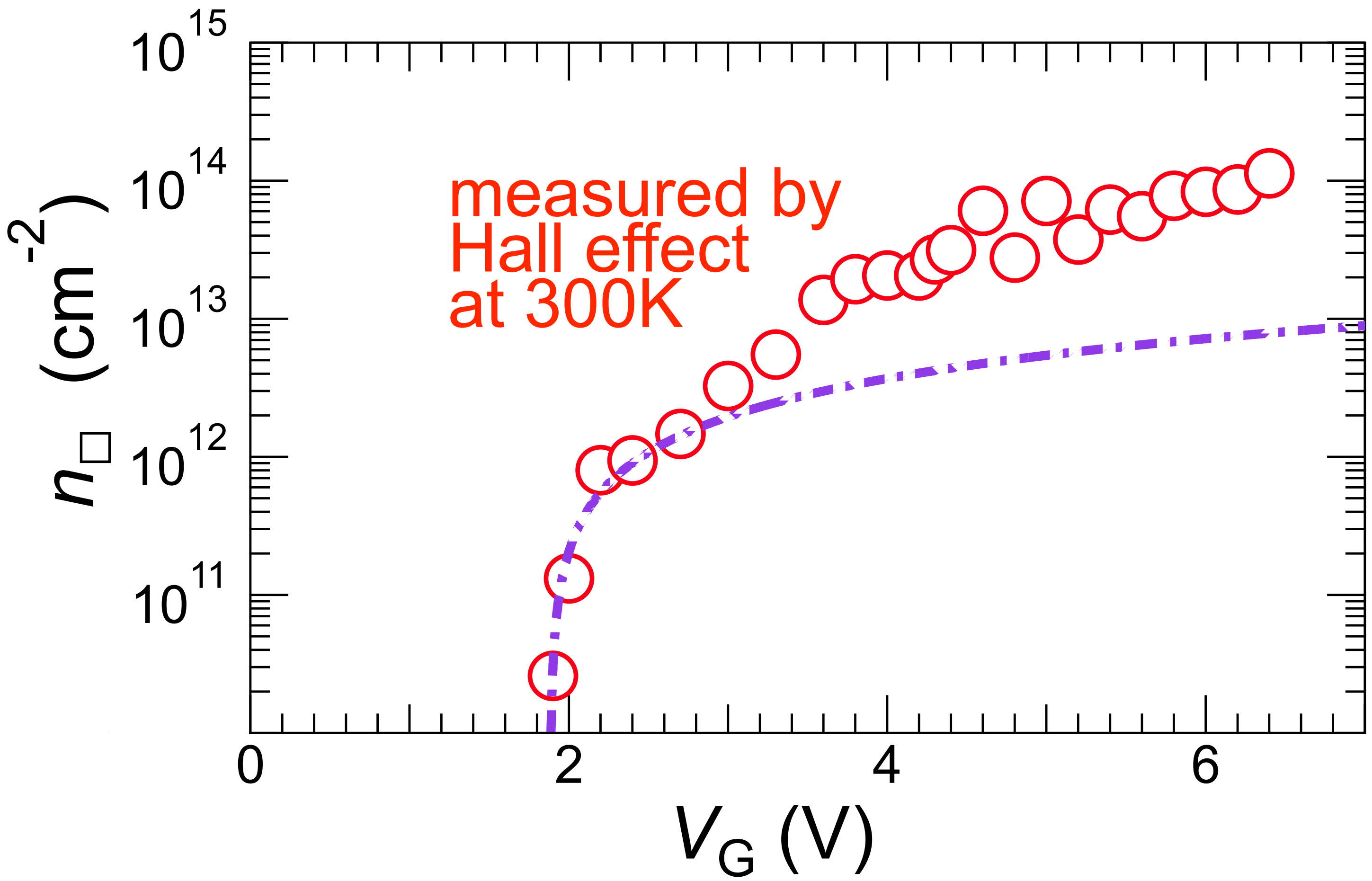
$n_\square$ can be larger than $C_\square^{\mathrm{ins}} V_\mathrm{G}/e$



$$e n_\square = C_\square V_\mathrm{G}$$
$$= \left(\frac{1}{C_\square^{\mathrm{ins}}} + \frac{1}{C_\square^{\mathrm{sub}}} \right)^{-1} V_\mathrm{G}$$

	exotic **metal**?	$\cdots$	ideal **metal** perfect screening	$\cdots$	ideal **insulator** no screening
$C_\square^{\mathrm{sub}}$	< 0 negative capacitance	$\cdots$	∞	$\cdots$	0 $\because \ \frac{\varepsilon}{d} \to 0$ for $d \to \infty$
$n_\square$	$> C_\square^{\mathrm{ins}} V_\mathrm{G}/e$	$\cdots$	$C_\square^{\mathrm{ins}} V_\mathrm{G}/e$	$\cdots$	0

Negative capacitance !?

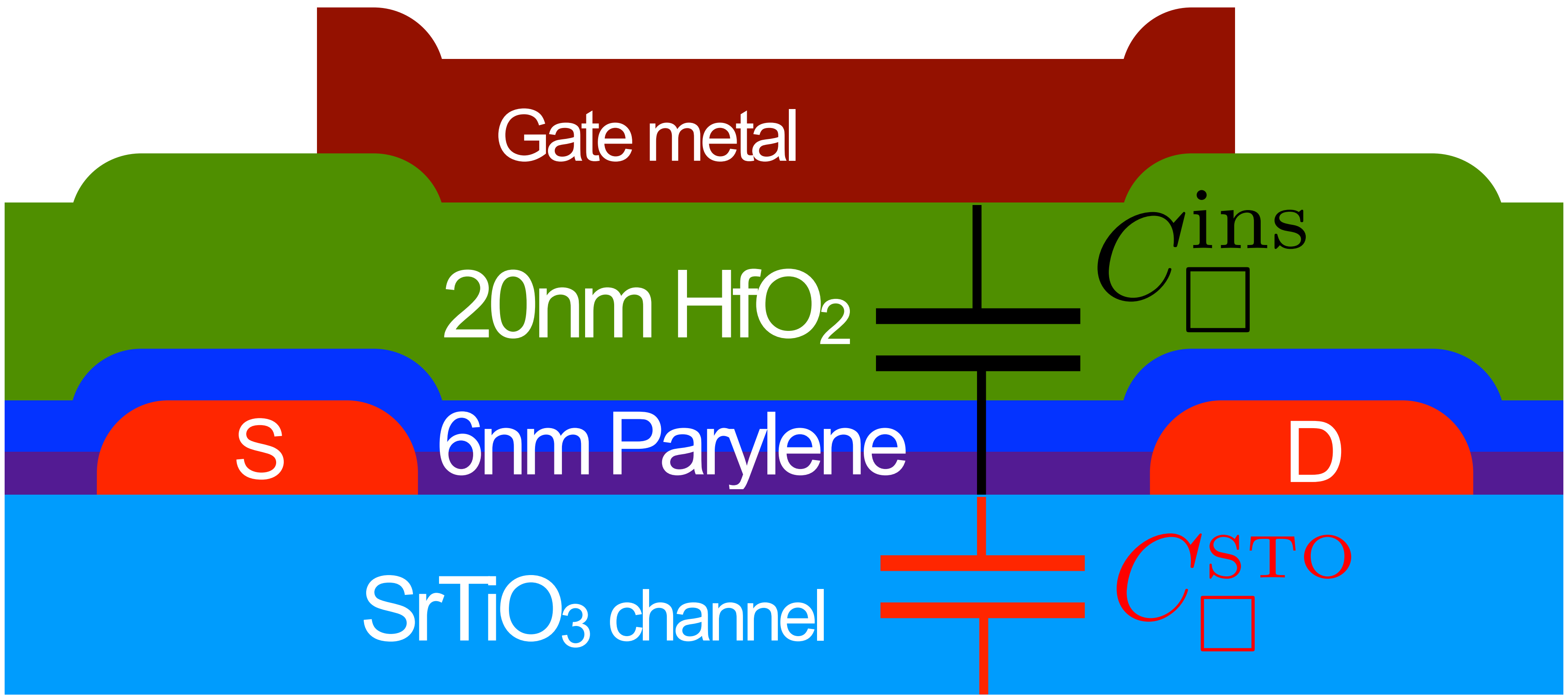


$$n_{\square} > C_{\square}^{\mathrm{ins}} V_{\mathrm{G}}/e$$

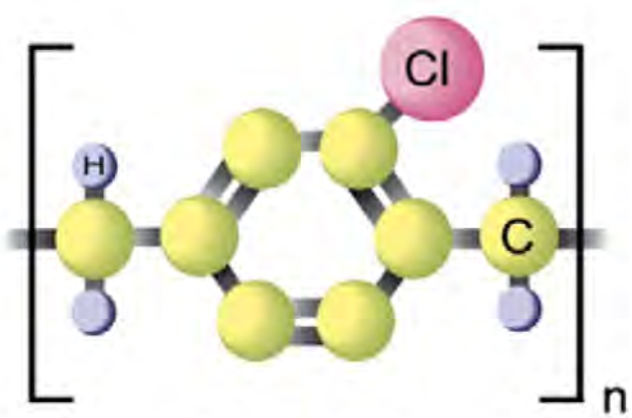
$$en_{\square} = C_{\square} V_{\mathrm{G}}$$
$$= \left(\frac{1}{C_{\square}^{\mathrm{ins}}} + \frac{1}{C_{\square}^{\mathrm{sub}}} \right)^{-1} V_{\mathrm{G}}$$

$$C_{\square}^{\mathrm{sub}} < 0$$

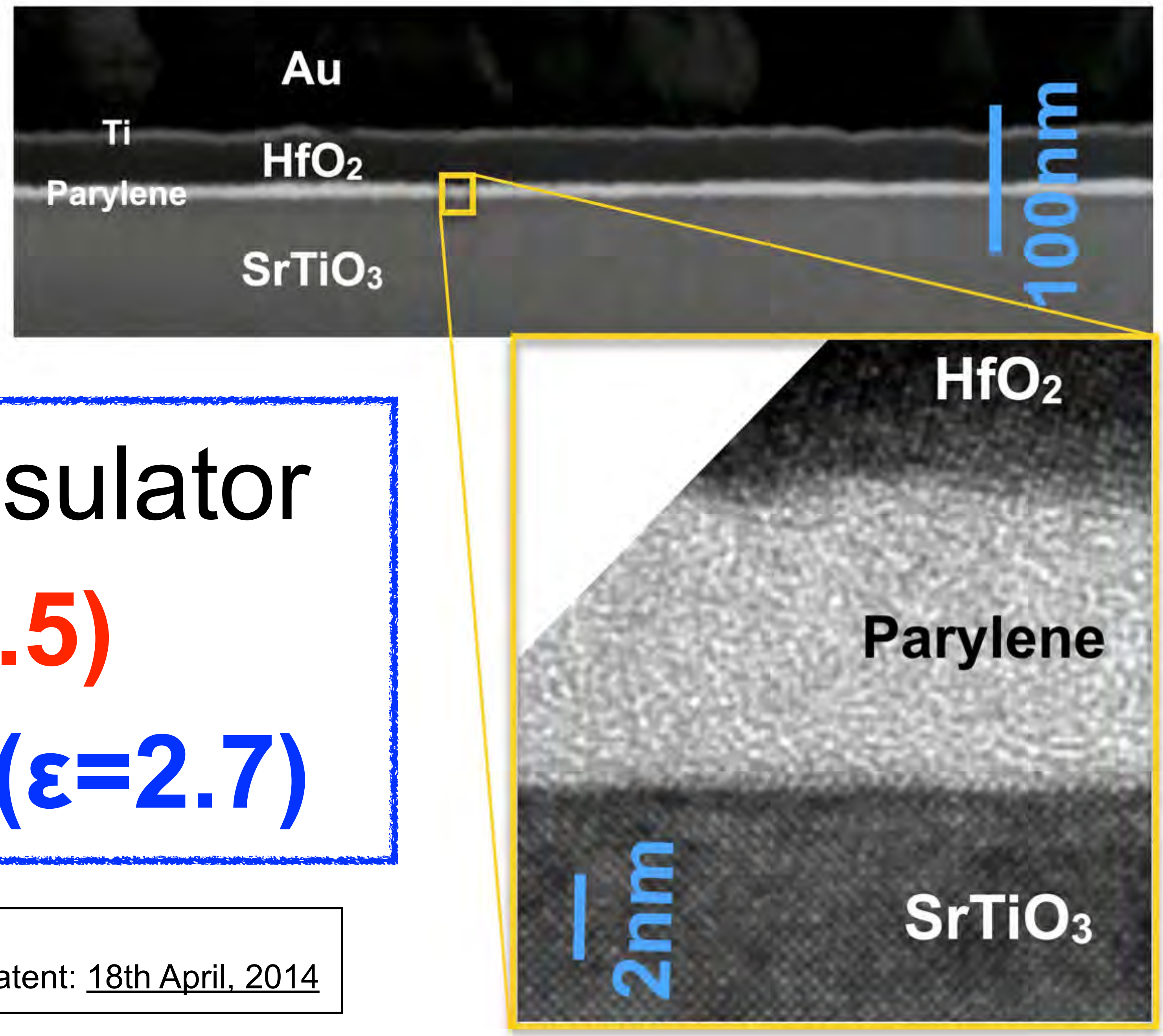
HfO_2 / Parylene bilayer gate insulator



HfO_2 / Parylene bilayer gate insulator



Parylene C



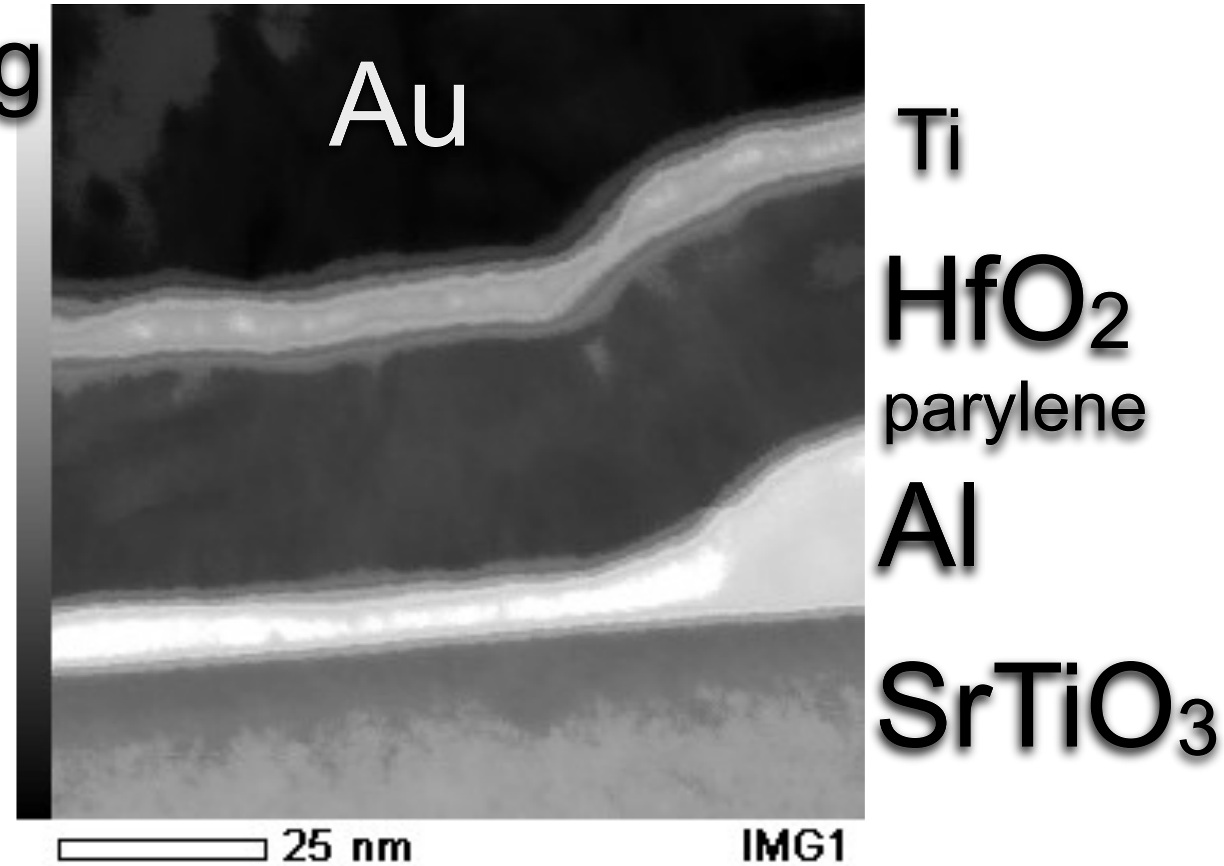
Hybrid gate insulator

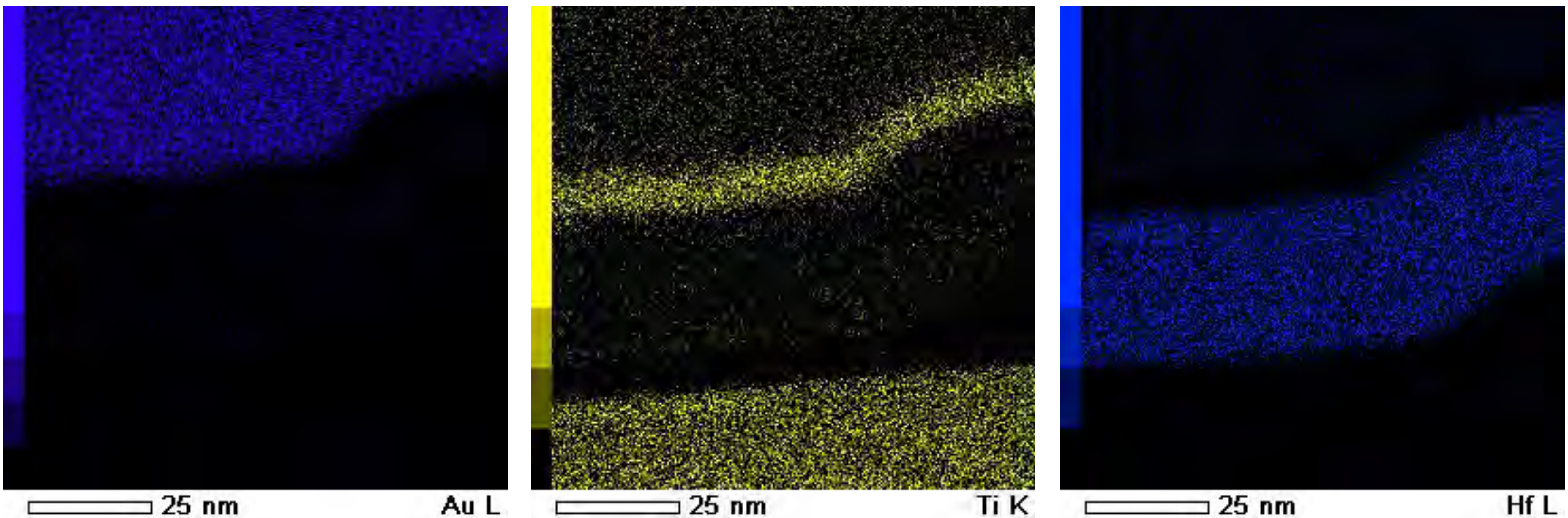
HfO_2 (ε = 21.5)
+
Parylene-C (ε=2.7)

Isao Inoue and Hisashi Shima,
Japan Patent Number: **5522688**, Date of Patent: 18th April, 2014

