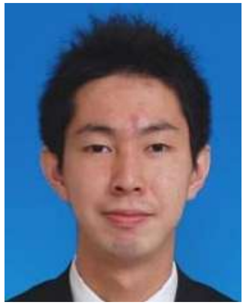
Quantum mechanical shift current

Masashi Kawasaki[1,2]

[1]Quantum Phase Electronics Center (QPEC)&Department of Applied Physics, University of Tokyo
[2]RIKEN Center for Emergent Matter Science (CEMS)


M. Nakamura
RIKEN [2]


H. Hatada
Univ Tokyo[1]


M. Sotome
RIKEN[2]


N. Ogawa
RIKEN[2]


T. Morimoto
UC Berkeley
→ Univ Tokyo[1]


N. Nagaosa
RIKEN[2,1]


Y. Tokura
RIKEN[2,1]

S. Horiuchi[3], S. Inagaki[1], S. Ishibashi[3], T. Kurumaji[2],
D. Shindo[2], T. Tanigaki[4], H. S. Park[2], F. Kagawa[1]

[3]National Institute of Advanced Industrial Science and Technology
[4]Hitachi High Technologies

Outline

Bulk photovoltaic effect → Shift current

History, Intuitive view & theory

Quantum mechanical motion of carriers

$LaFeO_3/SrTiO_3$: Interface-engineered ferroelectric

Current opposite to *E* field

M. Nakamura *et al*. Phys. Rev. Lett. **116** 156801 (2016)

TTF-CA: Organic ferroelectric

Polarization by not ions but electrons is the issue

M. Nakamura *et al*. Nature Commun. **8**, 281 (2017)

SbSI: Inorganic ferroelectric (steady state)

Electrode device physics uncover majority carrier action

M. Nakamura *et al*. Appl. Phys. Lett. **113**, 232901 (2018)

SbSI: Inorganic ferroelectric (dynamics)

Quantitative agreement with theory

M. Sotome, N. Ogawa *et al*. PNAS 116, 1929 (2019)

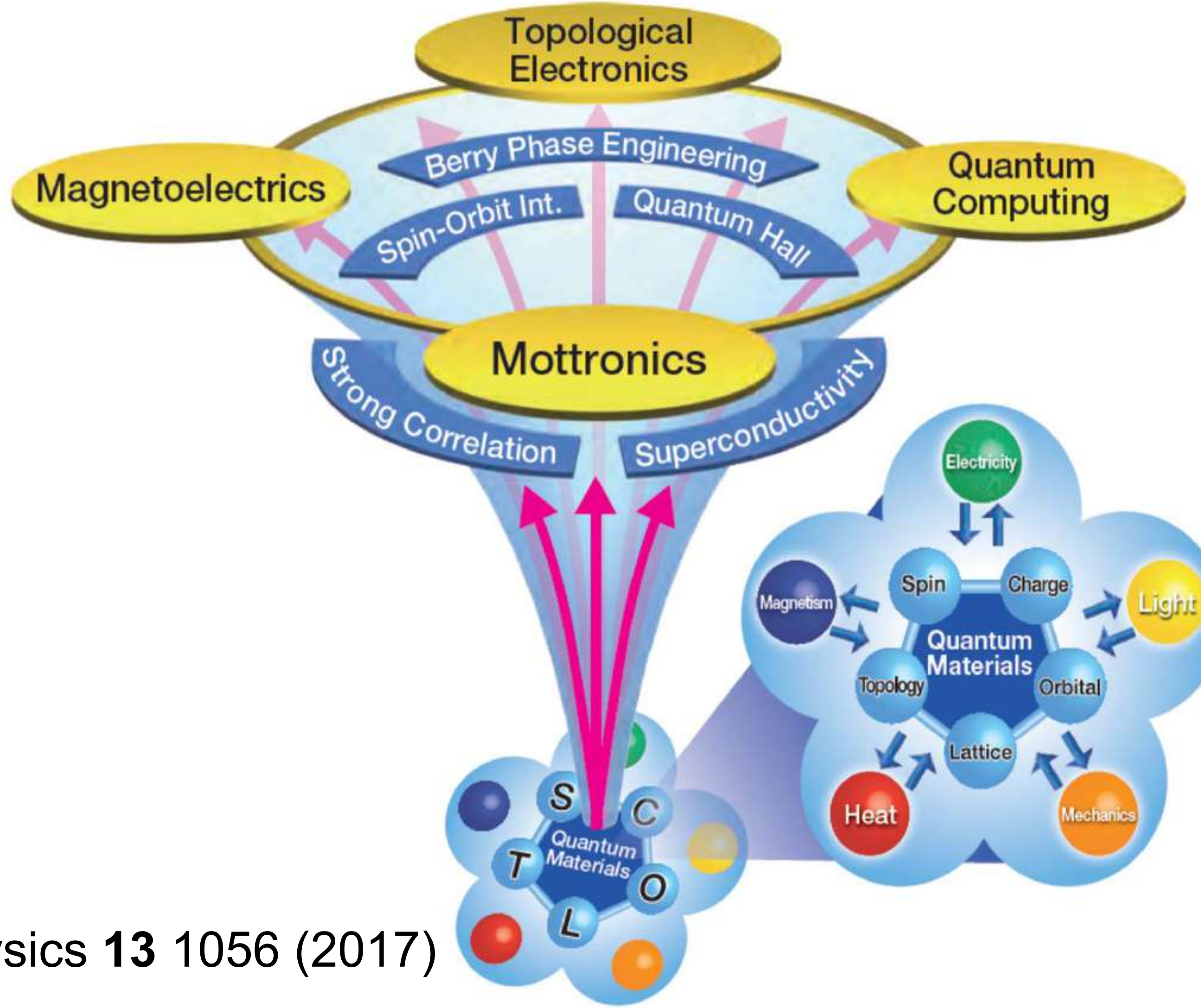
nature physics

REVIEW ARTICLES

PUBLISHED ONLINE: 25 SEPTEMBER 2017 | DOI: 10.1038/NPHYS4274

Emergent functions of quantum materials

Yoshinori Tokura[1,2]*, Masashi Kawasaki[1,2] and Naoto Nagaosa[1,2]

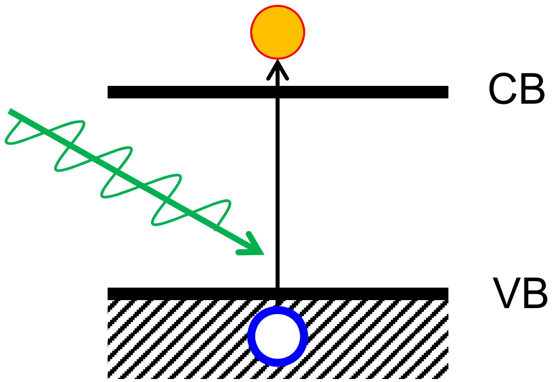


Nature Physics **13** 1056 (2017)