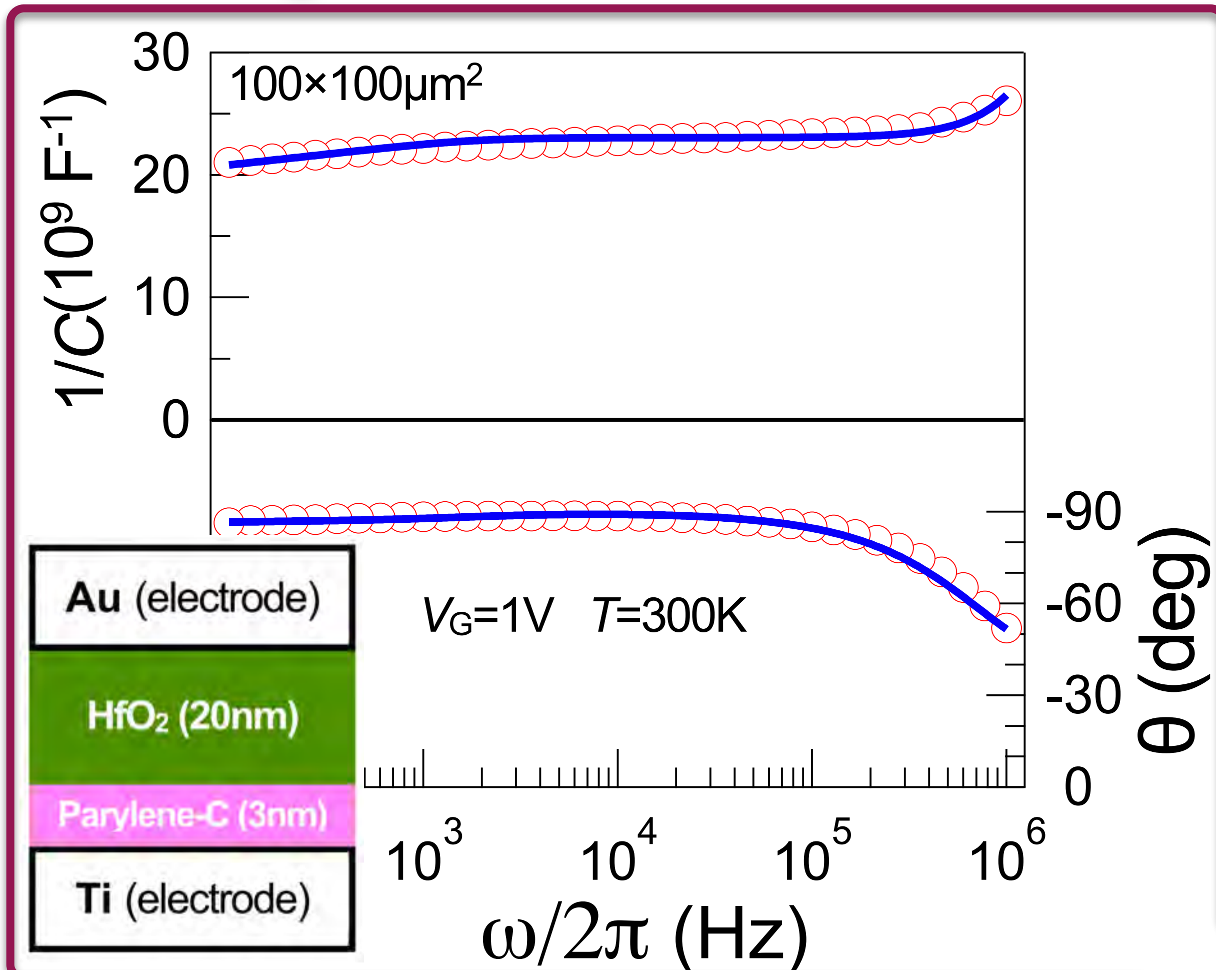
STEM-EDS mapping

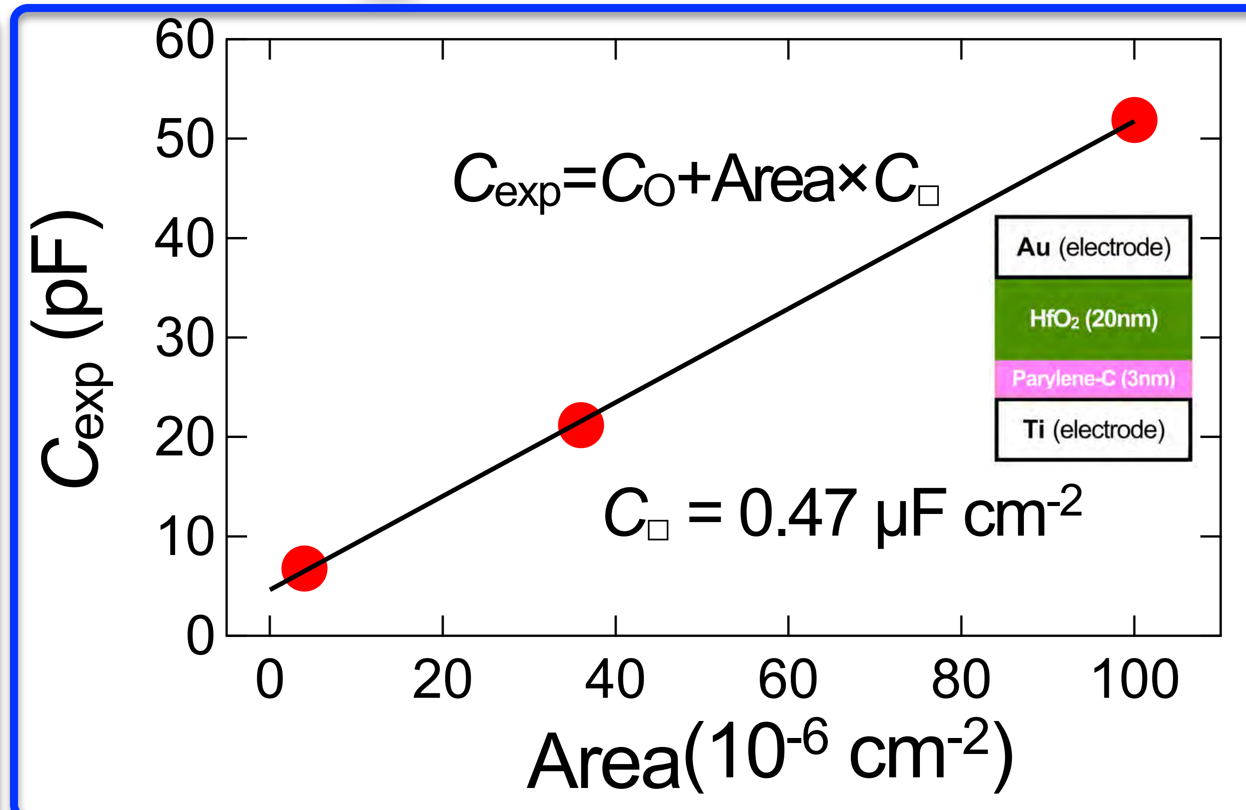
No mixture of each layer

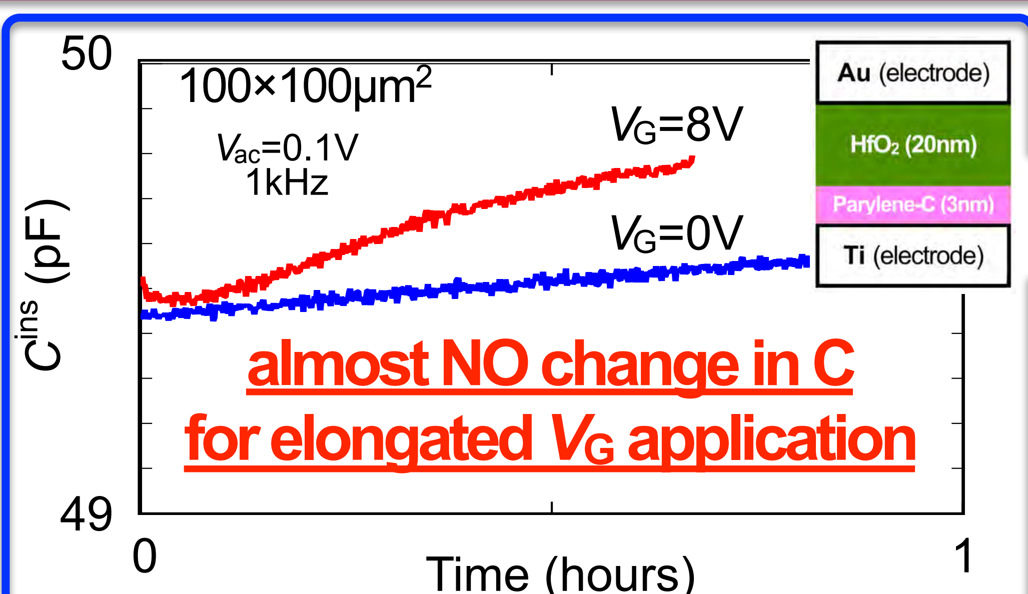




Capacitance of the gate insulator

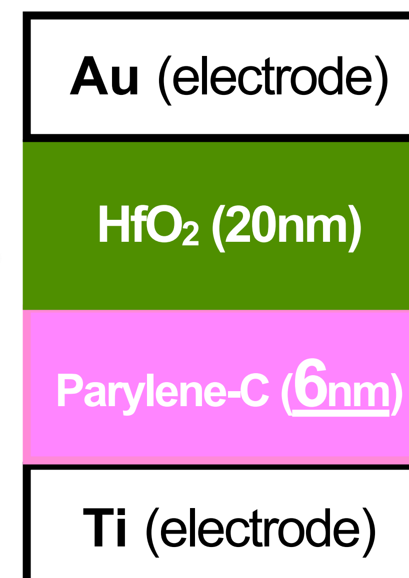




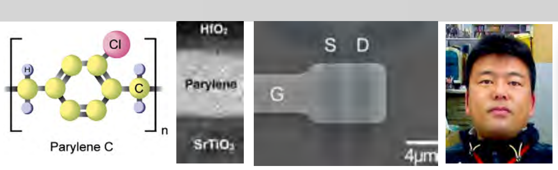


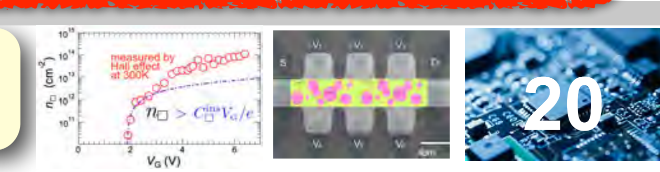
$$\varepsilon_{\mathrm{parylene}} = 2.7$$

$$\varepsilon_{\mathrm{HfO_2}} = 21.5$$

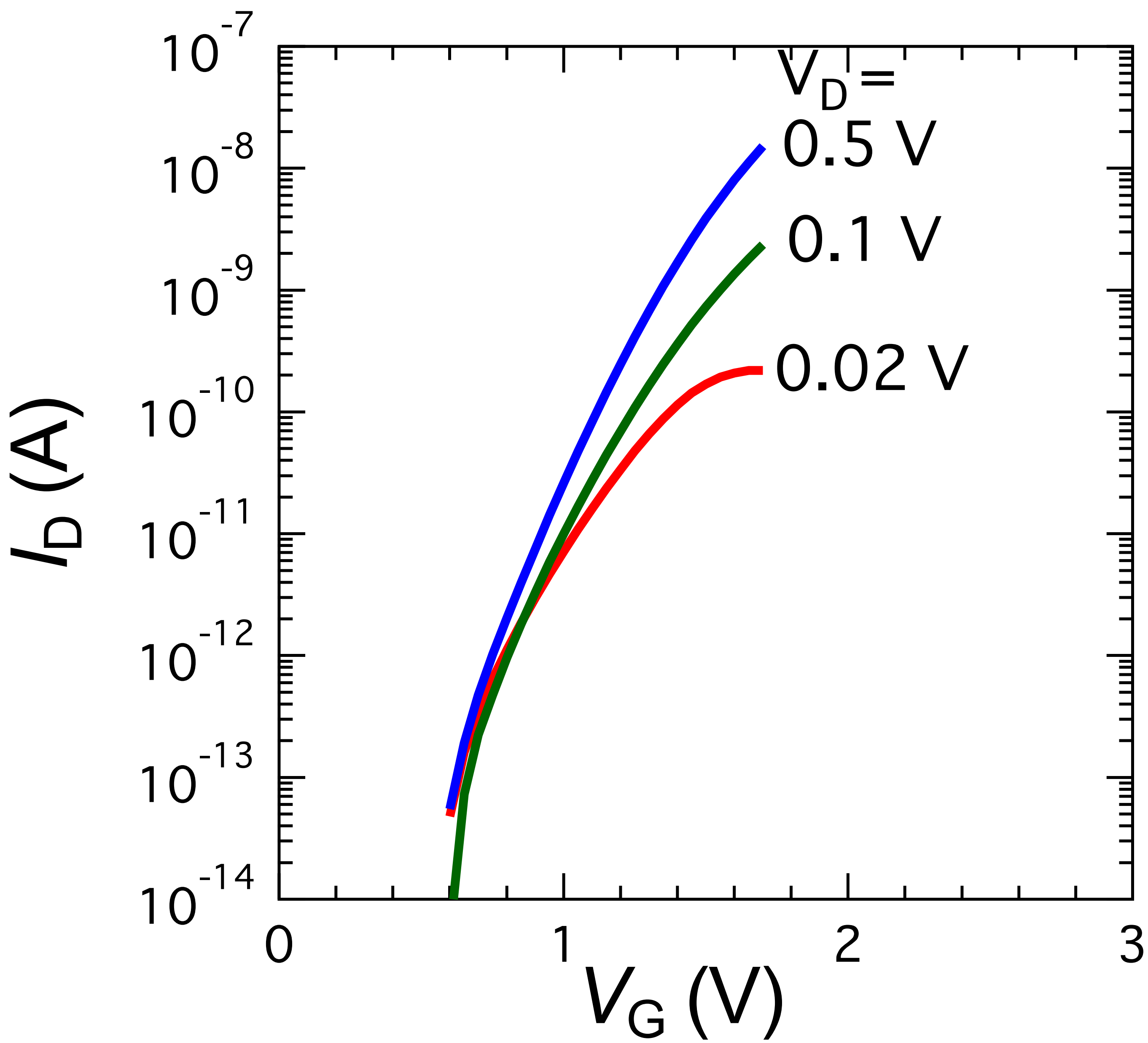


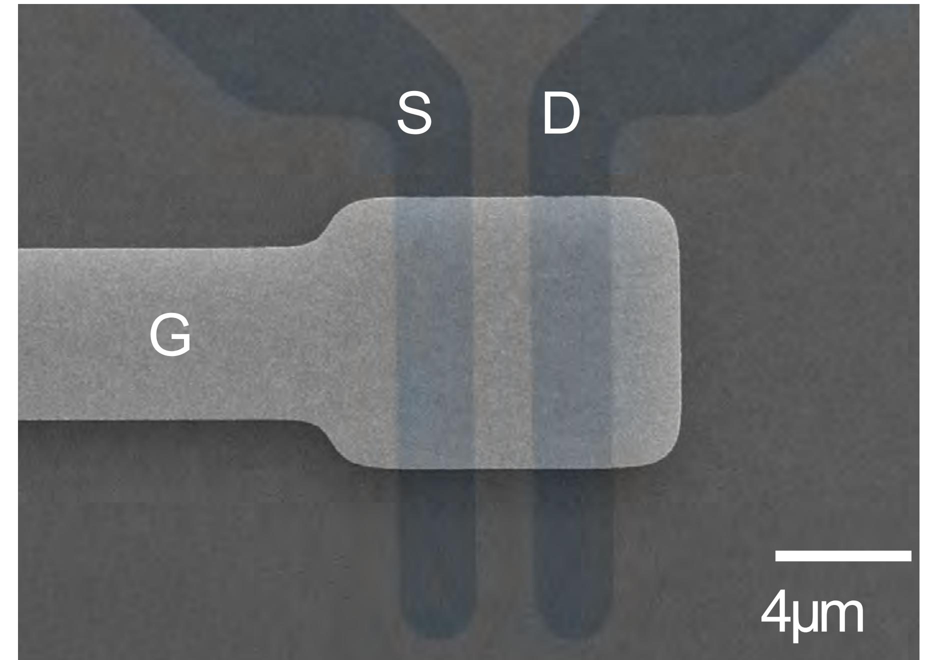
$$C^{\mathrm{ins}}_{\square} = 0.28\,\mu\mathrm{F}/\mathrm{cm}^2$$