Photovoltaic effect

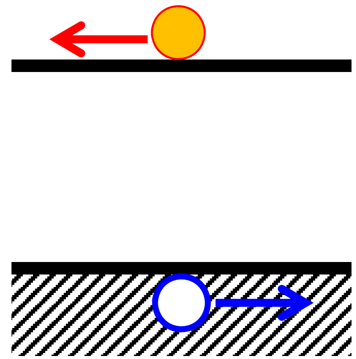
Photocurrent generation process

1. Photo-generation of e-h pairs



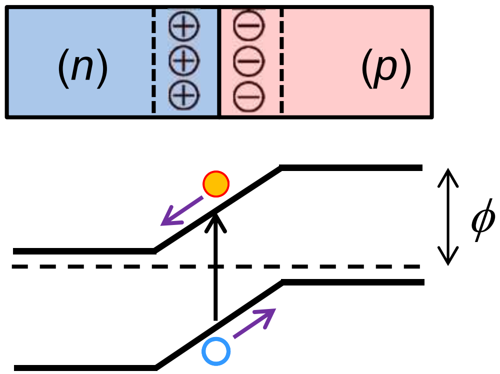
Law of mass action
$np \sim 10^{20}$ cm^{3} (in case Si)
If $n \sim 10^{17}$, $p \sim 10^{3}$
under equilibrium
$\Delta n \sim \Delta p \sim 10^{15}$ cm^{-3}
under photoexcitation

2. Separation of e-h pairs



Interface photovoltaic effect

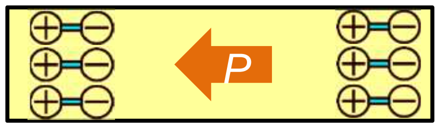
p-n junction

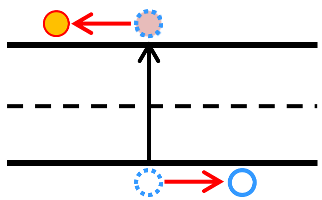


Drift + Diffusion current
Minority carriers have to survive

Bulk photovoltaic effect

non-centrosymm. crystal





Shift current

Photovoltaic effect: history

1839: E. Becquerel (photovoltaic effect in electrolytic cell)

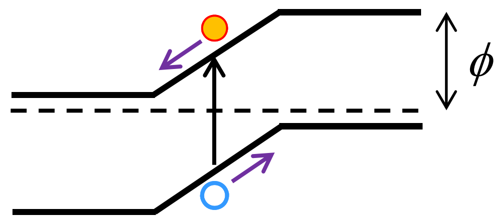
1876: W.G. Adams & R. E. Day (solid selenium)

1923: Albert Einstein (Nobel Prize for photoelectric effect)

1954: Bell lab. (silicon solar cell)

1962: Sharp (radio with solar cell)

p-n / Schottky junction



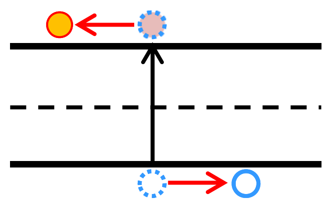
1960s: Anomalous bulk photovoltaic effect in SbSI, $BaTiO_3$

1979-: Theory based on shift current

2012: 1st-principles calc. on $BaTiO_3$ (as shift current), Rappe et al

2016: RIKEN, new theoretical formalism (Floquet), Nagaosa et al.

Ferroelectrics



Classical picture: uncompensated electric field

Electrostatic potential in Ferroelectrics

No surface screening

Spontaneous Polarization

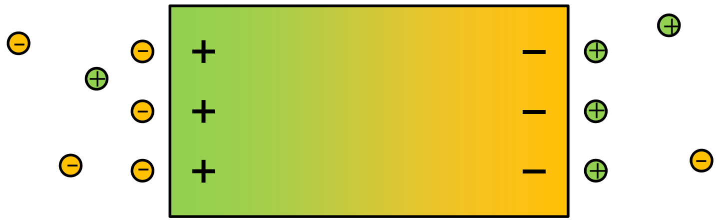
P = 30 μC/cm^2

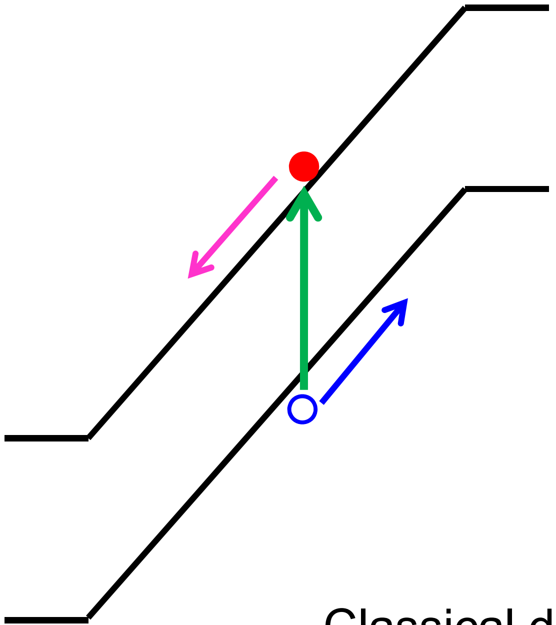
Bound Charge Density

$n = P/e$ = 2 X10^{14} cm^{-2}

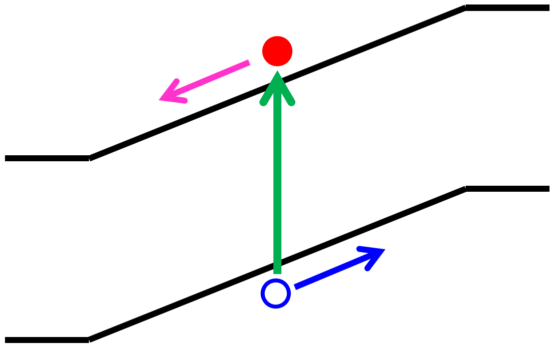
Electric field: 50 MV/cm

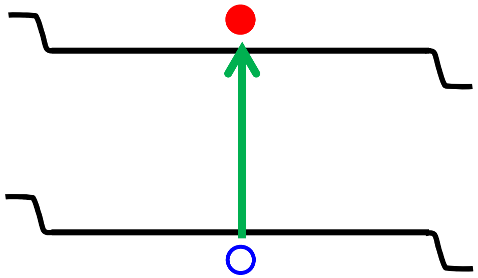
Perfect screening





Reality



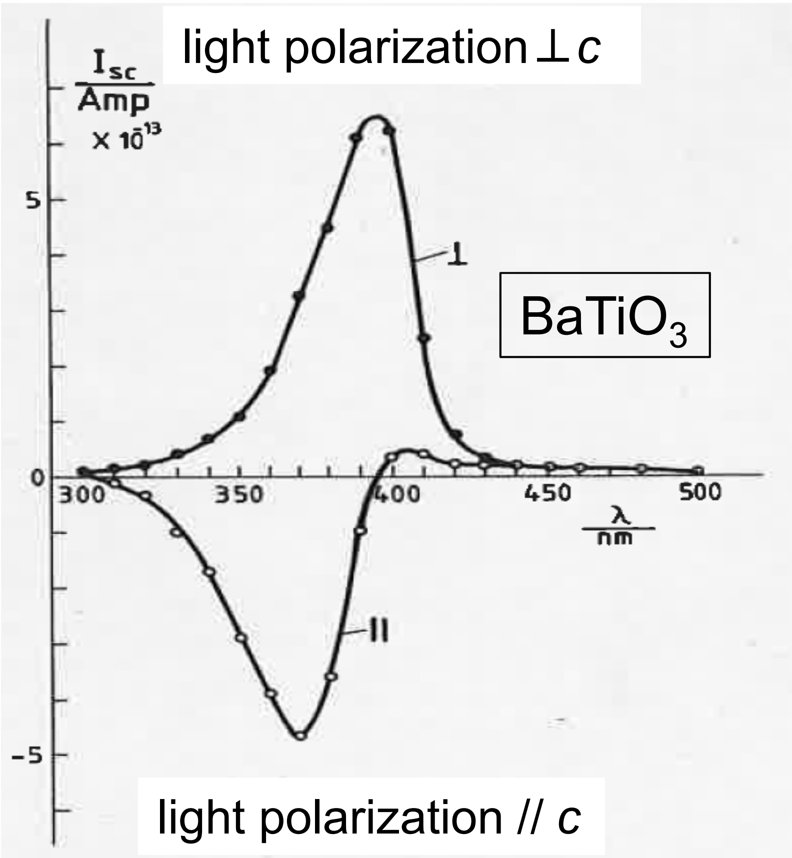


Classical drift current

No current

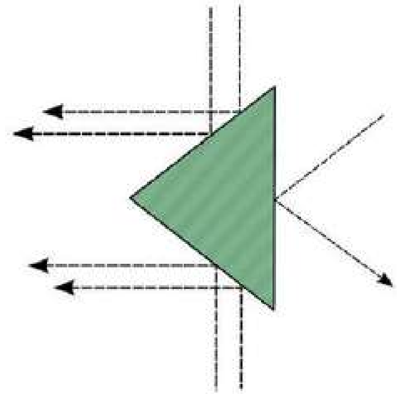
Research on bulk photovoltaic effect

Light polarization dependence
Open circuit voltage > Bandgap

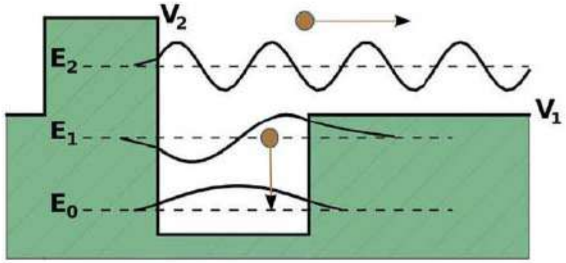


W. T. H. Koch *et al.*, Ferroelectrics **13**, 305 (1976)

Asymmetric carrier scattering



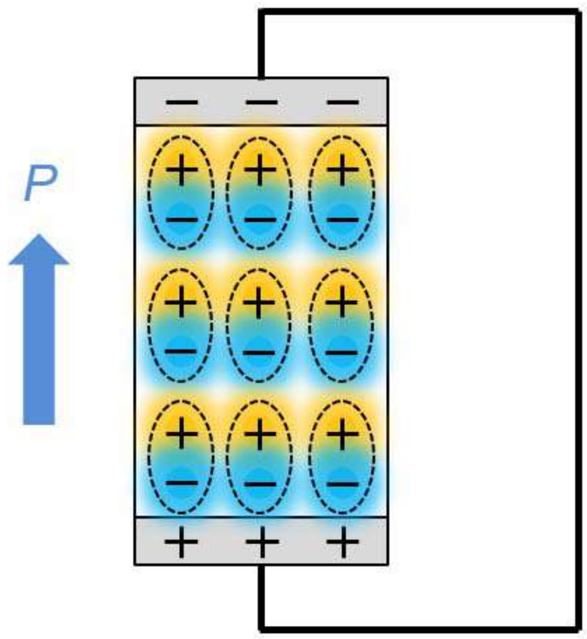
Asymmetric carrier generation



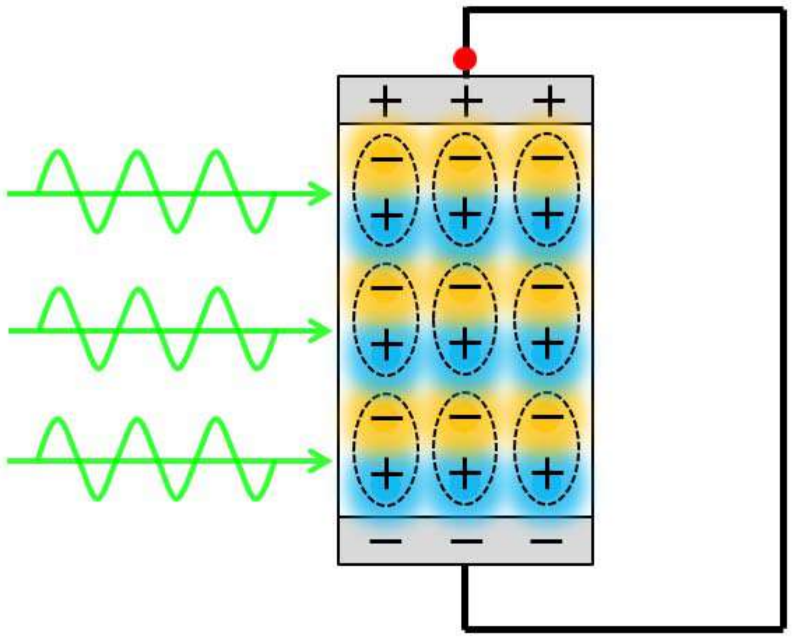
K. T. Butler *et al.*, Energy Env. Sci. **8**, 838 (2015)

Displacement current vs. Shift current

Displacement current
upon polarization reversal



Optical pumping of
shift current



First exact formulation of bulk photovoltaic effect

Formulation of current generation from non-linear optical process using perturbation theory

R. von Baltz and W. Kraut Phys. Rev. B **23**,5590 (1981)

Shift current

- ✓ Second-order nonlinear optical effect

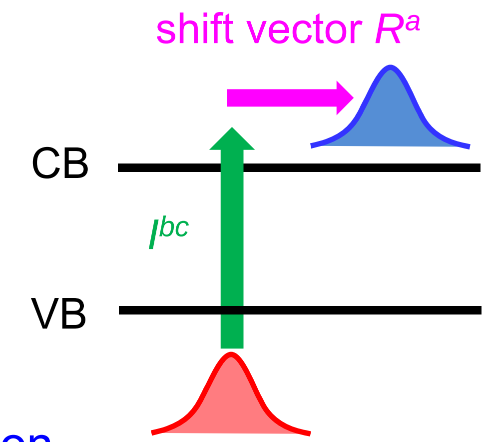
$$J^a_{\text{shift}} = \sigma^{abc} E^b(\omega) E^c(-\omega)$$

- ✓ Current induced by the change of wave function upon photoexcitation

$$\sigma^{abc} = e \sum_{cv} \int_{\text{BZ}} d\boldsymbol{k}\, \underbrace{I^{bc}(c, v, \boldsymbol{k}, \omega)}_{\text{transition intensity}}\, \underbrace{R^a(c, v, \boldsymbol{k})}_{\text{shift vector}}$$