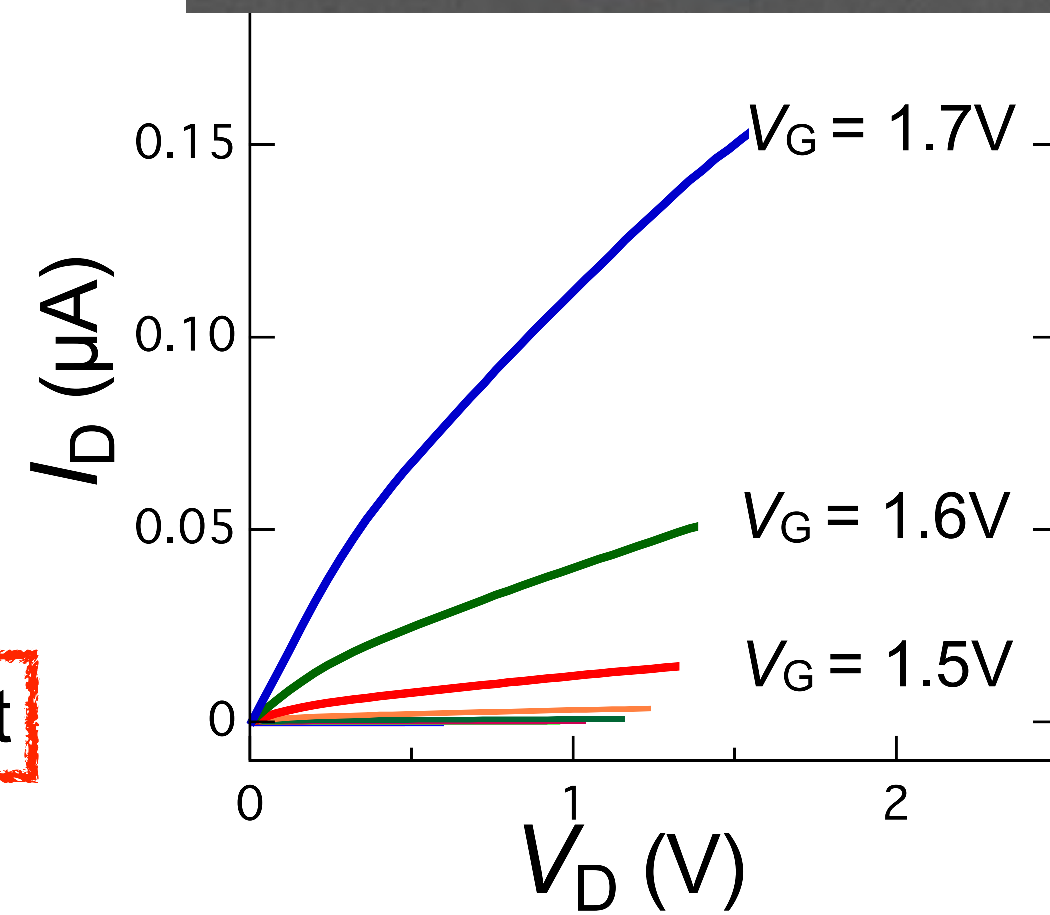




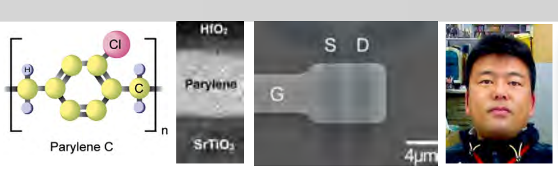
FET characteristics

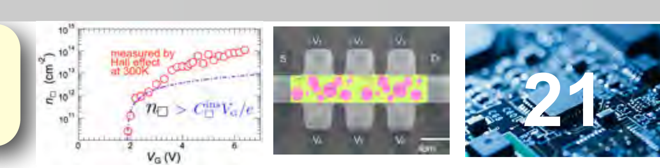




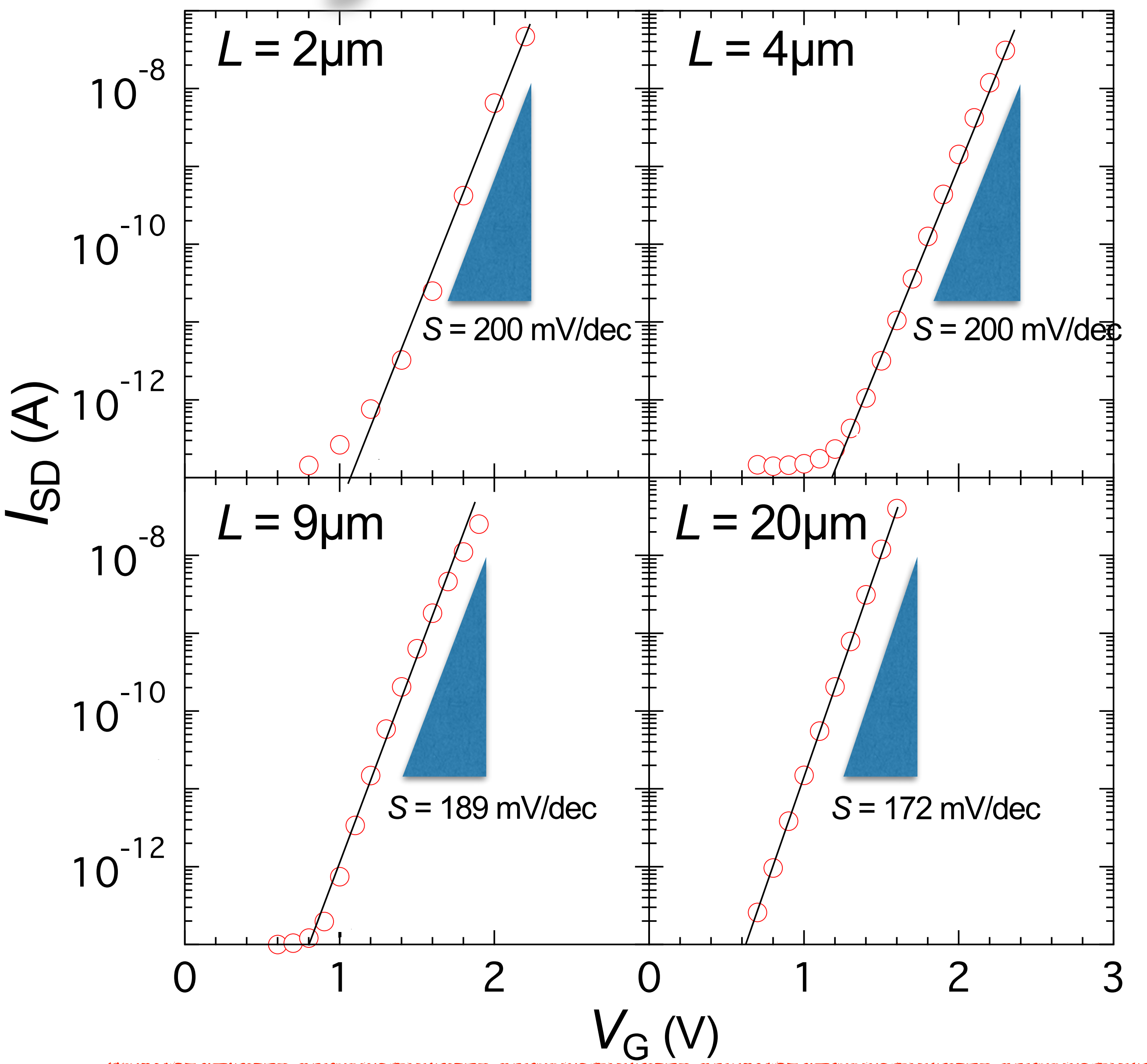


Drastic modulation of the drain current





Very small sub-threshold swing



$$I_D \propto \exp\left[-\frac{E_{gap}-\mu-e\varphi}{k_B T}\right]$$ ...... only the thermally excited carriers can contribute the transport.

$$\boxed{S = \frac{\Delta V_G}{\Delta(\log_{10} I_D)}}$$ ...... definition

$$= \frac{d\varphi}{d(\log_{10} I_D)} \times \frac{dV_G}{d\varphi}$$ ...... φ is the surface potential

$$= \ln(10) I_D \frac{d\varphi}{dI_D} \times \frac{dV_G}{d\varphi}$$

$$= \underbrace{\boxed{\ln(10)\frac{k_B T}{e}}}_{\text{transport factor}} \underbrace{\boxed{\left(1+\frac{C_\square^{STO}}{C_\square}\right)}}_{\text{body factor}}$$ ...... because $n_\square = (1/C_\square + 1/C_\square^{STO})^{-1} V_G$

$\varphi = n_\square / C_\square^{STO} = (1 + C_\square^{STO}/C_\square)^{-1} V_G$

S=170mV/dec is extremely small ! (~100mV/dec even for Si FET).

Therefore

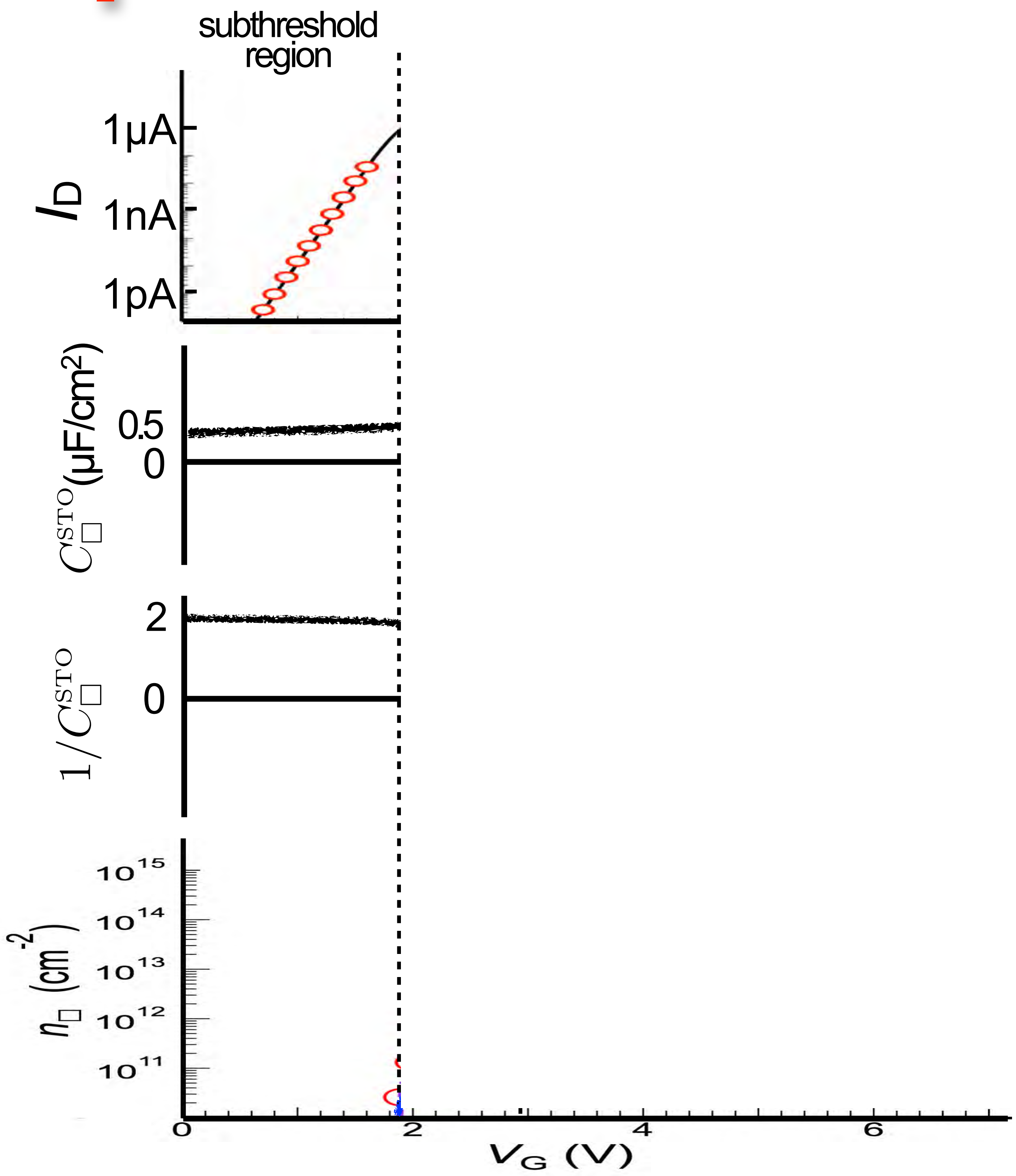
$$170\,\mathrm{mV/dec} = \boxed{60\,\mathrm{mV/dec}} \times \boxed{\left(1+\frac{C_\square^{STO}}{C_\square^{ins}}\right)}$$

$$C_\square^{STO} = 1.8 \times C_\square^{ins}$$

$$= 0.50\,\mu\mathrm{F/cm}^2$$

Small *S* means $C_\square^{STO} \rightarrow 0$ very clean channel !!

A possible scenario of gating $SrTiO_3$

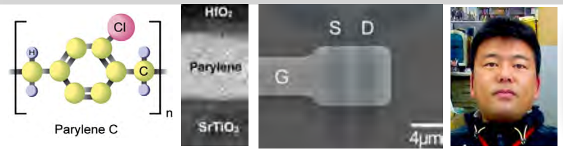


$$en_\square = C_\square(V_G - V_{fb})$$
$$= \left(\frac{1}{C_\square^{ins}} + \frac{1}{C_\square^{STO}}\right)^{-1}(V_G - V_{fb})$$

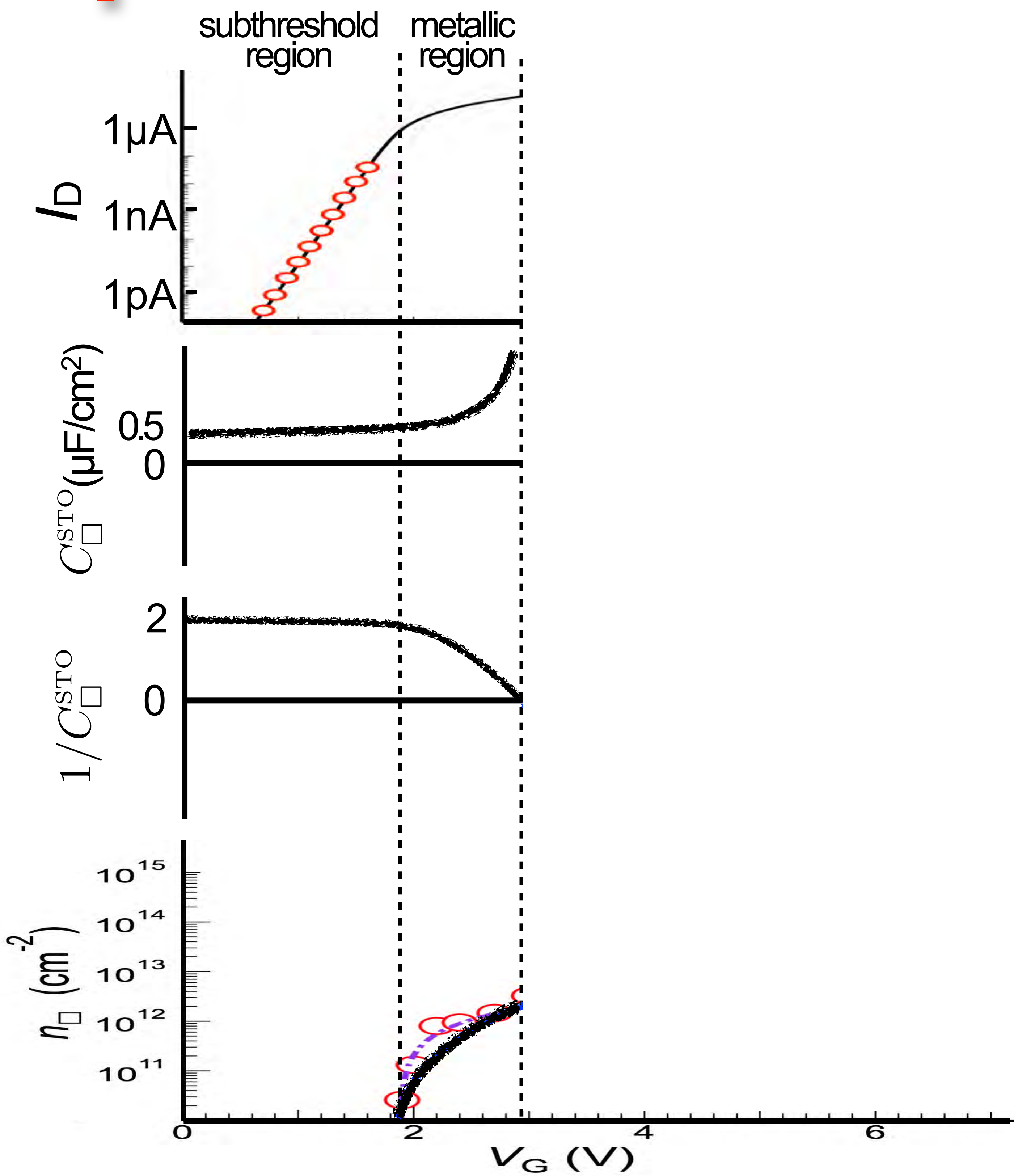
$0.28\,\mu F/cm^2$

$0.50\,\mu F/cm^2$

unchanged



A possible scenario of gating $SrTiO_3$



$$
\begin{aligned}
en_\square &= C_\square(V_G - V_{fb}) \\
&= \left(\frac{1}{C_\square^{ins}} + \frac{1}{C_\square^{STO}}\right)^{-1}(V_G - V_{fb})
\end{aligned}
$$

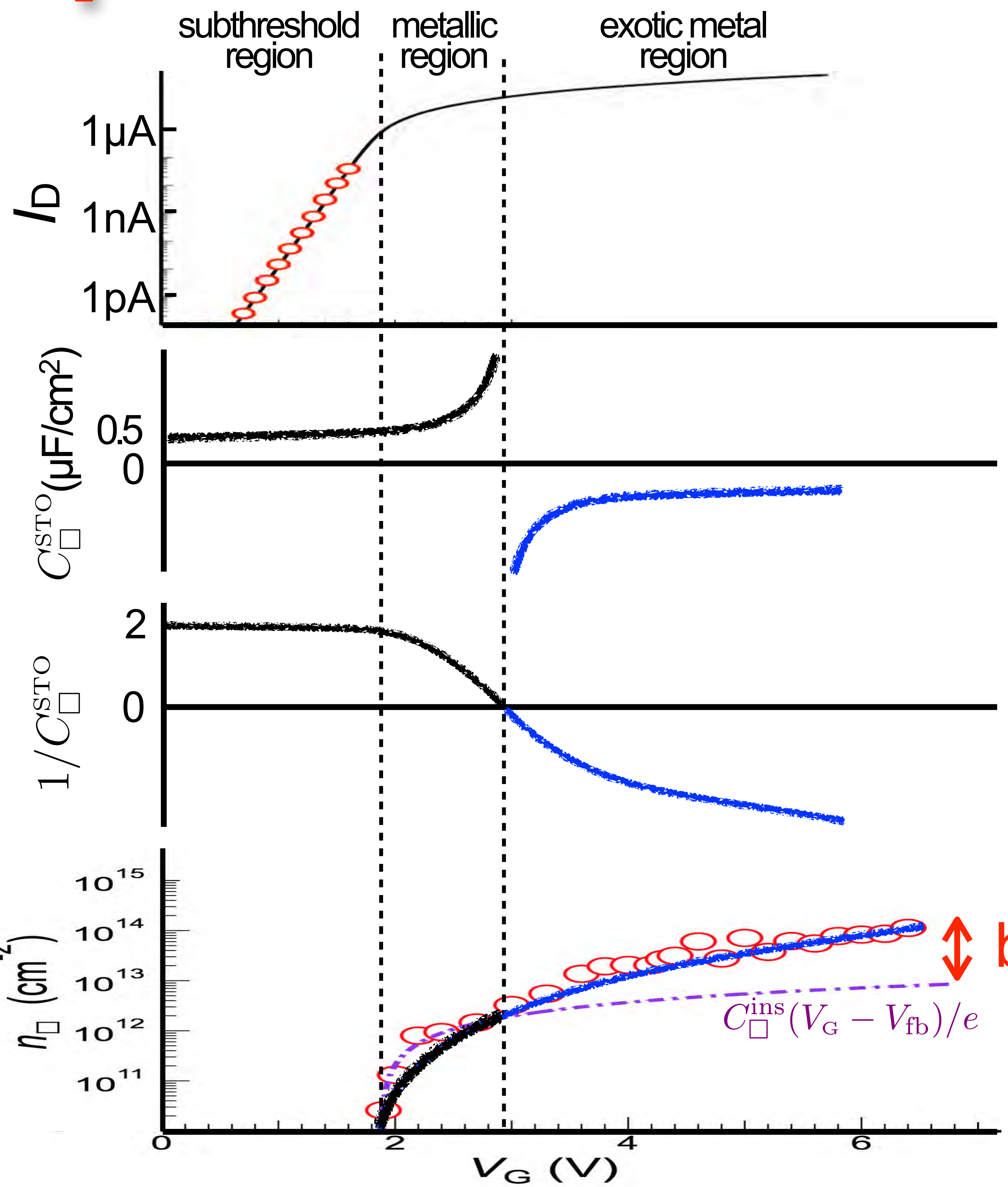
$0.28\,\mu\mathrm{F/cm}^2$

unchanged

$0.50\,\mu\mathrm{F/cm}^2$

∞

A possible scenario of gating $SrTiO_3$



$$en_\square = C_\square(V_G - V_{\mathrm{fb}})$$

$$= \left(\frac{1}{C_\square^{\mathrm{ins}}} + \frac{1}{C_\square^{\mathrm{STO}}}\right)^{-1}(V_G - V_{\mathrm{fb}})$$

$0.28\,\mu\mathrm{F/cm}^2$

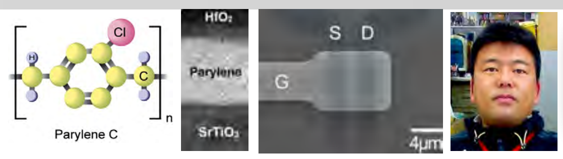
<u>unchanged</u>

$0.50\,\mu\mathrm{F/cm}^2$

∞

<u>negative !</u>

big deviation can be explained?