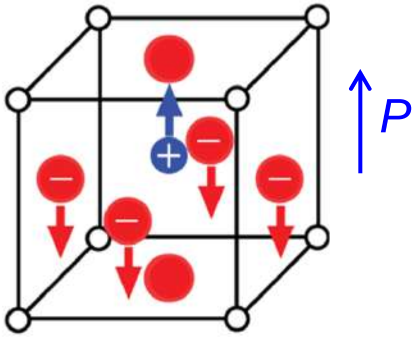
$$R^a = -[A^a_{cc} - A^a_{vv}] - \frac{\partial \phi_{cv}}{\partial k^a}$$

$$A^a_{nn} = i \langle u_n | \frac{\partial}{\partial k^a} | u_n \rangle$$ Berry connection



Origin of electric polarization

1. Ionic displacement (P_{ion})



$$P_{\text{ion}} = \frac{e}{V_{\text{cell}}} \sum_i Z_i^{\text{ion}} \mathbf{r}_i$$

cf. Born effective charge

Ti : +7 O : −5

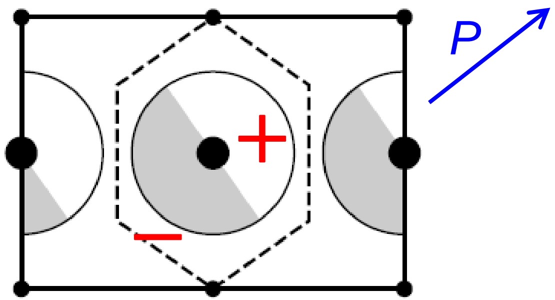
Ph. Ghosez, PRB (1995)

$BaTiO_3$

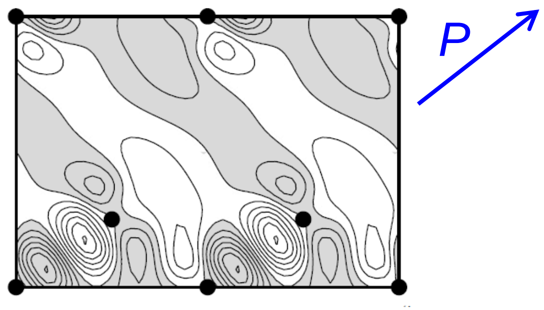
Exp. 26 μC/cm^2

P_{ion} 17 μC/cm^2

2. Asymmetry in the distribution of electrons (P_{ele})



simple case



real materials

Polarization cannot be unambiguously determined in real space

"Physics of Ferroelectrics: A Modern Perspective" ed. by C. H. Ahn, K. M. Rabe, and J. M. Triscone

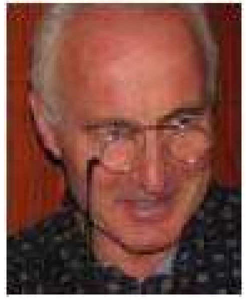
Modern theory of polarization

Description of electronic polarization using momentum-space representation

R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993)

R. Resta, Rev. Mod. Phys. **66**, 899 (1994)


D. Vanderbilt


R. Resta

Wannier function $$w_n(\mathbf{r}-\mathbf{R}) = \frac{V}{(2\pi)^3}\int_{BZ} d^3\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{R}}\underline{\psi_{\mathbf{k}n}(\mathbf{r})}$$

Bloch function

Position operator in momentum space $$\mathbf{r} = -i\frac{\partial}{\partial \mathbf{k}}$$

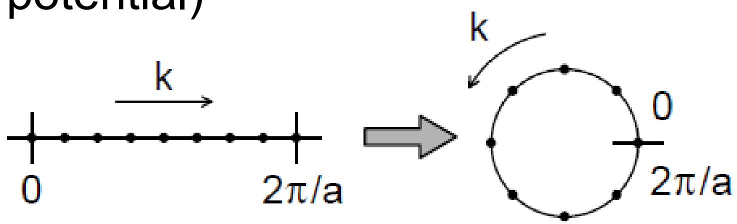
$$P_{\mathrm{ele}} = e\langle w_n|\mathbf{r}|w_n\rangle = \frac{e}{(2\pi)^3}\sum_{n=\mathrm{occupied}}\int_{BZ} d^3\mathbf{k}\, A_n(\mathbf{k})$$

$$A_n(\mathbf{k}) = -i\langle u_n|\frac{\partial}{\partial \mathbf{k}}|u_n\rangle$$ Berry connection

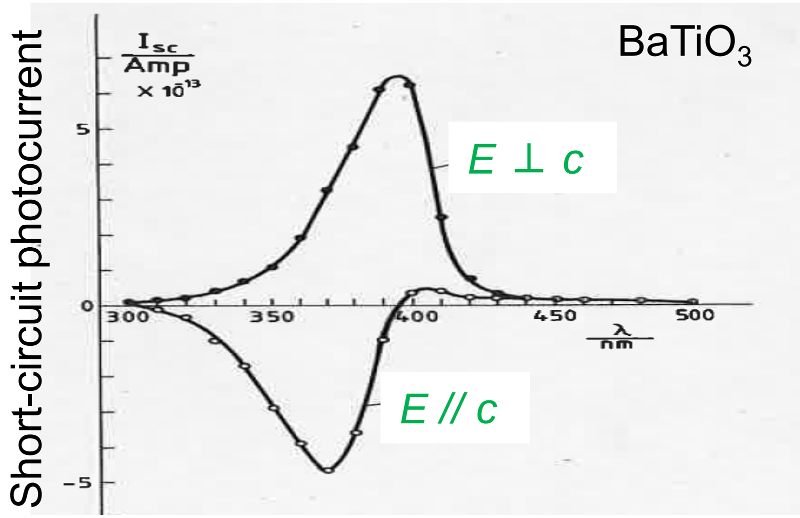
(Vector potential)

$$\phi = \oint dk A(k) = 2\pi m$$

Berry phase

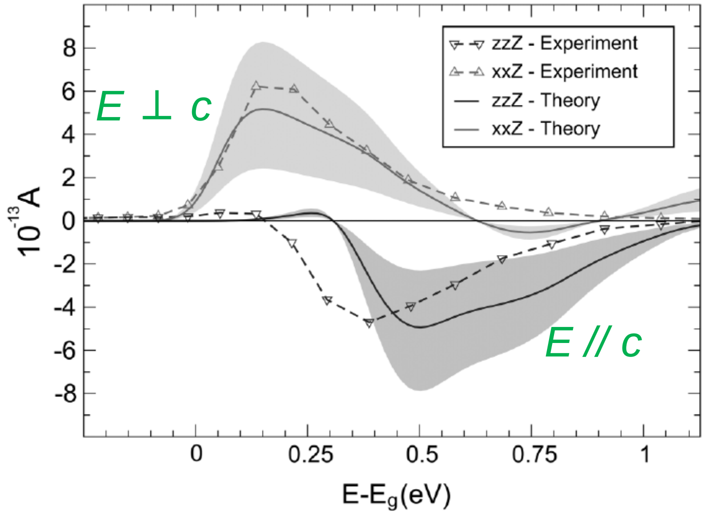


Quantum mechanical picture: shift current



W. T. H. Koch *et al*., Ferroelectrics **13**,305 (1976)

First-principles calculation



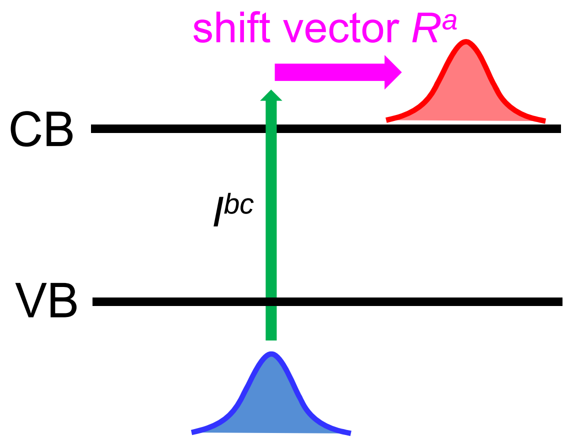
S. M. Young, M. Rappe, Phys.Rev.Lett.**109**,116601 (2012)

$$J^a_{\text{shift}} = \sigma^{abc} E^b(\omega) E^c(-\omega)$$

$$\sigma^{abc} = e \sum_{cv} \int_{\text{BZ}} d\boldsymbol{k} I^{bc}(c, v, \boldsymbol{k}, \omega) R^a(c, v, \boldsymbol{k})$$

$$R^a = -[A^a_{cc} - A^a_{vv}] - \frac{\partial \phi_{cv}}{\partial k^a}$$

$$A^a_{nm} = i \langle u_n | \frac{\partial}{\partial k^a} | u_m \rangle$$ (Berry connection)



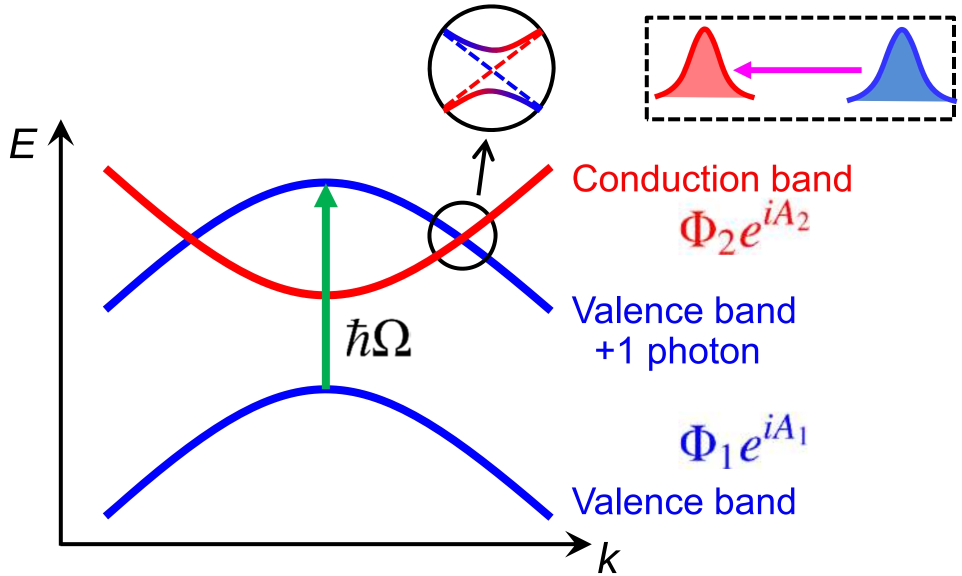
R. von Baltz and W. Kraut, Phys. Rev. B **23**, 5590 (1981)

Clarification of topological nature of shift current

T. Morimoto and N. Nagaosa Sci. Adv. **2**, e1501524 (2016)

Floquet formalism of Shift current

$J_{\mathrm{shift}} \propto A_2 - A_1$



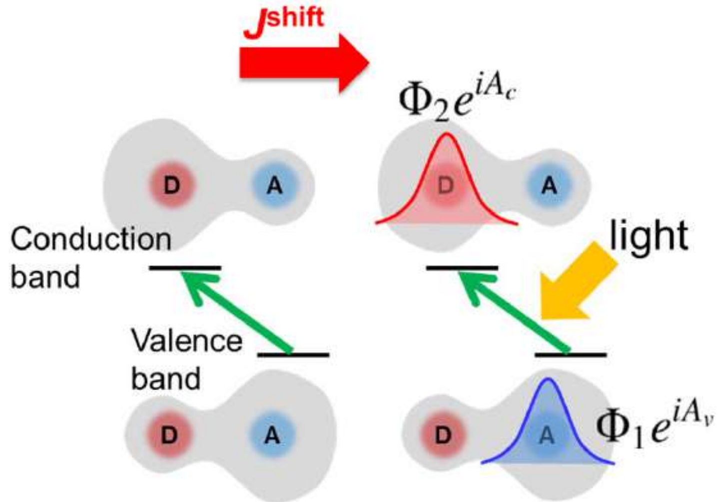
$$J_\lambda^{\mathrm{shift}} = \sigma_{\lambda\mu\nu} E_\mu(\omega) E_\nu(-\omega)$$

$$\sigma_{\lambda\mu\nu} \propto A_\lambda^c - A_\lambda^v$$

$$A_\lambda^n = -i < u_n | \frac{\partial}{\partial k_\lambda} | u_n >$$

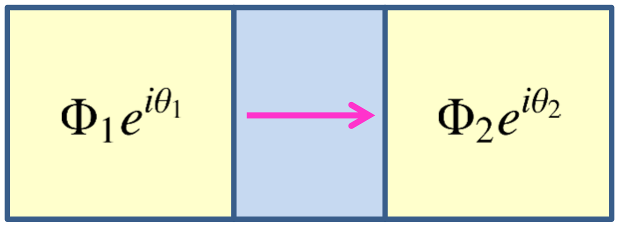
Berry connection

Topological current:
Robust against scattering



cf. Josephson current

S. C. Insulator S. C.



$J_{\mathrm{Josephson}} \propto \sin(\theta_2 - \theta_1)$

Bulk photovoltaic effect in oxide FE

LETTER

Nature **503**, 509 (2013)

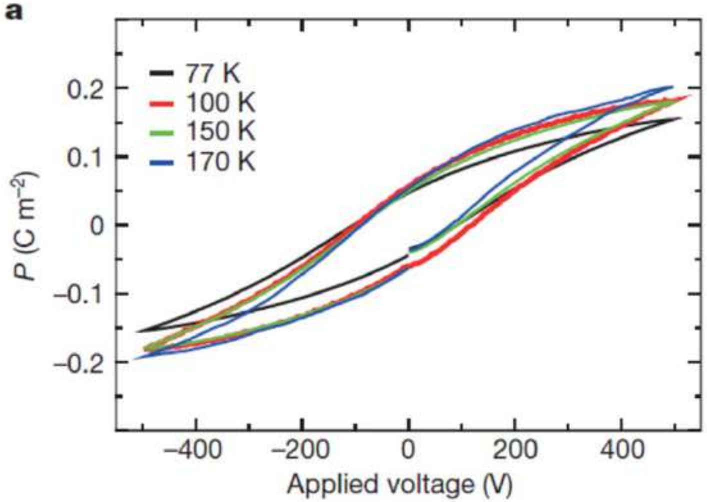
doi:10.1038/nature12622

Perovskite oxides for visible-light-absorbing ferroelectric and photovoltaic materials