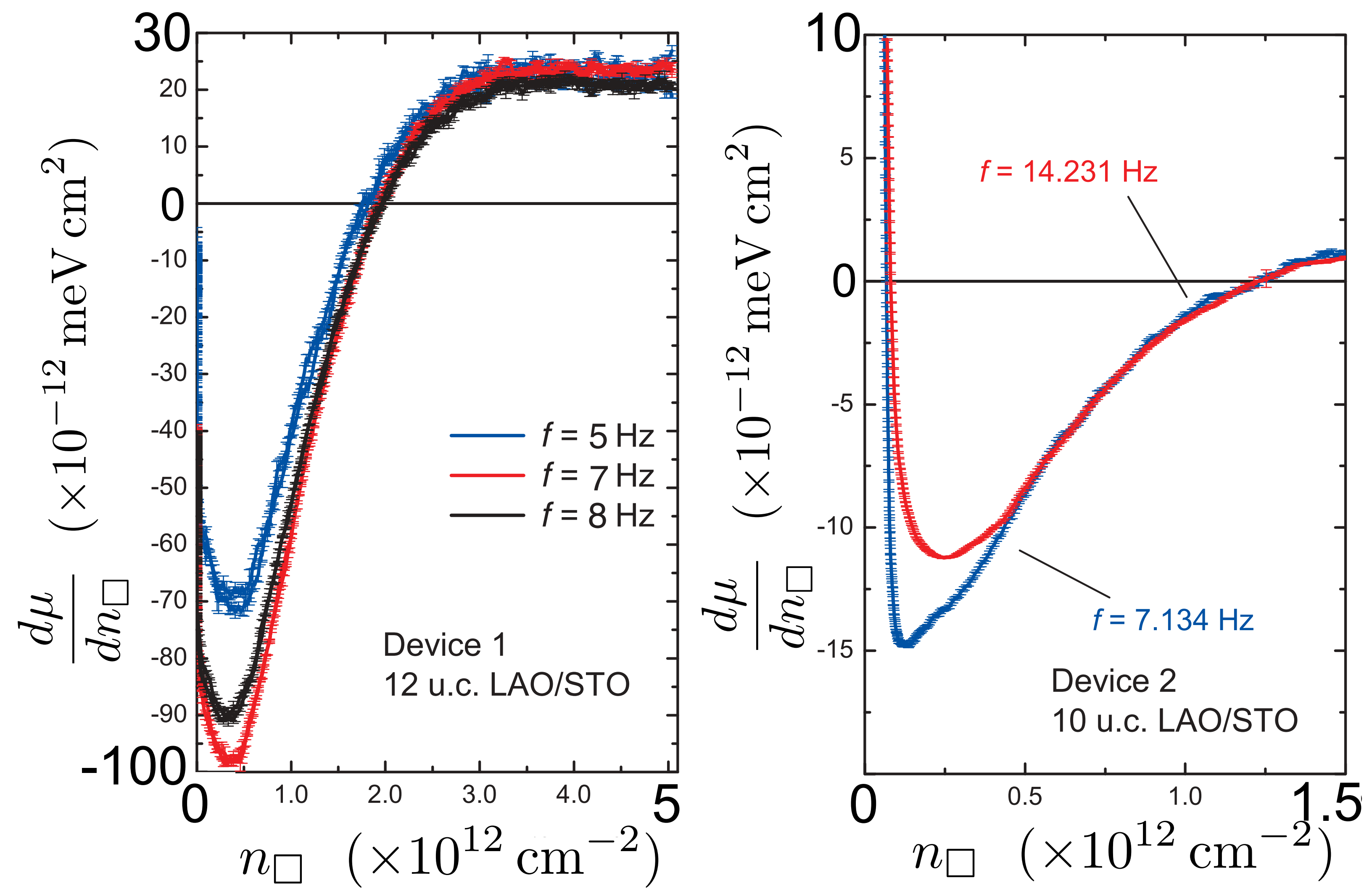


Negative C in $LaAlO_3/SrTiO_3$

Negative C (negative charge compressibility) is **not** a strange phenomenon.

There have been many reports in literature so far.

Even $SrTiO_3$ shows it in the $LaAlO_3/SrTiO_3$ interface.



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$$\frac{d\mu}{dn_\square} = \frac{e^2}{C_\square^{\mathrm{STO}}}$$

What's the origin of negative C?

JOURNAL OF APPLIED PHYSICS **106**, 064504 (2009)

Calculation of the capacitances of conductors: Perspectives for the optimization of electronic devices

Thilo Kopp[a] and Jochen Mannhart
Center for Electronic Correlations and Magnetism, Institute of Physics, Universität Augsburg, D-86135 Augsburg, Germany

$$A/C^{(2\mathrm{D})} - AC_{\mathrm{geom}}^{-1} = \sum_i \frac{\varkappa_i^{-1}}{(en_i)^2}$$

$$4\pi\epsilon_0 A/C_{\mathrm{geom}} = \frac{4\pi d}{\epsilon_r}$$

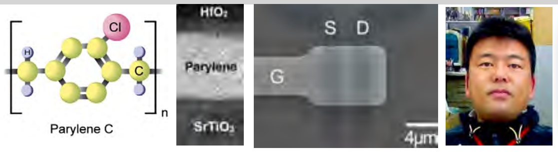
geometric term (gate insulator)

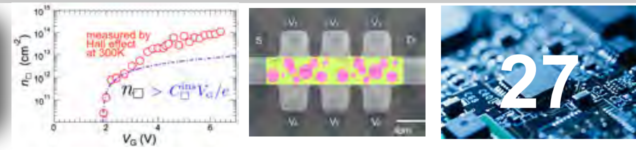
$$4\pi\epsilon_0 A/C_{\mathrm{kin},i}^{(2\mathrm{D})} = \frac{\pi a_B}{m_i^\star/m} = \frac{4\pi\epsilon_0}{e^2}\frac{1}{\rho_i^{(2\mathrm{D})}(\varepsilon_F)}$$

Hartree term

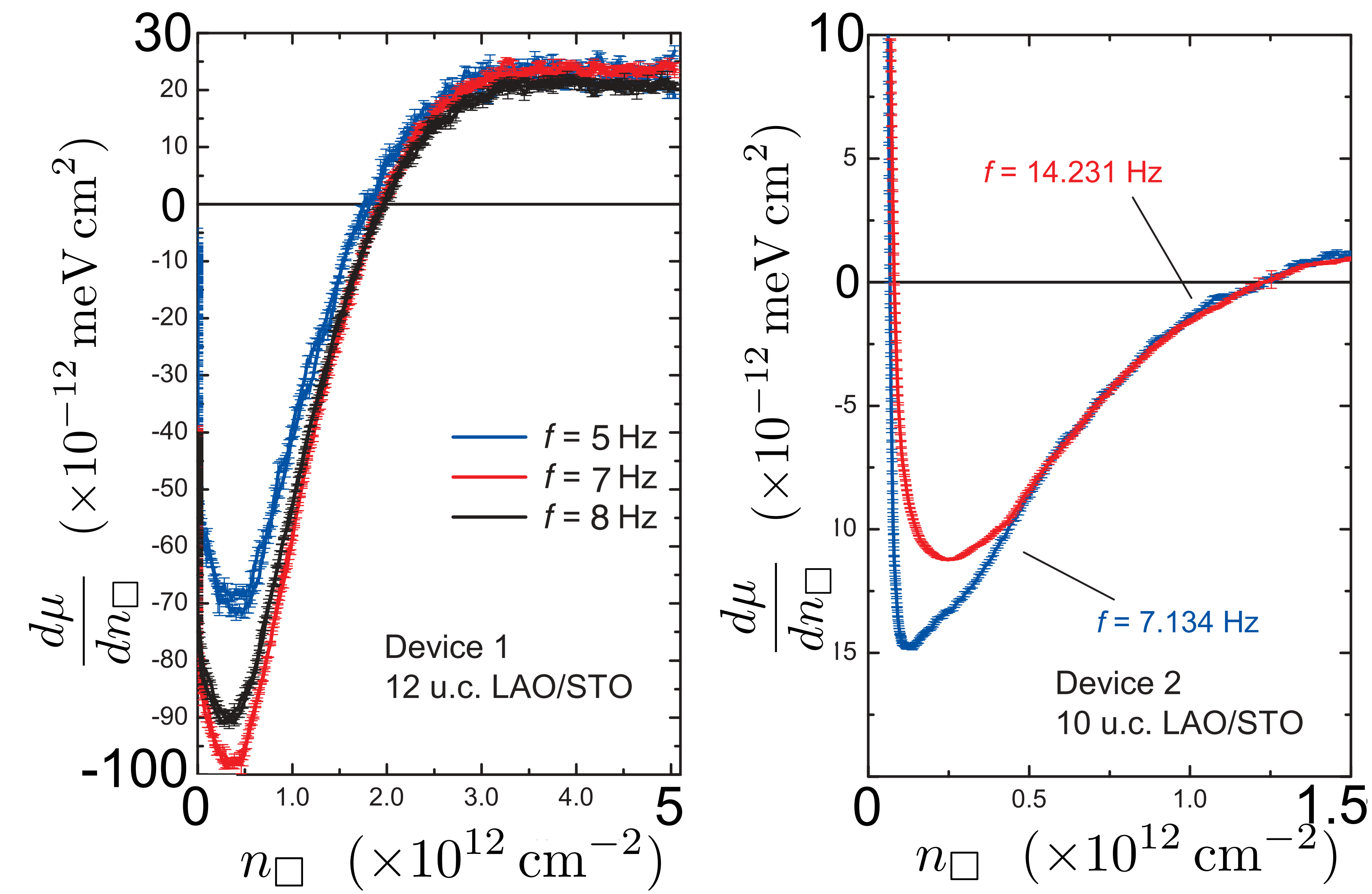
$$4\pi\epsilon_0 A/C_{\mathrm{x},i}^{(2\mathrm{D})} = -\left(\frac{2}{\pi}\right)^{1/2}\frac{1}{\sqrt{n_i}}\frac{1}{\epsilon_{\mathrm{eff},i}}$$

Fock term
negative!!





Only for <u>dilute</u> carrier density

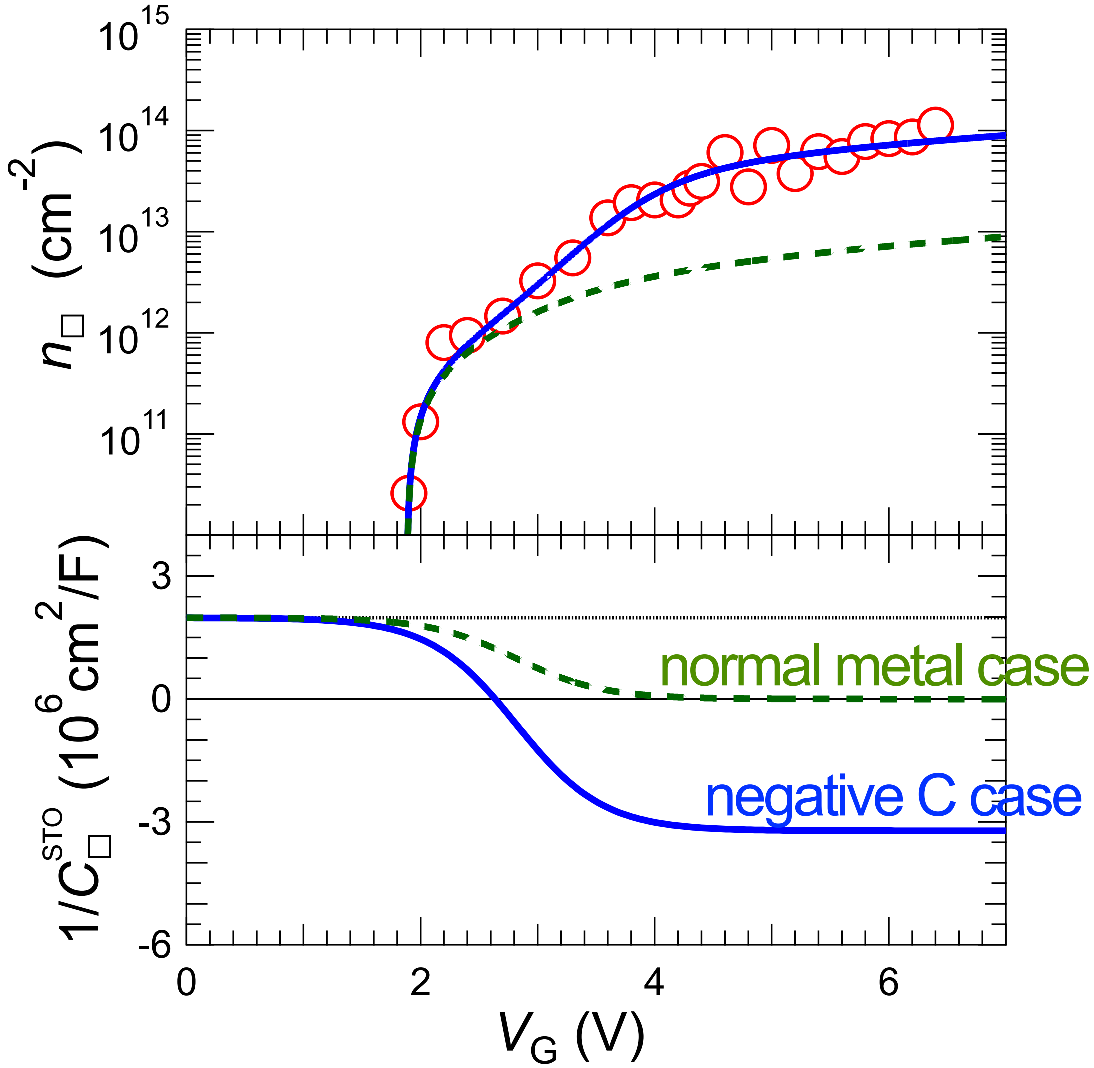


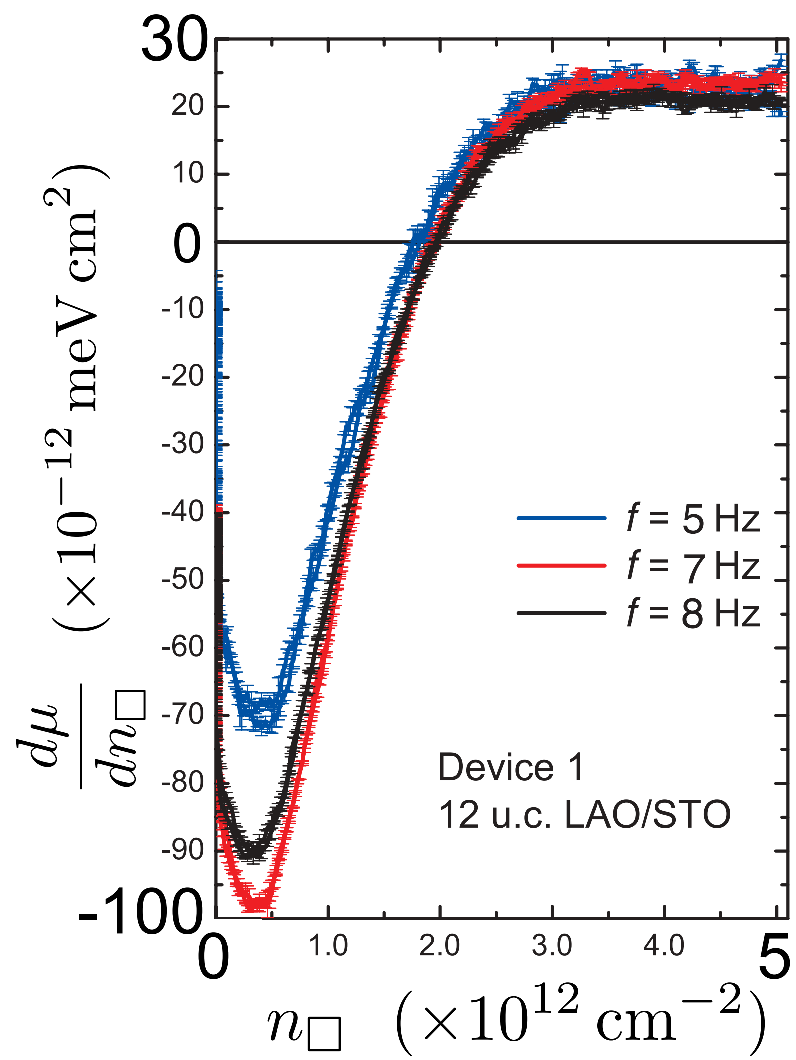
Lu Li *et al. Science* **332**, 825 (2011)

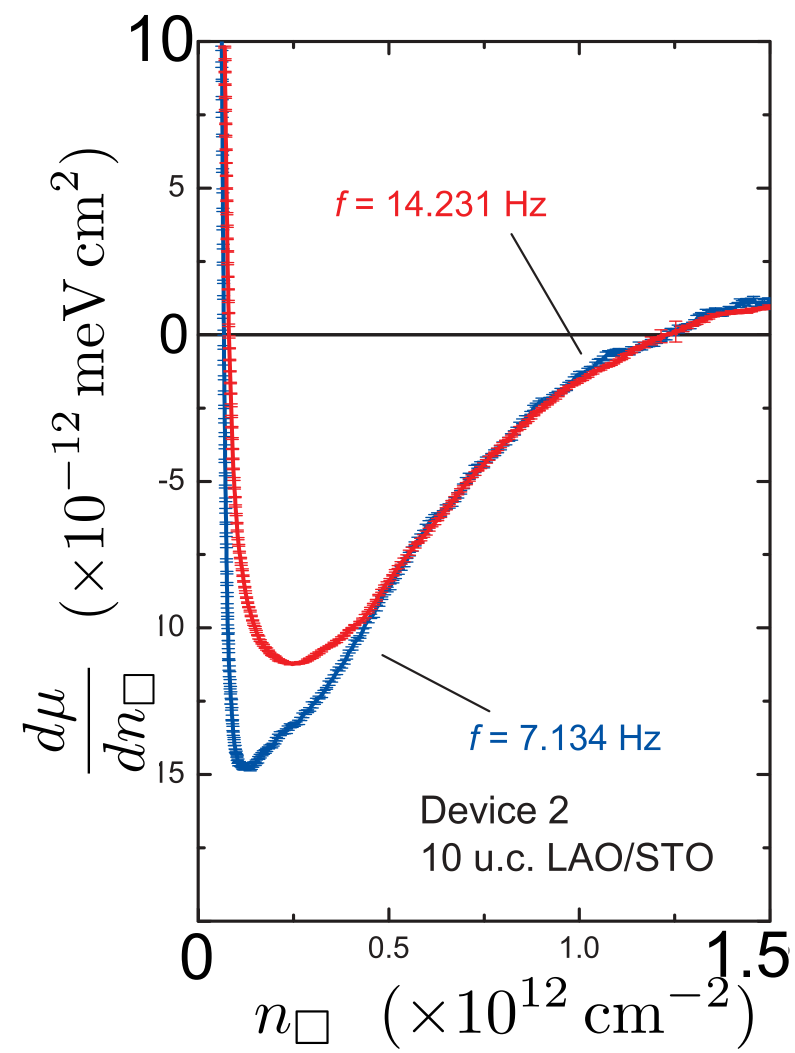
$$\frac{e^2}{C_\square^{\mathrm{STO}}} = \frac{d\mu}{dn_\square} = -0.15\times 10^{-13} \sim -1.0\times 10^{-13}\,\mathrm{eV\,cm^2}$$

$$\text{for}\quad n_\square \sim 10^{11}\,\mathrm{cm^{-2}}$$

Our carrier density is too large?!