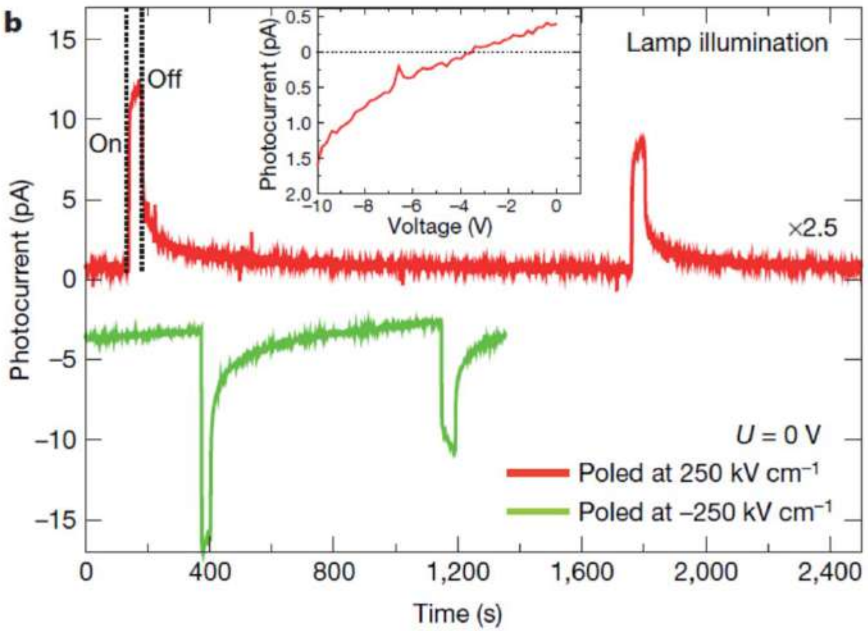
Ilya Grinberg[1], D. Vincent West[2], Maria Torres[3], Gaoyang Gou[1], David M. Stein[2], Liyan Wu[2], Guannan Chen[3], Eric M. Gallo[3], Andrew R. Akbashev[3], Peter K. Davies[2], Jonathan E. Spanier[3] & Andrew M. Rappe[1]

$$[KNbO_3]_{1-x}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_x \text{ (KBNNO)}$$

a

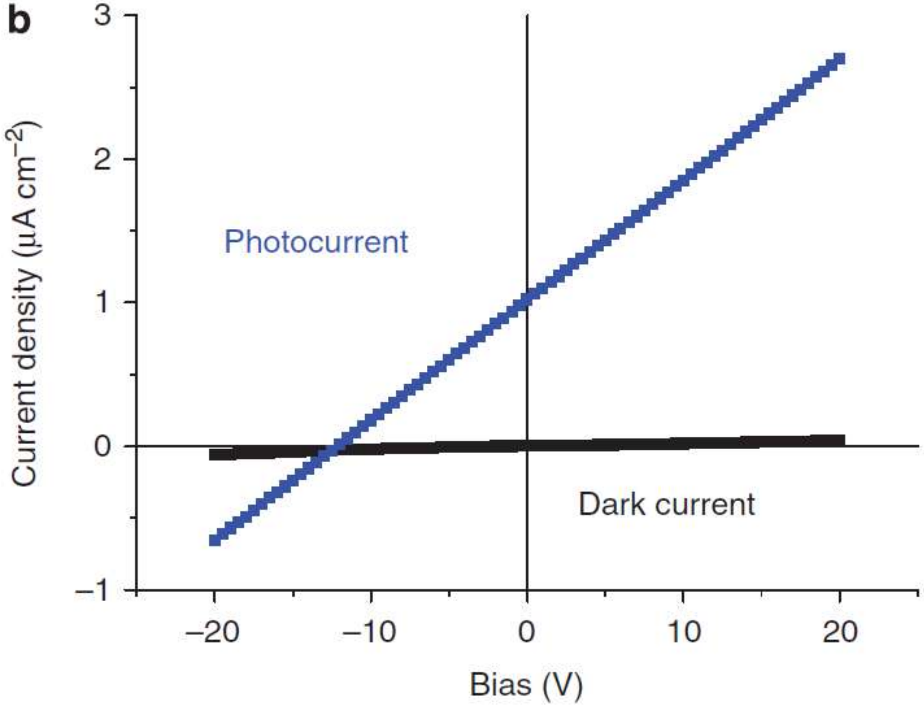


b



Photovoltaic effect in polar oxides

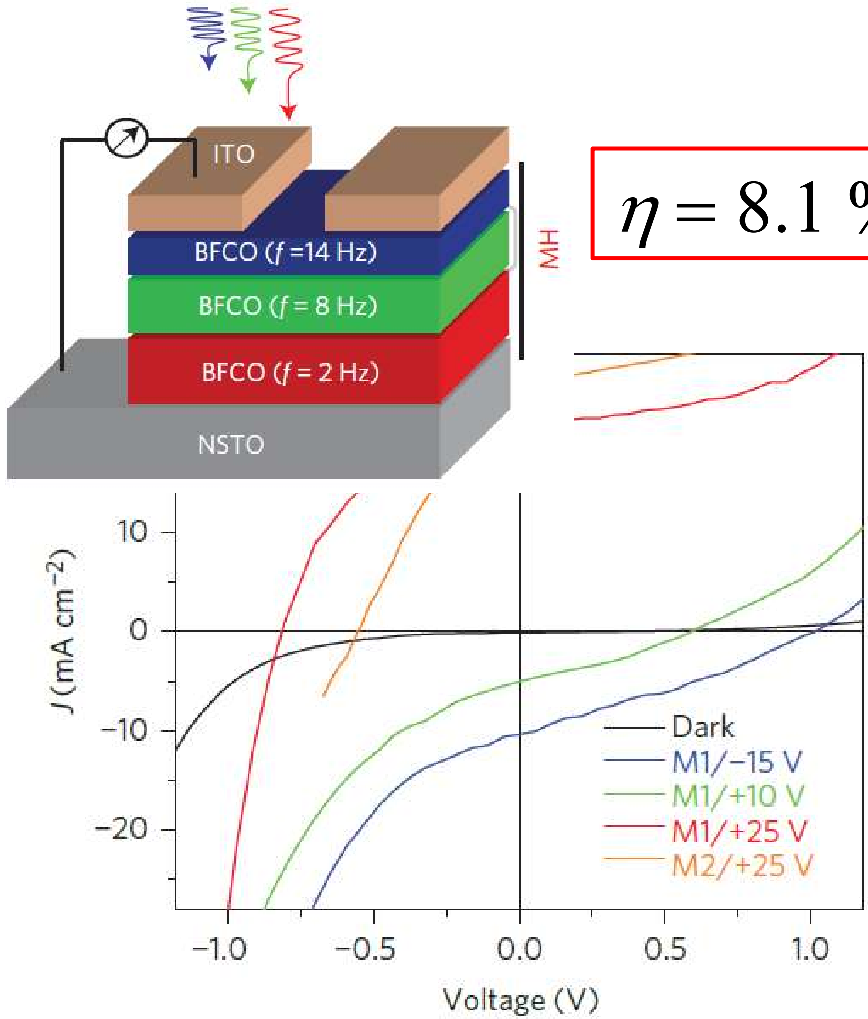
$BiFeO_3$ Single crystal



M. Alexe *et al.*
Nat. Commun. **2**, 256 (2011)

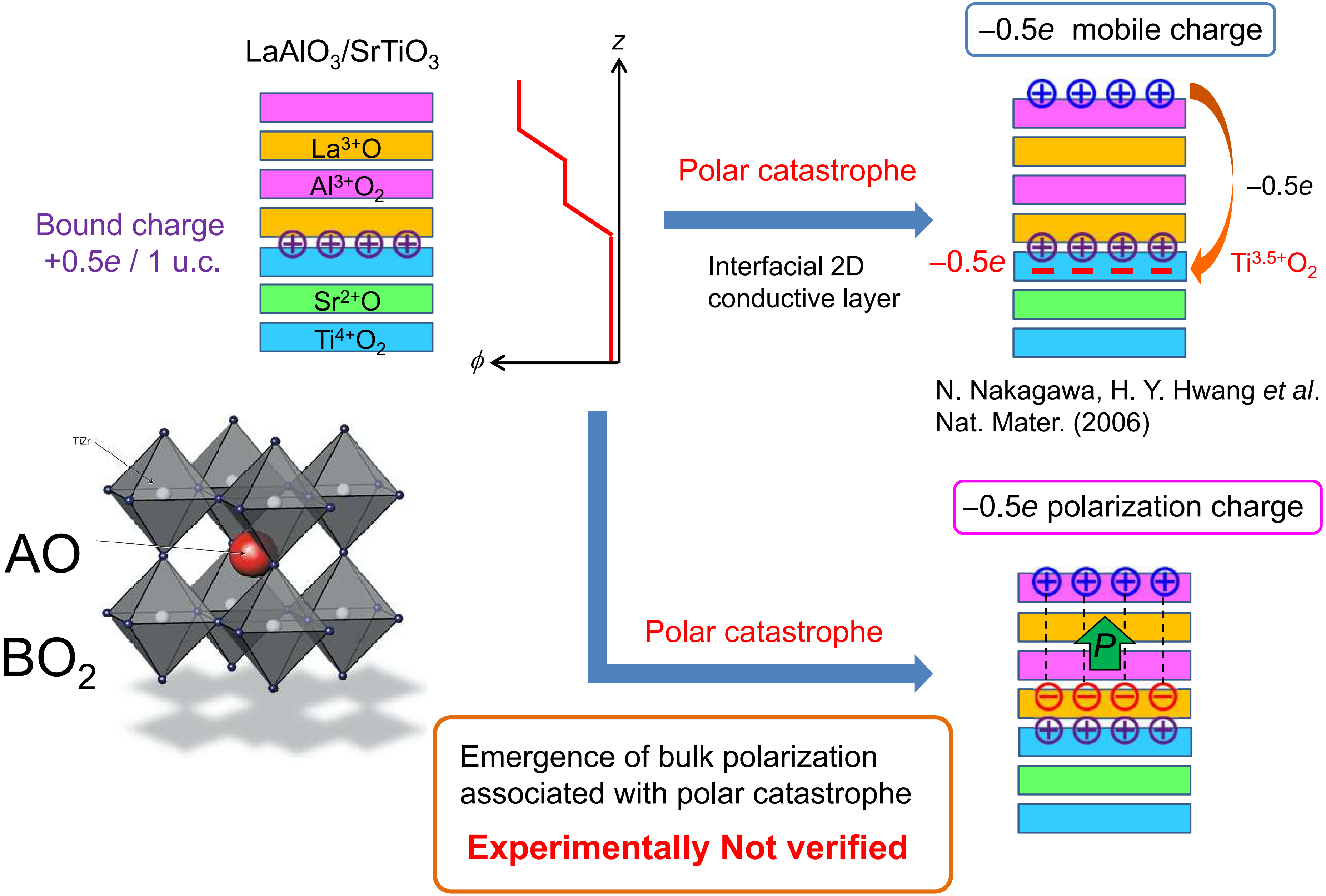
Multilayer junction $Bi(Fe,Cr)O_3$

$$\eta = 8.1\ \%$$



R. Nechache *et al*.
Nat. Photonics **9,** 61 (2015)

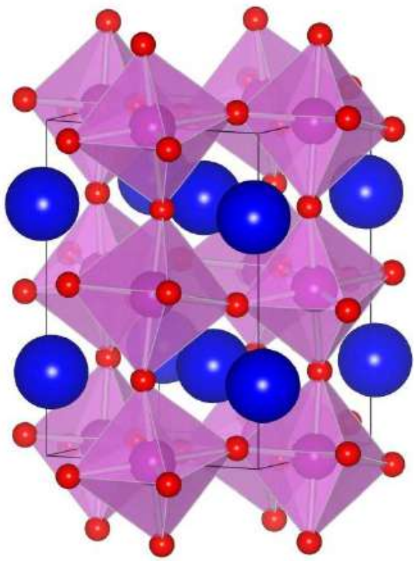
Interface-driven polar state in oxides



Target material : $LaFeO_3$

Crystal structure

Orthorhombic perovskite

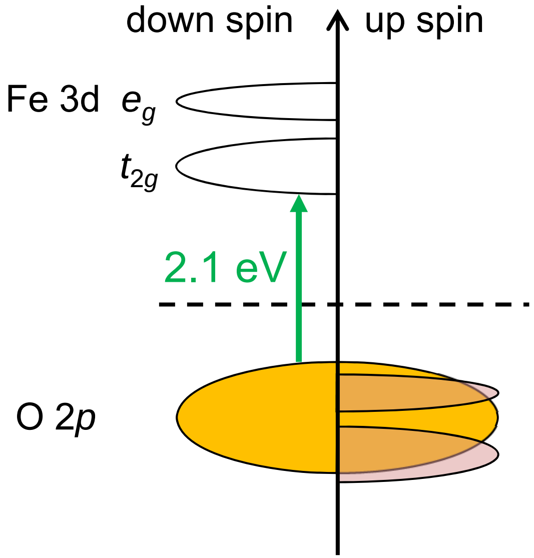


Centrosymmetric

Non polar

Electronic structure

Fe^{3+} (d^5 high spin)

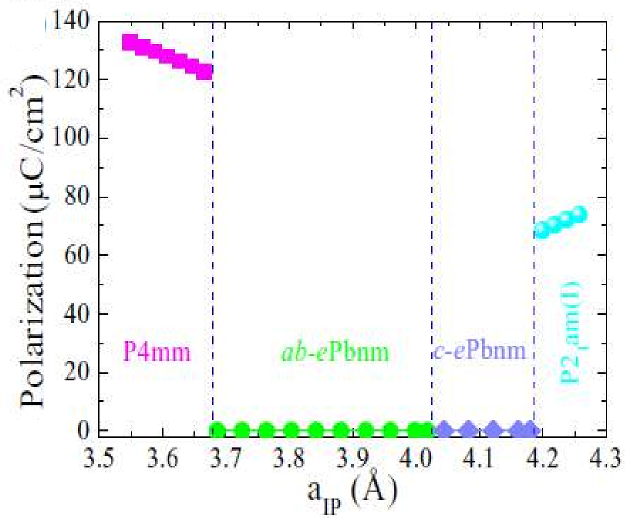


Highly resistive Mott insulator

Large absorption for visible light (cf. $BiFeO_3$ E_g = 2.8 eV)