Our data

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$$\frac{e^2}{C_\square^{\mathrm{STO}}} = \frac{d\mu}{dn_\square} = -5.2 \times 10^{-13}\,\mathrm{eV\,cm^2}$$

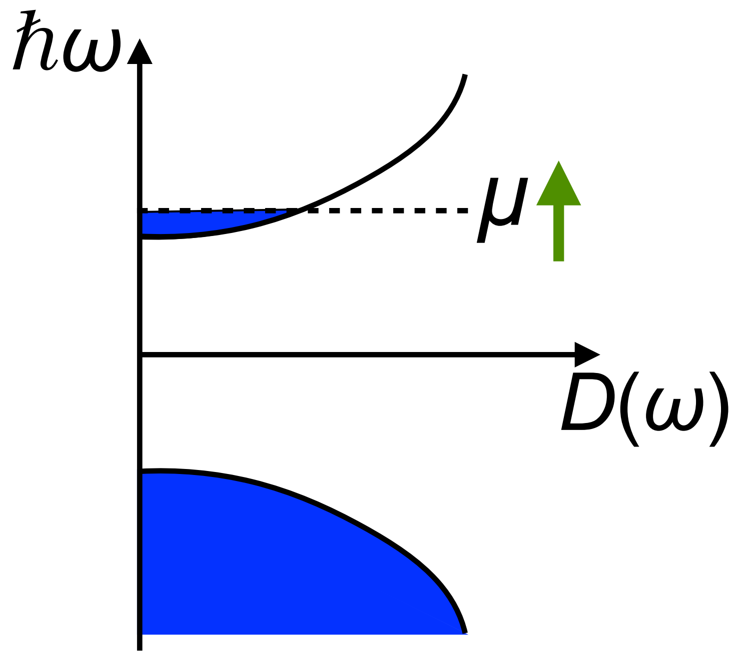
for $n_\square \sim \underline{10^{14}\,\mathrm{cm^{-2}}}$

$$\frac{e^2}{C_\square^{\mathrm{STO}}} = \frac{d\mu}{dn_\square} = -0.15 \times 10^{-13} \sim -1.0 \times 10^{-13}\,\mathrm{eV\,cm^2}$$

for $n_\square \sim \underline{10^{11}\,\mathrm{cm^{-2}}}$

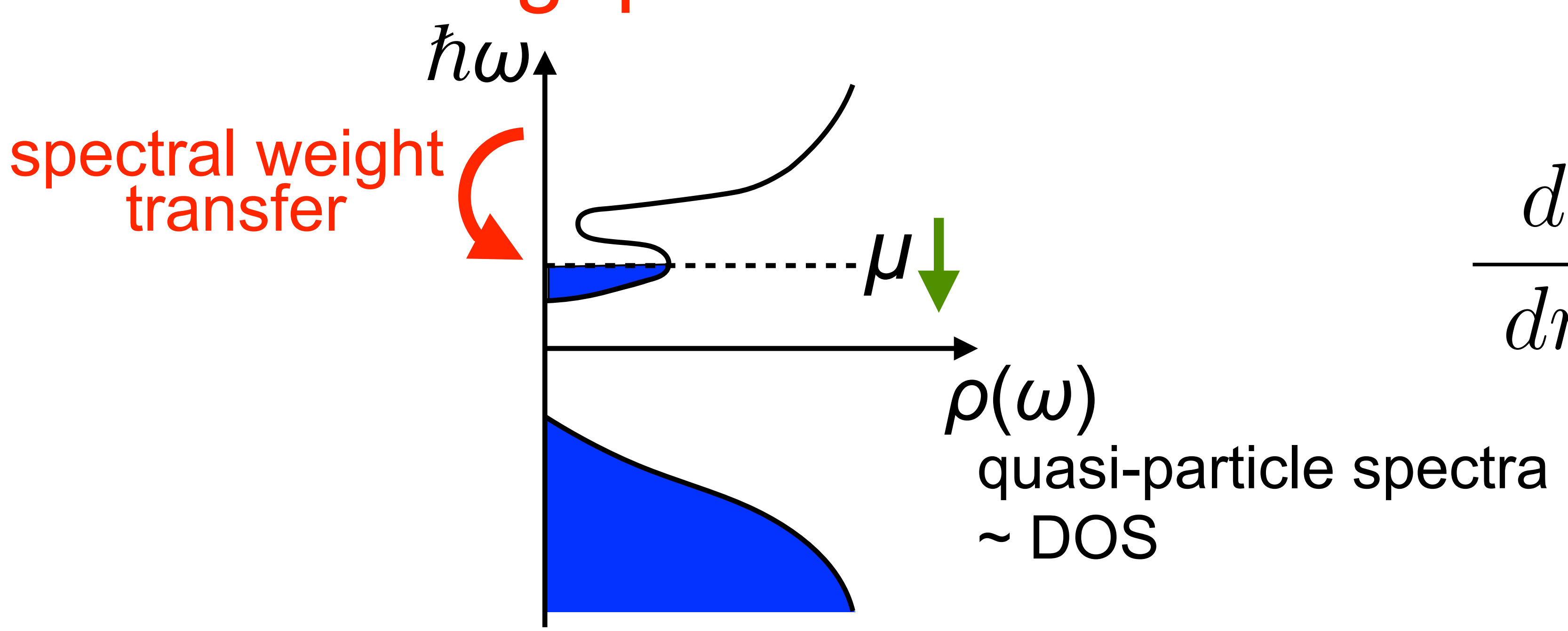
Other mechanisms of negative C

Rigid band shift



$$\frac{d\mu}{dn_{\square}} > 0$$

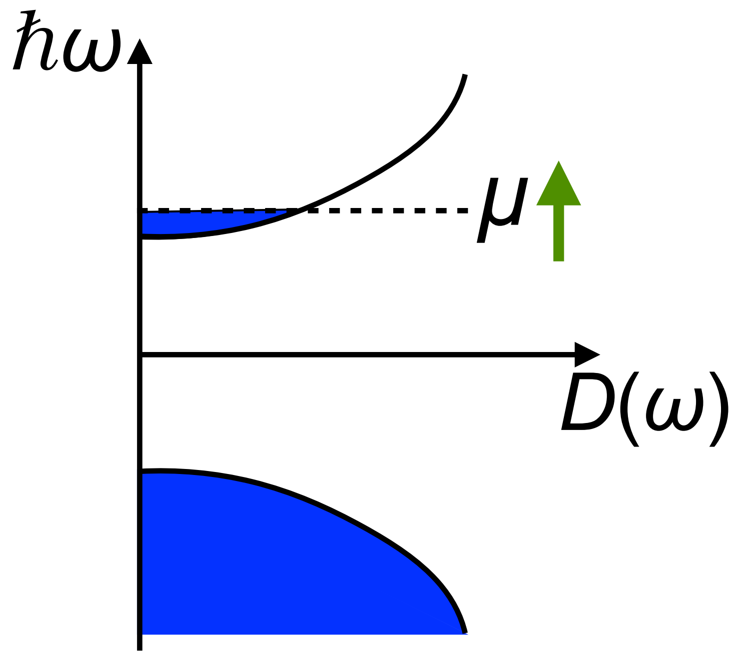
Correlation gap closure



$$\frac{d\mu}{dn_{\square}} < 0$$

Other mechanisms of negative C

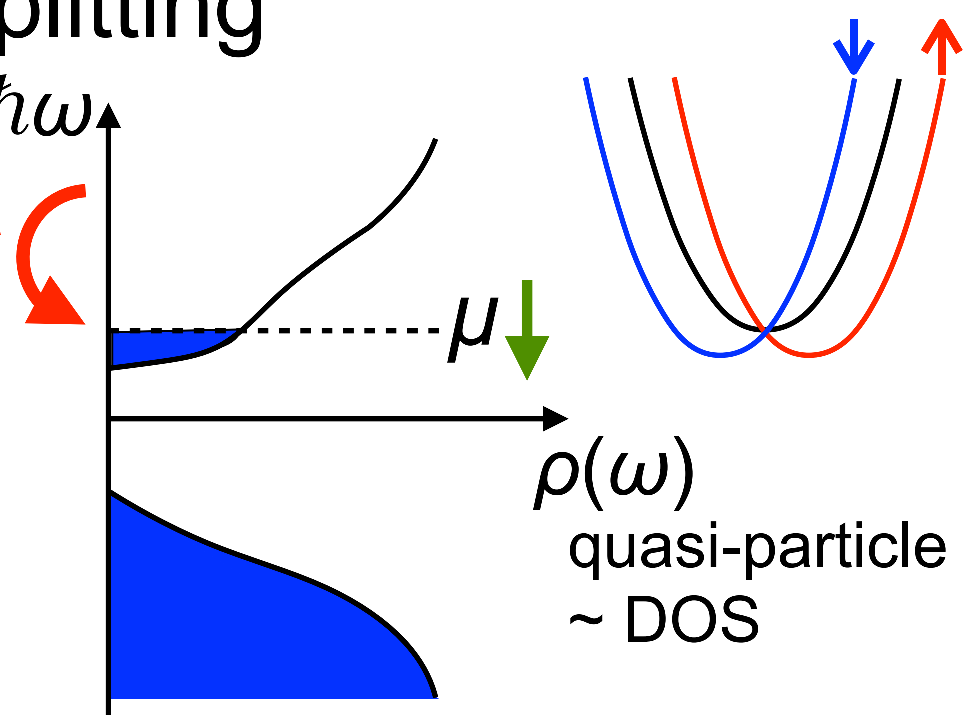
Rigid band shift



$$\frac{d\mu}{dn_\square} > 0$$

Rashba splitting

spectral weight transfer



quasi-particle spectra
~ DOS

$$\frac{d\mu}{dn_\square} < 0$$

Still our $|C_{\square}^{\mathrm{STO}}|$ is too small !!
($\left|\frac{1}{C_{\square}^{\mathrm{STO}}}\right|$ is too large !!)

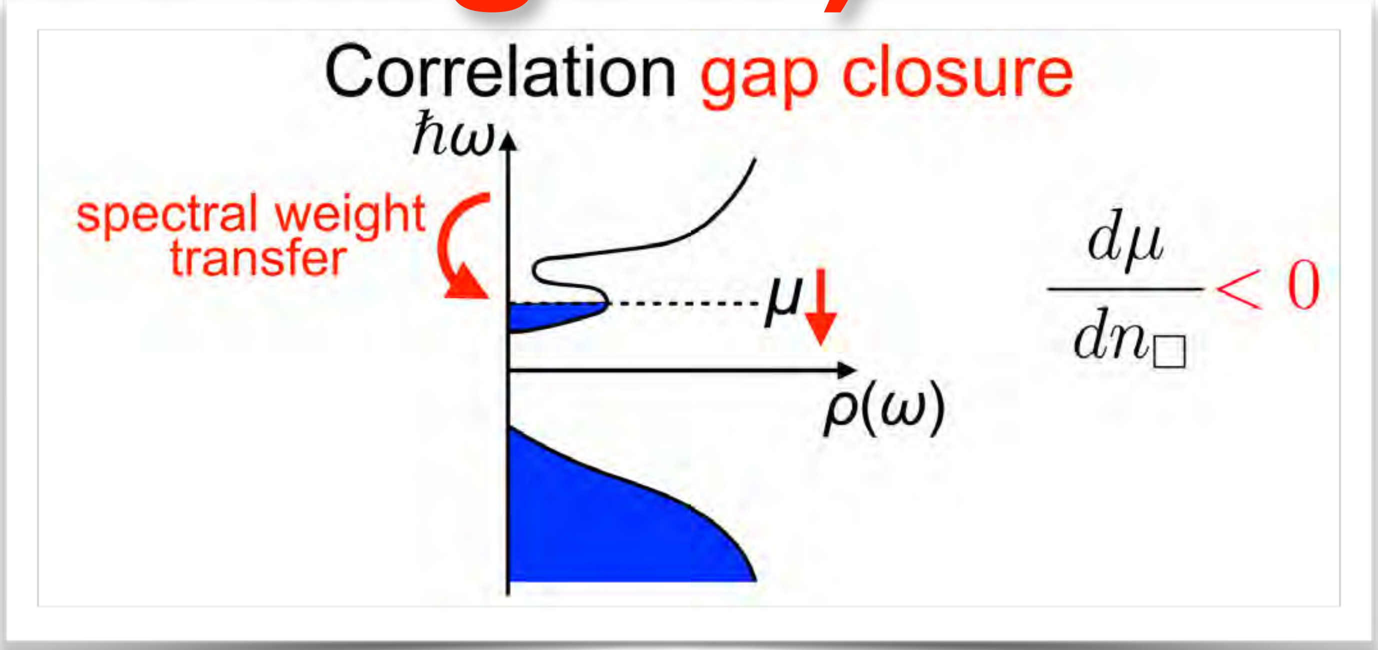
$$\frac{1}{C_{\square}^{\mathrm{STO}}} = -3.2 \times 10^{6}\,\mathrm{cm}^2/\mathrm{F}$$

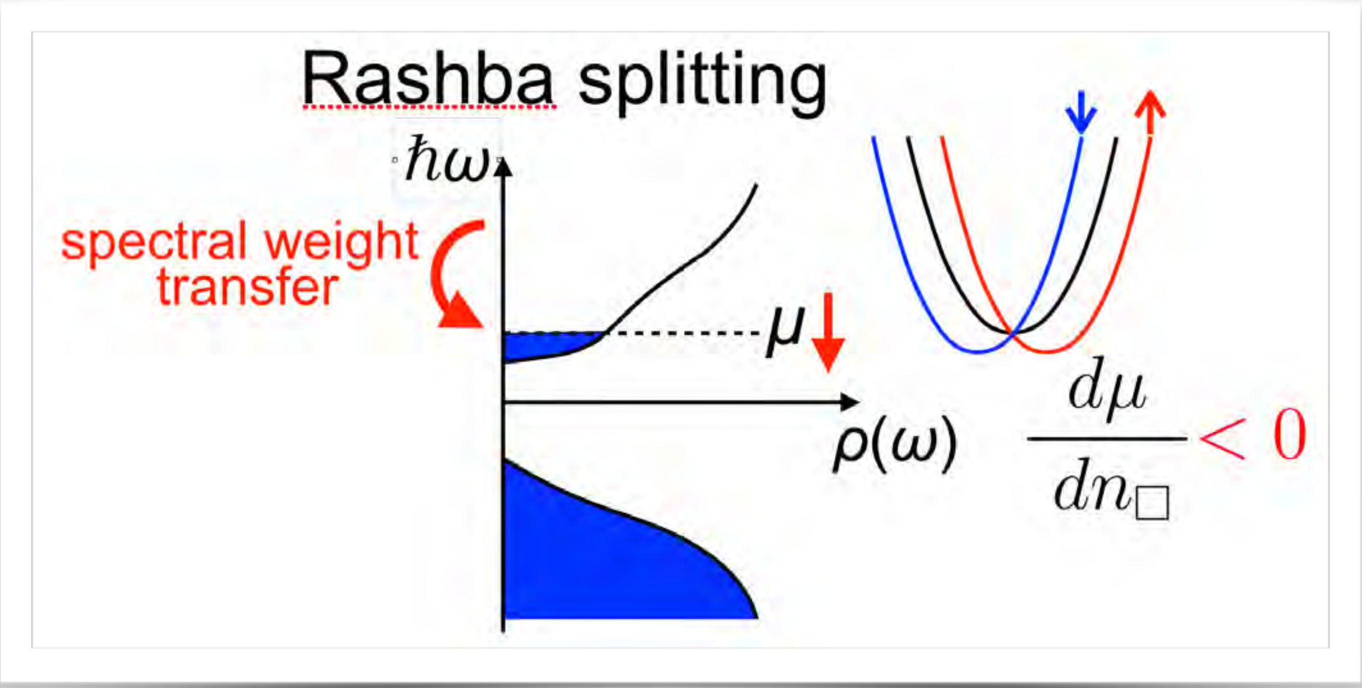
$$= \frac{1}{e^2}\frac{d\mu}{dn_{\square}}$$

$$\frac{d\mu}{dn_{\square}} = -5.1 \times 10^{-13}\,\mathrm{eV\,cm}^2$$

$$\text{for} \quad n_{\square} \sim 10^{14}\,\mathrm{cm}^{-2}$$

$$\Delta\mu = -51\,\mathrm{eV}$$





If $\left|\dfrac{1}{C_\square^{\mathrm{STO}}}\right|$ would be two-order smaller

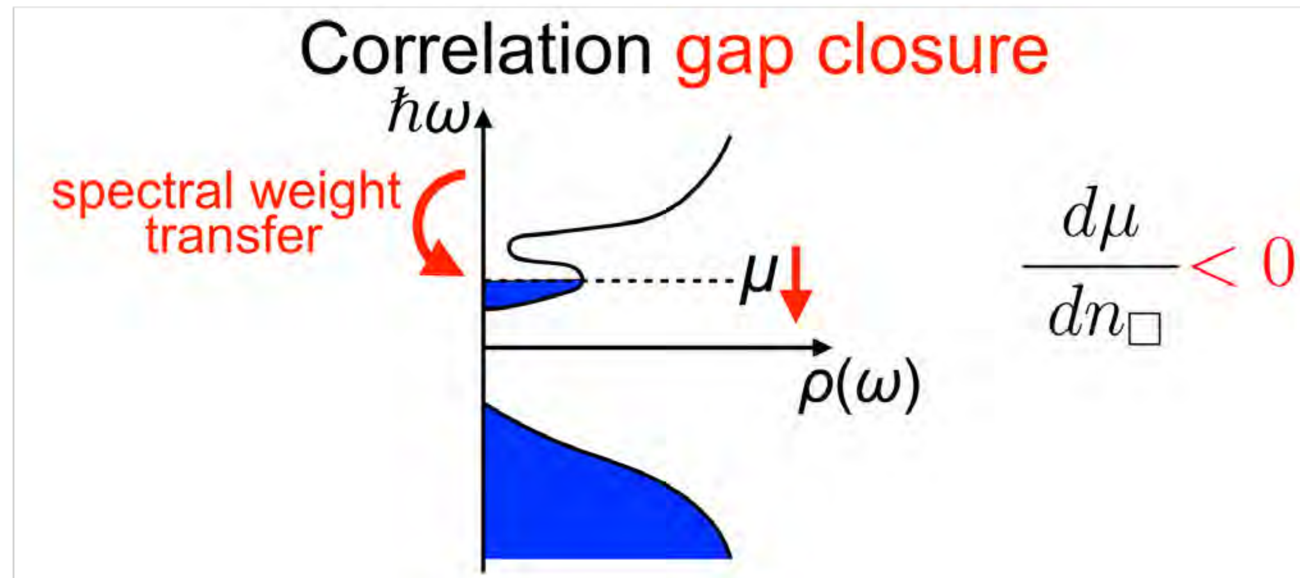
$$\frac{1}{C_\square^{\mathrm{STO}}} = -3.2 \times \overset{10^4}{\cancel{10^6}}\,\mathrm{cm}^2/\mathrm{F}$$

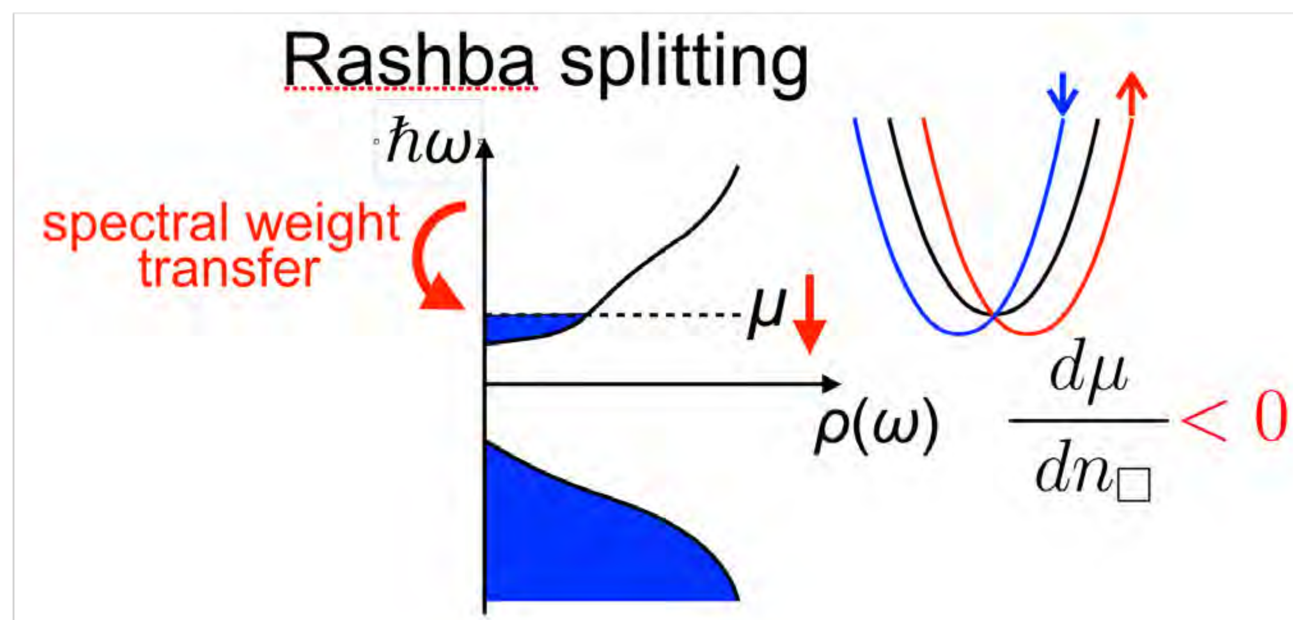
$$= \frac{1}{e^2}\frac{d\mu}{dn_\square}$$

$$\frac{d\mu}{dn_\square} = -5.1 \times \overset{10^{-15}}{\cancel{10^{-13}}}\,\mathrm{eV\,cm}^2$$

$$\text{for} \quad n_\square \sim 10^{14}\,\mathrm{cm}^{-2}$$

$$\Delta\mu = \overset{-0.5}{\cancel{-51}}\,\mathrm{eV}$$





that is, $\left|C_{\square}^{\mathrm{STO}}\right|$ would be two-order larger

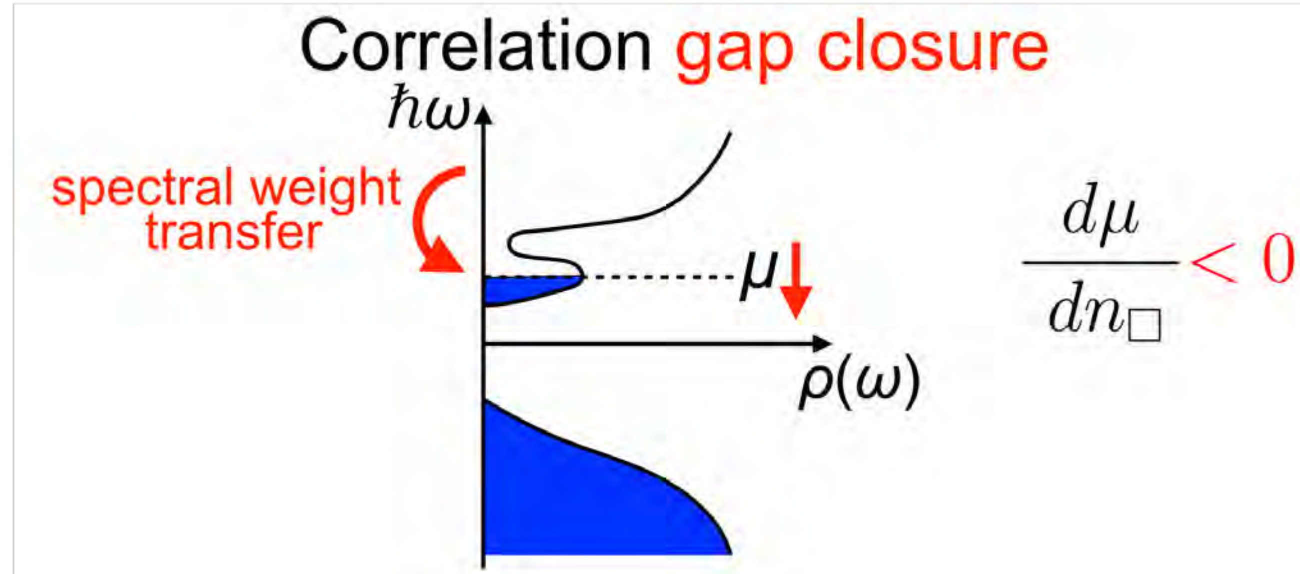
$$C_{\square}^{\mathrm{STO}} = -30\,\mu\mathrm{F/cm}^2$$

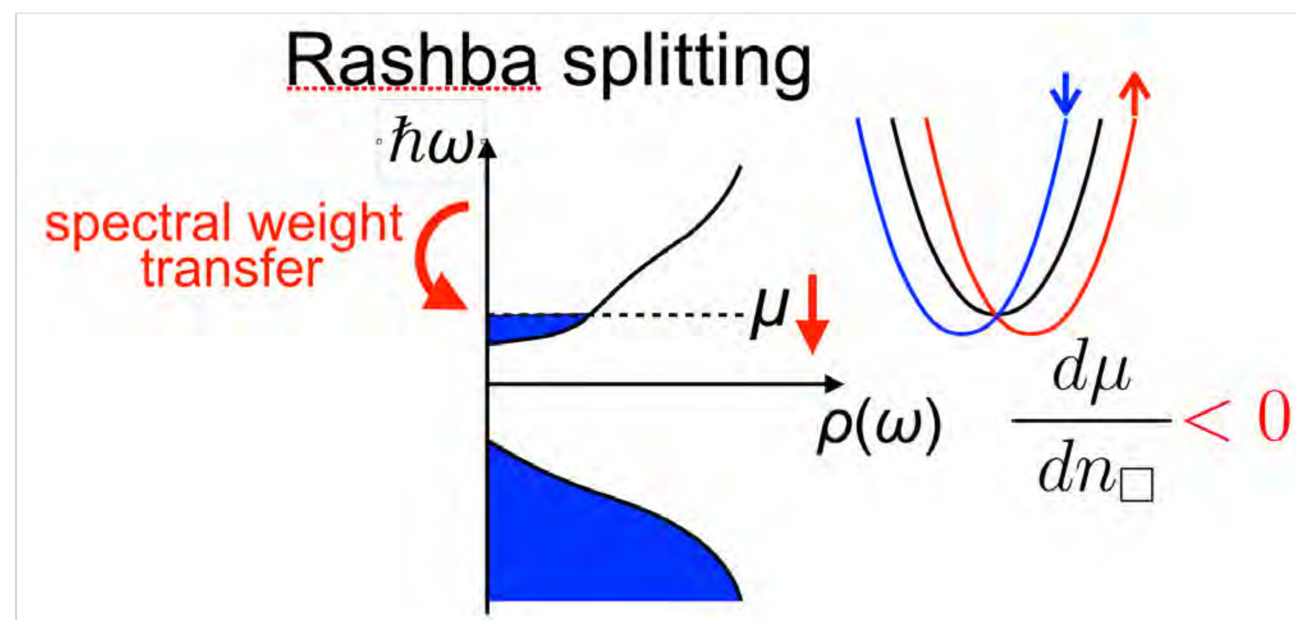
$$= \left(\frac{1}{e^2}\frac{d\mu}{dn_{\square}}\right)^{-1}$$

$$\frac{d\mu}{dn_{\square}} = -5.1\times 10^{-15}\,\mathrm{eV\,cm}^2$$

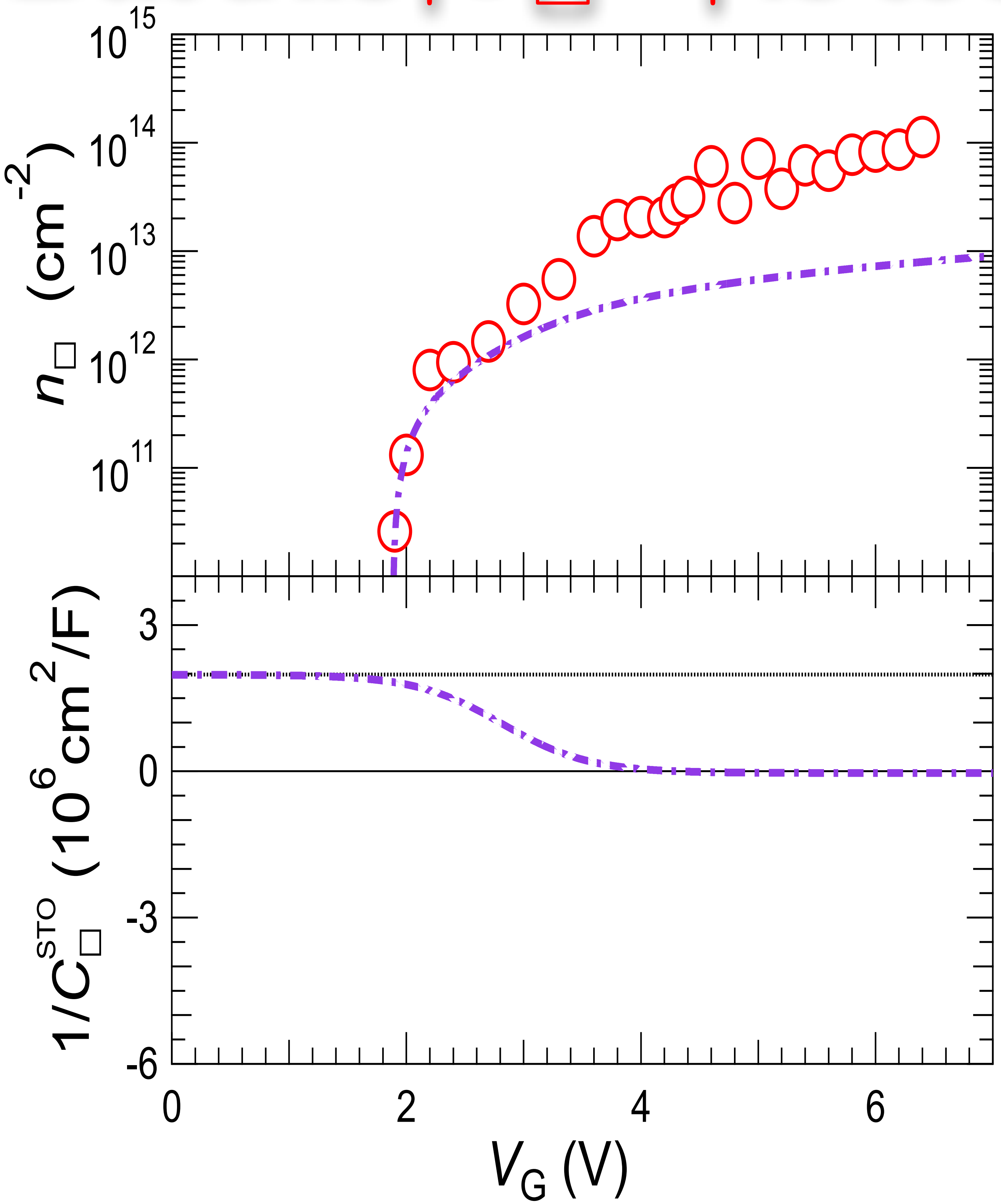
$$\text{for} \quad n_{\square} \sim 10^{14}\,\mathrm{cm}^{-2}$$

$$\Delta\mu = -0.5\,\mathrm{eV}$$





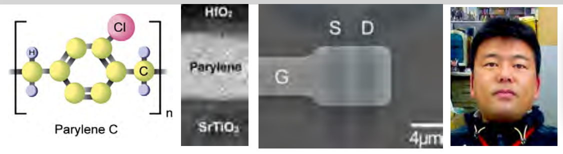
But this $|C_\square^{\rm STO}|$ is too large to enhance $n_\square$



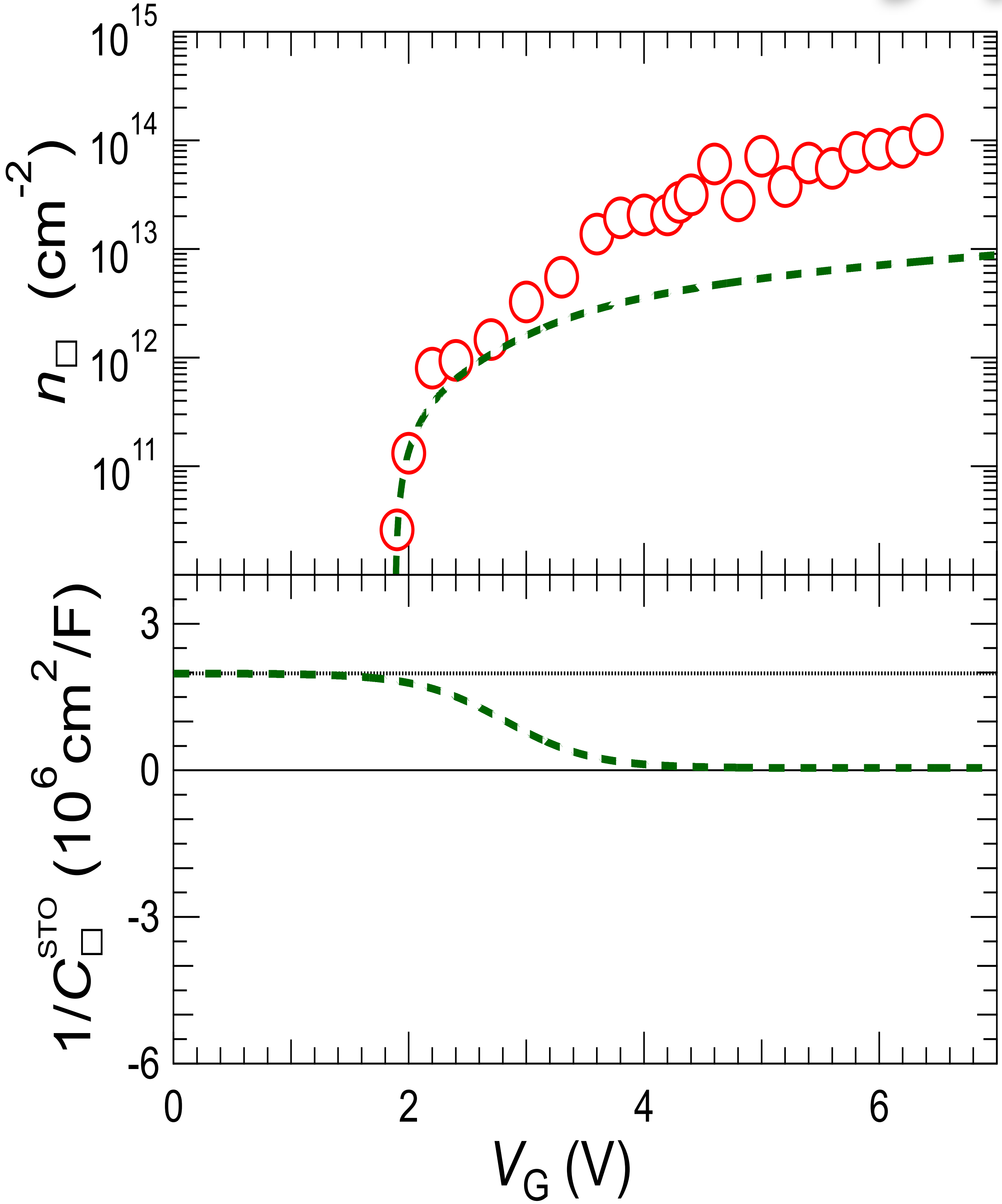
$C_\square^{\rm STO}$

$$C_\square^{\rm STO} = -30\,\mu{\rm F/cm^2}$$

$$\left|\frac{1}{C_\square^{\rm STO}}\right|$$ is too small !!



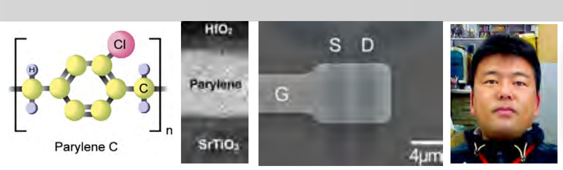
Ordinary positive $C_\square^{\mathrm{STO}}$

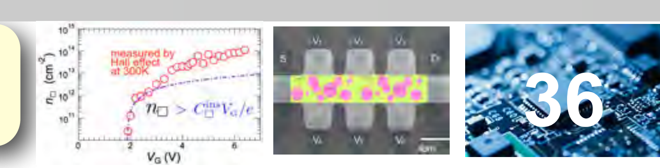


$C_\square^{\mathrm{STO}}$

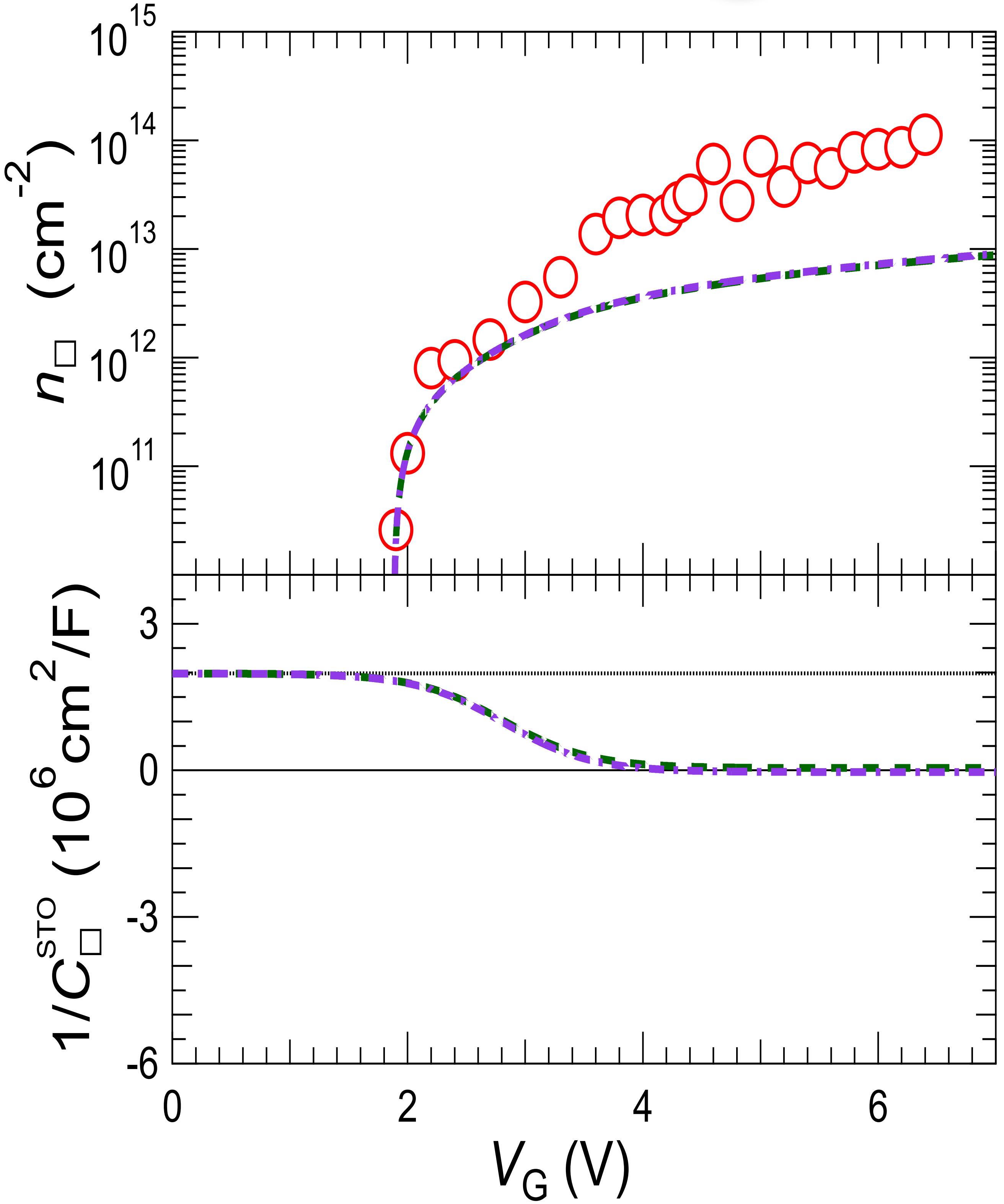
$C_\square^{\mathrm{STO}} = 20\,\mu\mathrm{F/cm^2}$

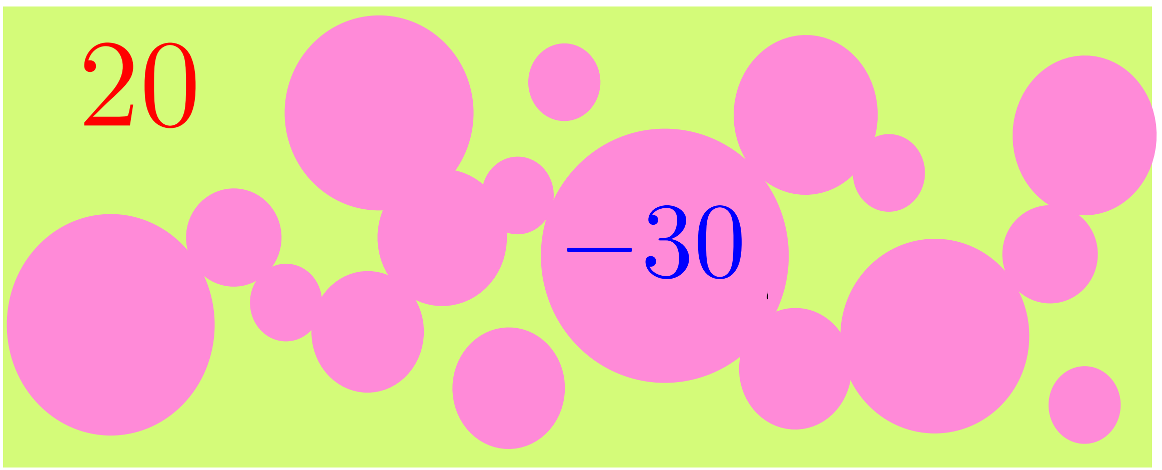
$\dfrac{1}{C_\square^{\mathrm{STO}}}$ is negligible





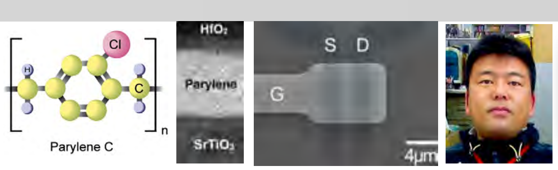
Inhomogeneous channel ?

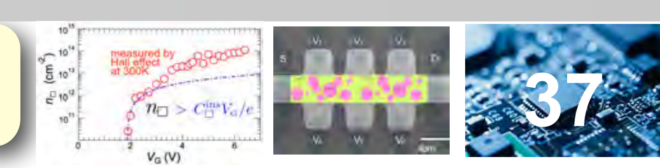




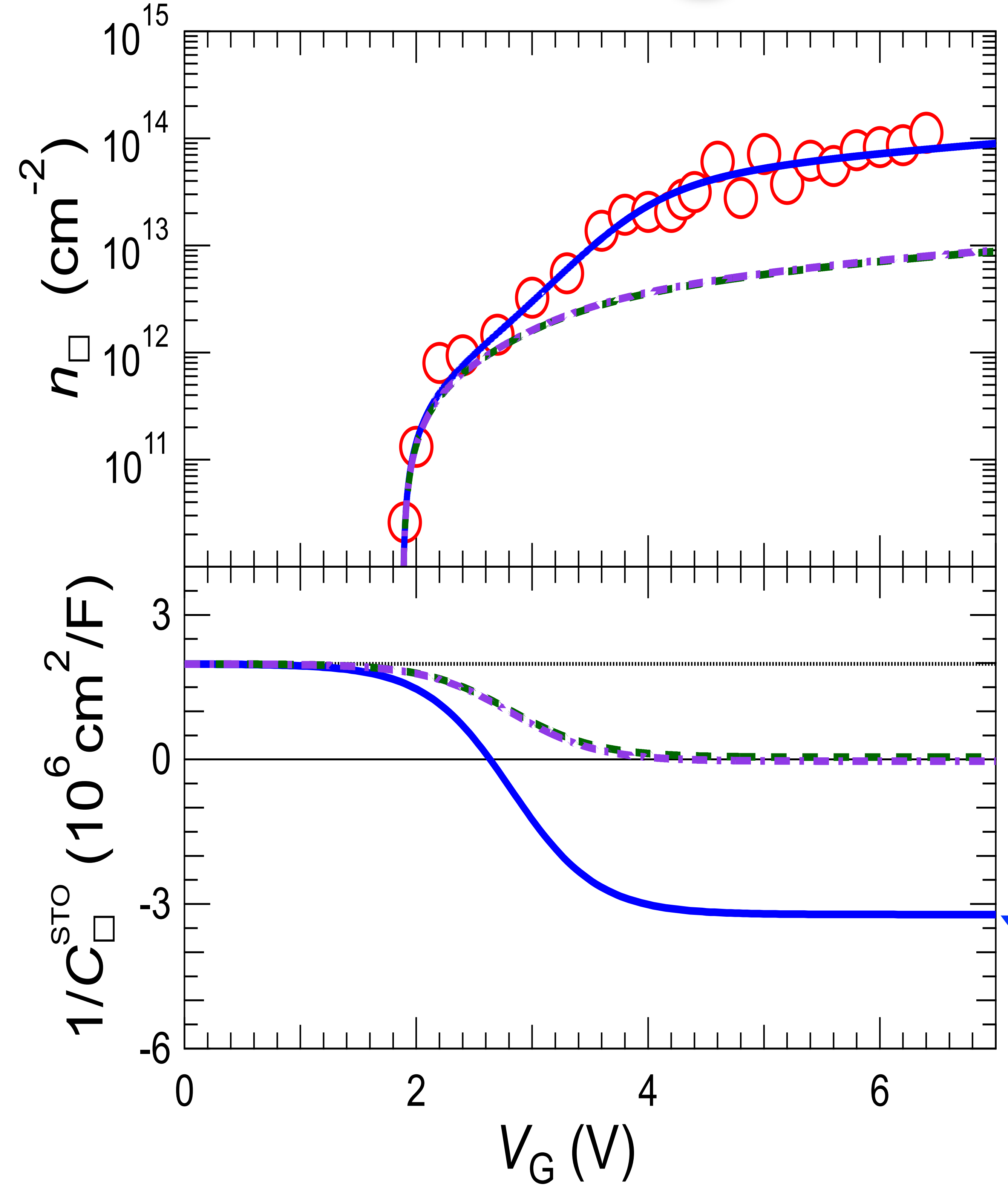
$$C_\square^{\mathrm{STO}} = 20\,\mu\mathrm{F}/\mathrm{cm}^2$$

$$C_\square^{\mathrm{STO}} = -30\,\mu\mathrm{F}/\mathrm{cm}^2$$

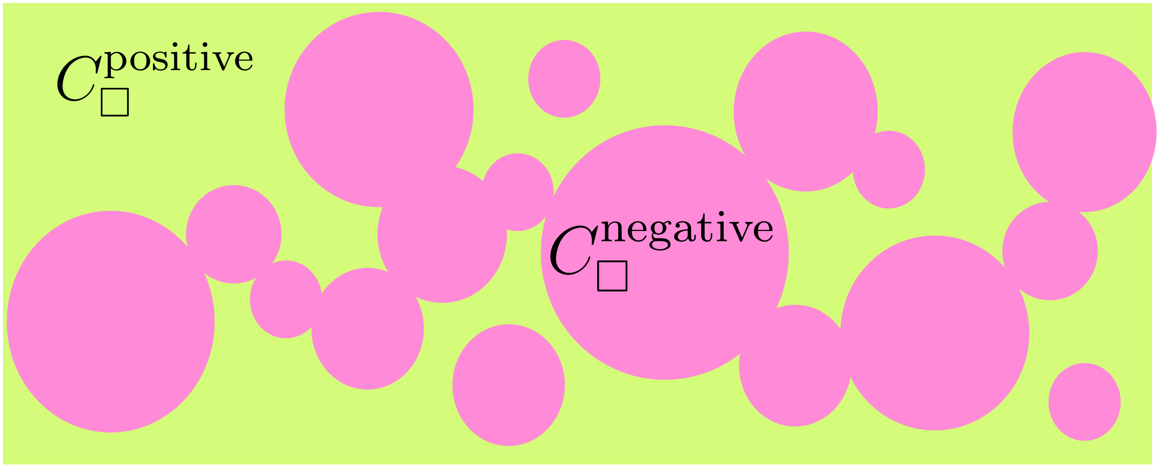




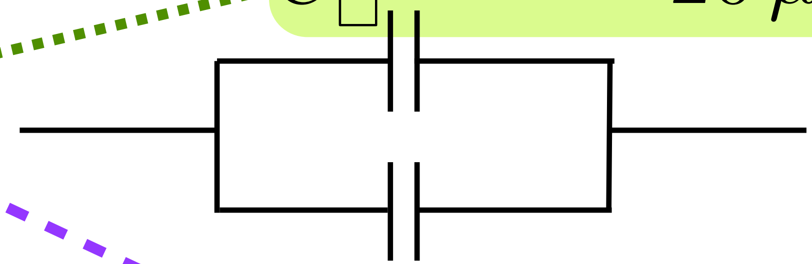
Inhomogeneity enhances $n_\square$



Large enhancement is due to inhomogeneity!



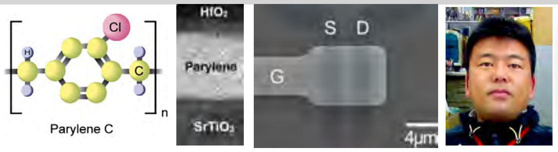
$$C_\square^{\rm positive} \simeq 20\,\mu{\rm F/cm^2}$$

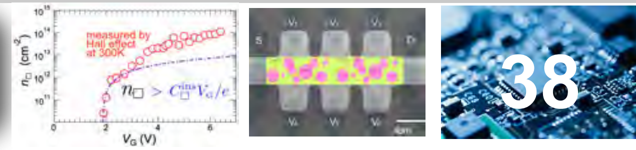


$$C_\square^{\rm negative} \simeq -30\,\mu{\rm F/cm^2}$$

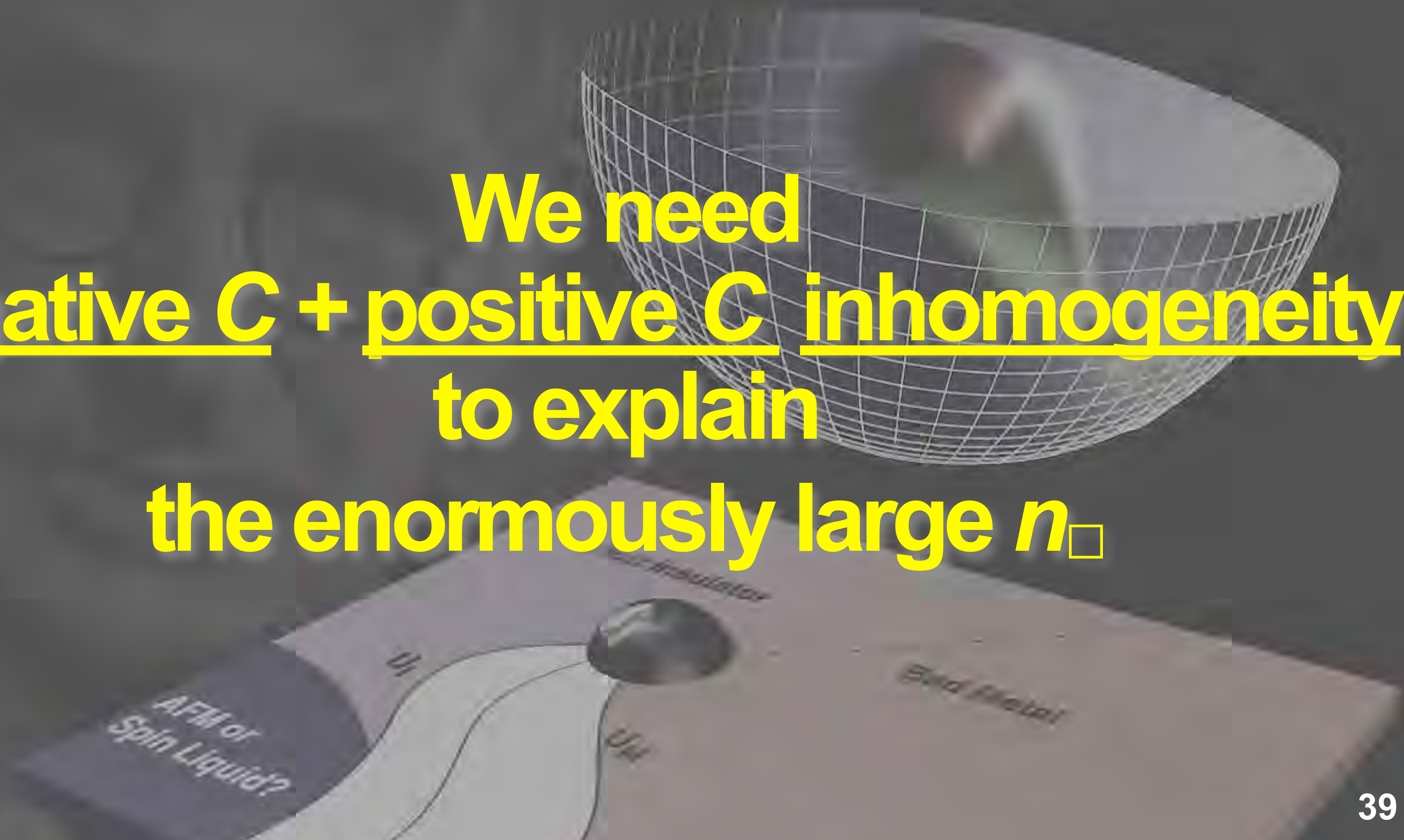
$$C_\square^{\rm STO} = (1-\xi)C_\square^{\rm positive} + \xi C_\square^{\rm negative}$$
$$= -0.31\,\mu{\rm F/cm^2}$$

for $\xi = 40\,\%$



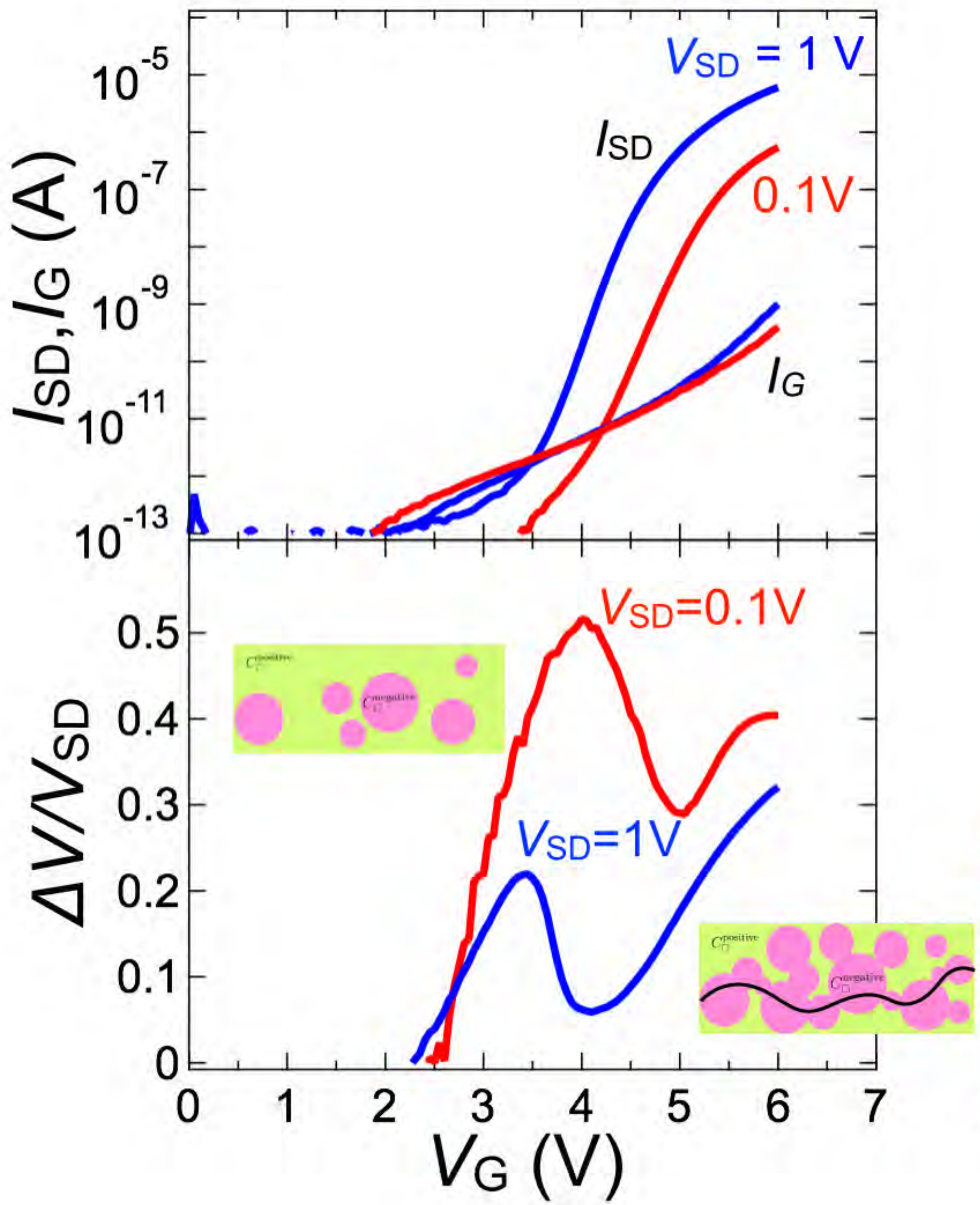


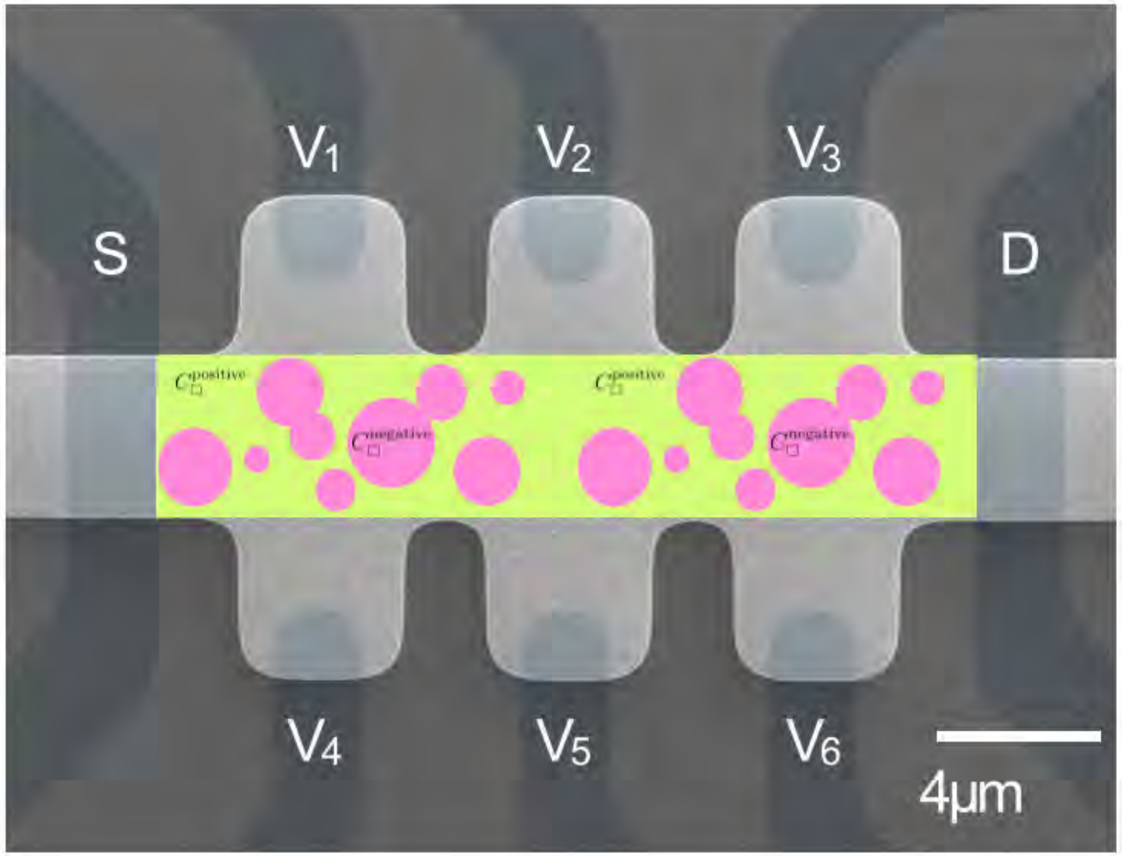
<u>Negative C</u> is <u>necessary</u>
but not enough!



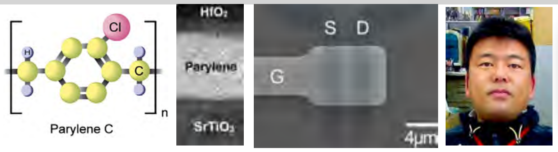
We need
<u>negative *C*</u> + <u>positive *C*</u> <u>inhomogeneity</u>
to explain
the enormously large *n*□

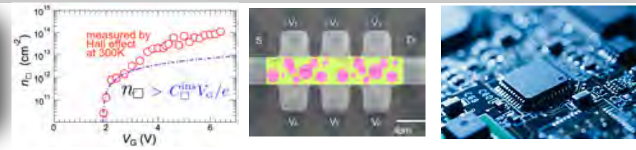
Evidence of the inhomogeneity



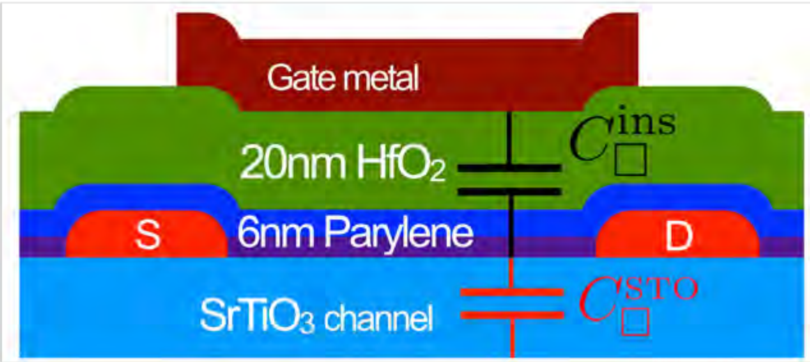


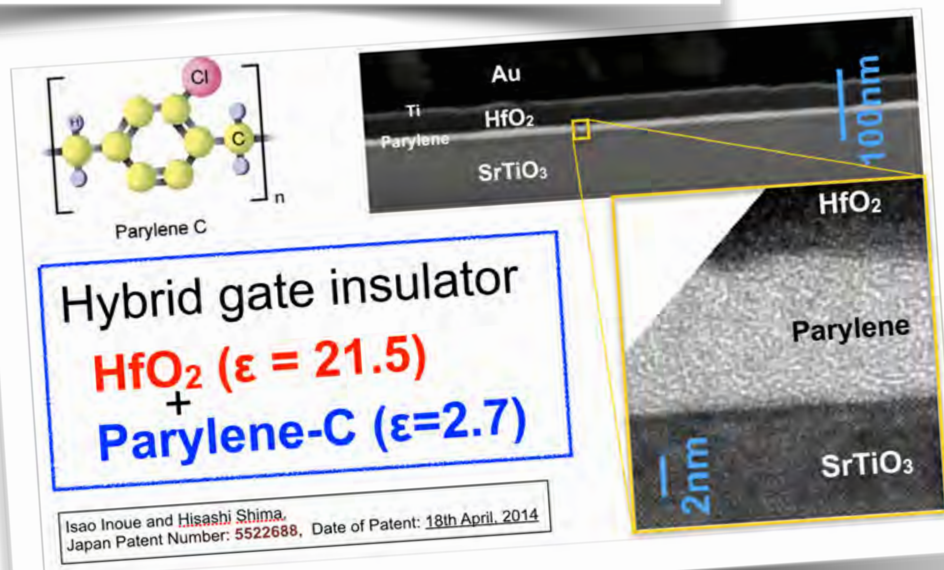
Inhomogeneous carrier distribution can be naturally ascribed to the negative C (**negative charge compressibility**)

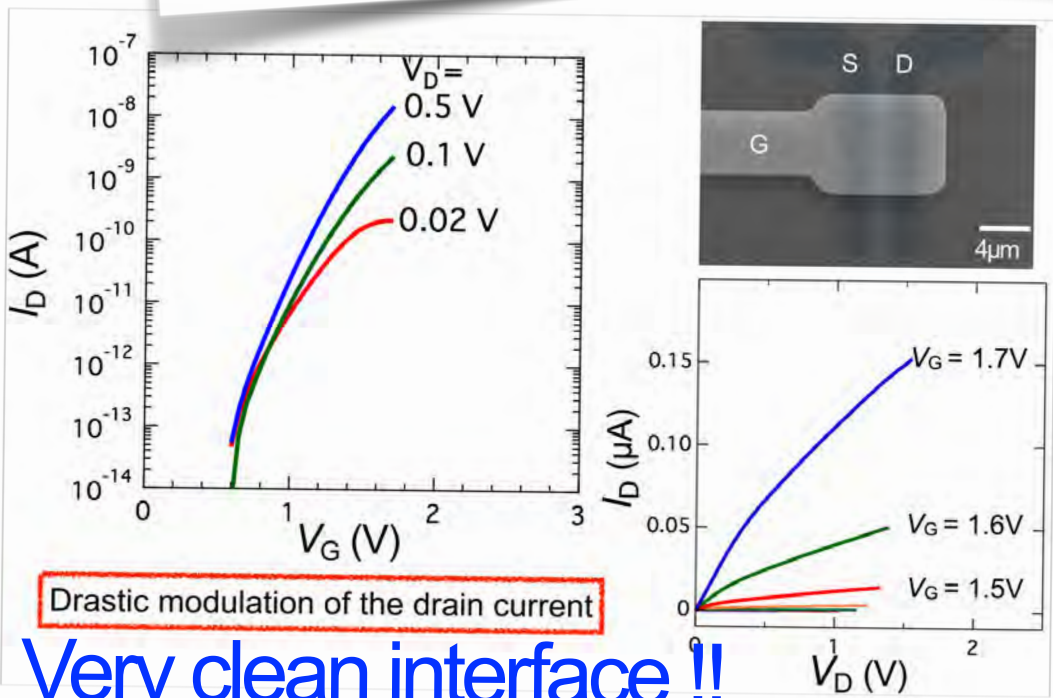




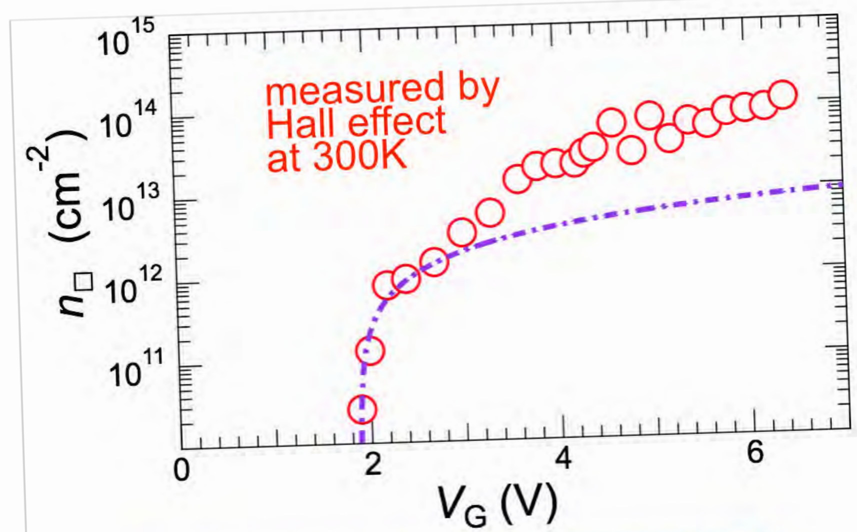
Summary







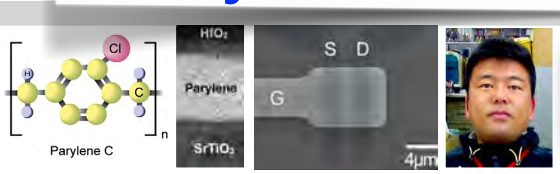
Very clean interface !!

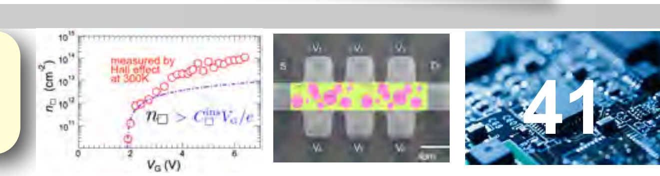


$n_\square > C_\square^{\rm ins} V_{\rm G}/e$

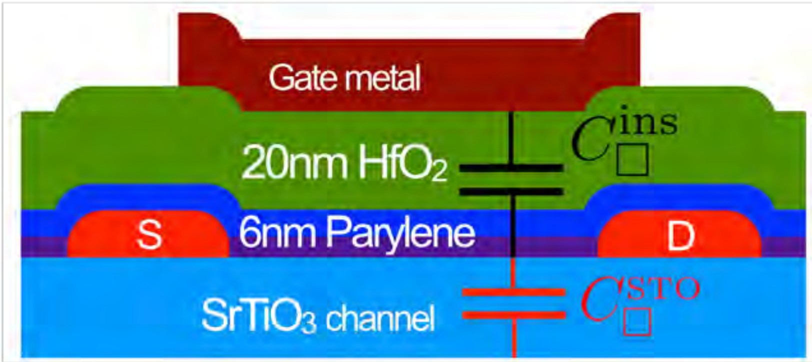
$$
\begin{aligned}
e n_\square &= C V_{\rm G} \\
&= \left(\frac{1}{C_\square^{\rm ins}} + \frac{1}{C_\square^{\rm sub}} \right)^{-1} V_{\rm G}
\end{aligned}
$$

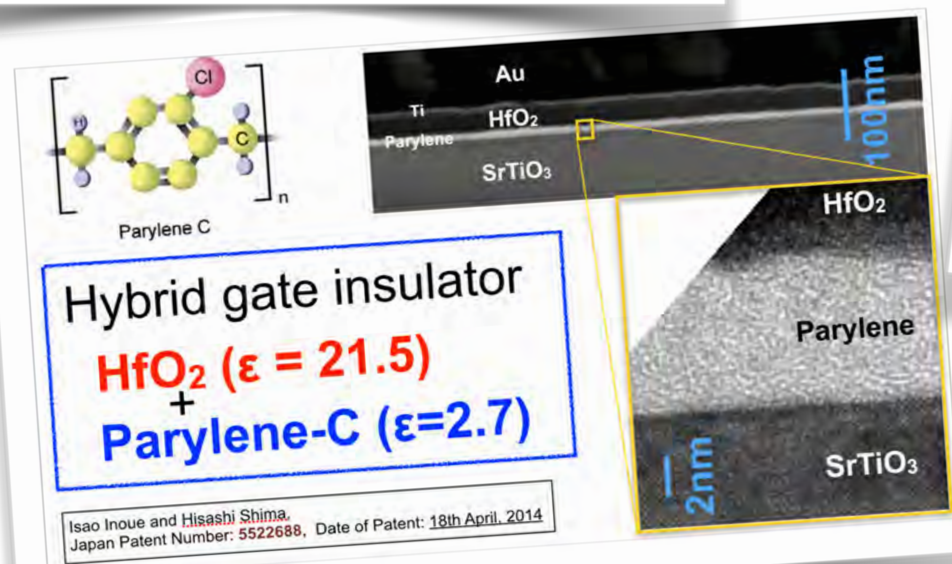
$C_\square^{\rm sub} < 0$

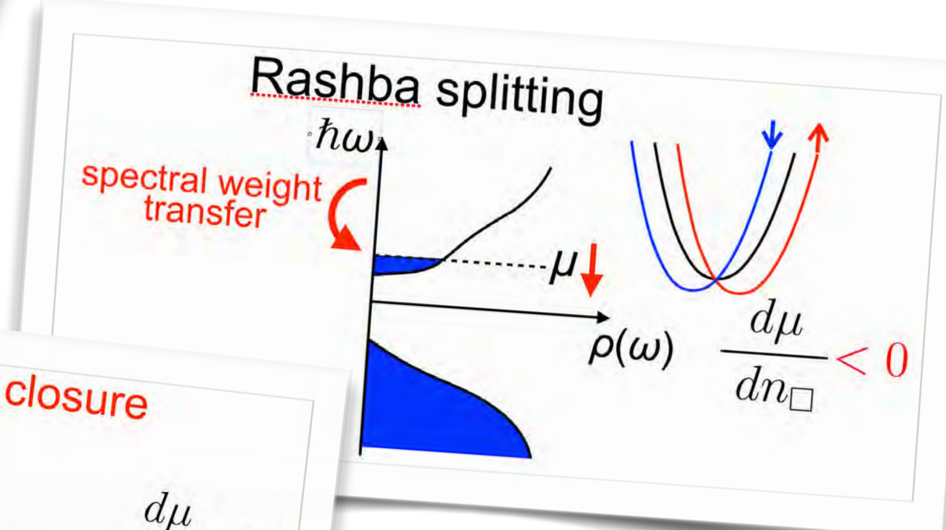


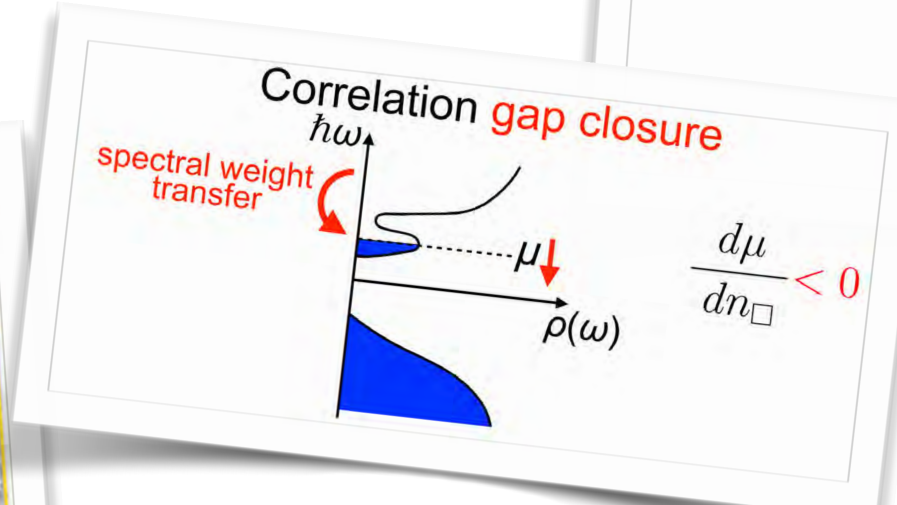


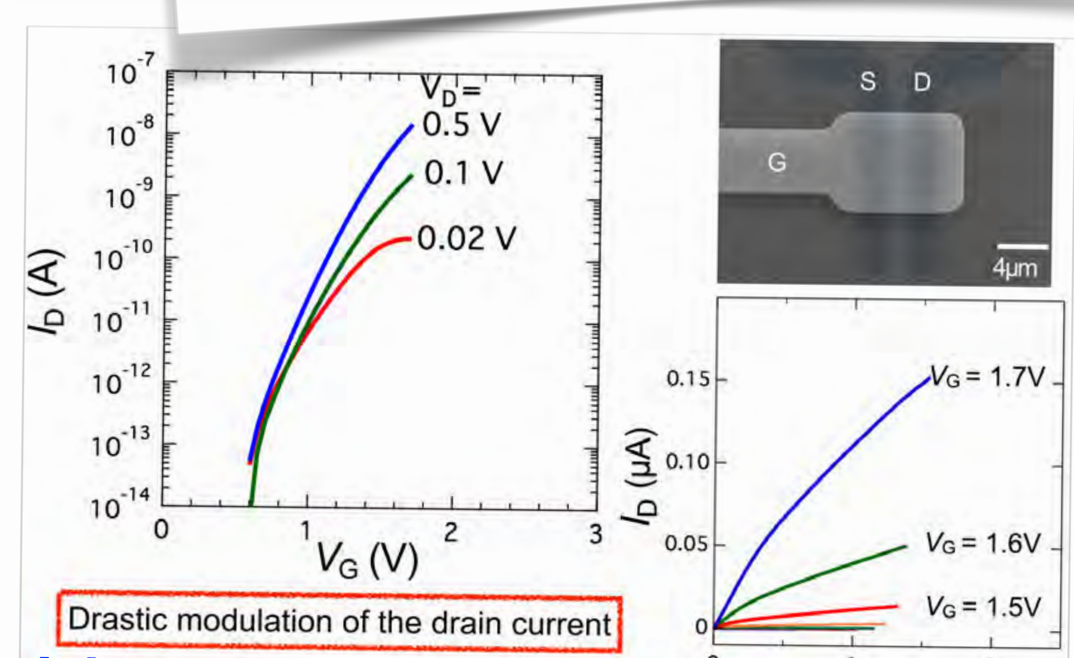
Summary











Very clean interface !!