Instability toward ferroelectric state

First-principles calculation of polarization in distorted $RFeO_3$

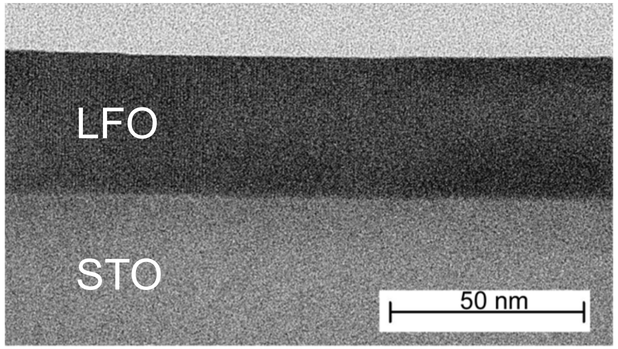


H. J. Zhao *et al*.,
J. Phys.: Condens. Matter (2014)

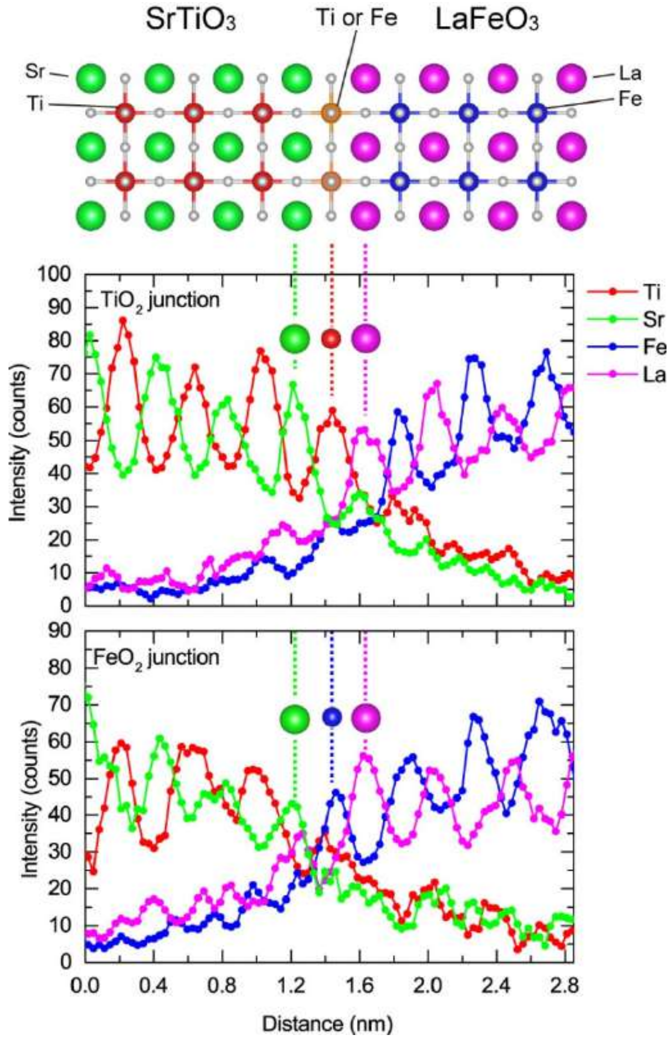
Fabrication of termination-controlled junction

$LaFeO_3$ / $SrTiO_3$ junction

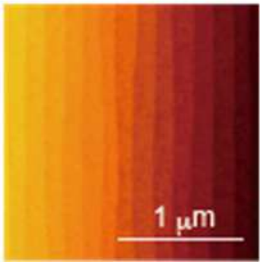
M. Nakamura *et al*. Phys. Rev. Lett. 116 156801 (2016)

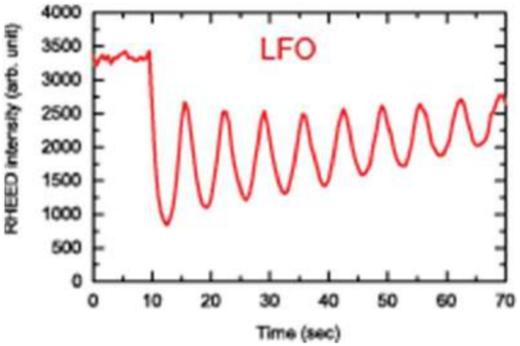


STEM-EDX

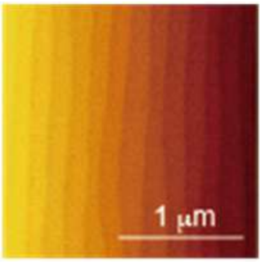


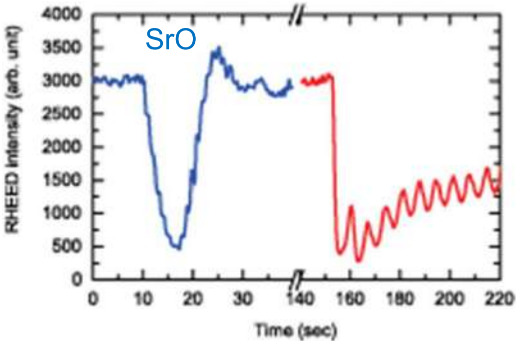
TiO_2 termination





SrO termination

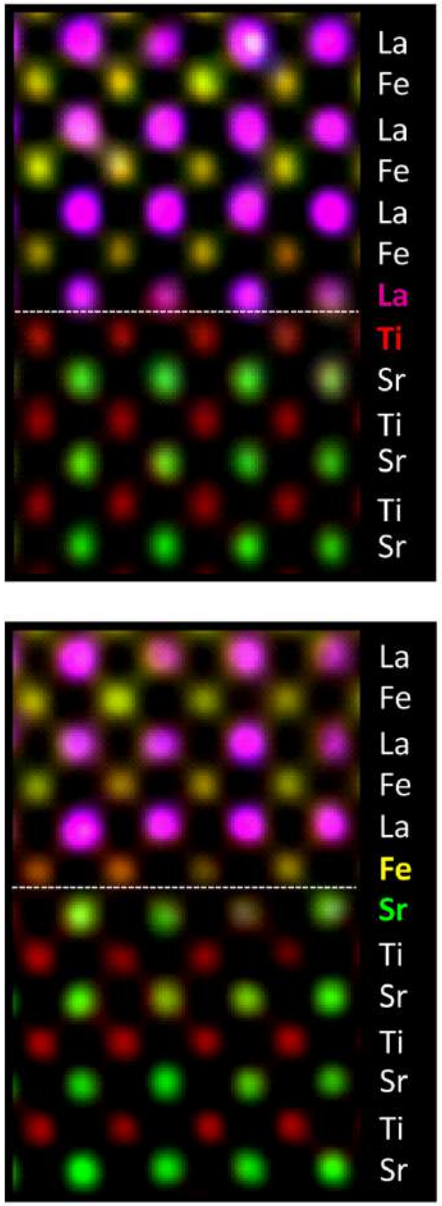


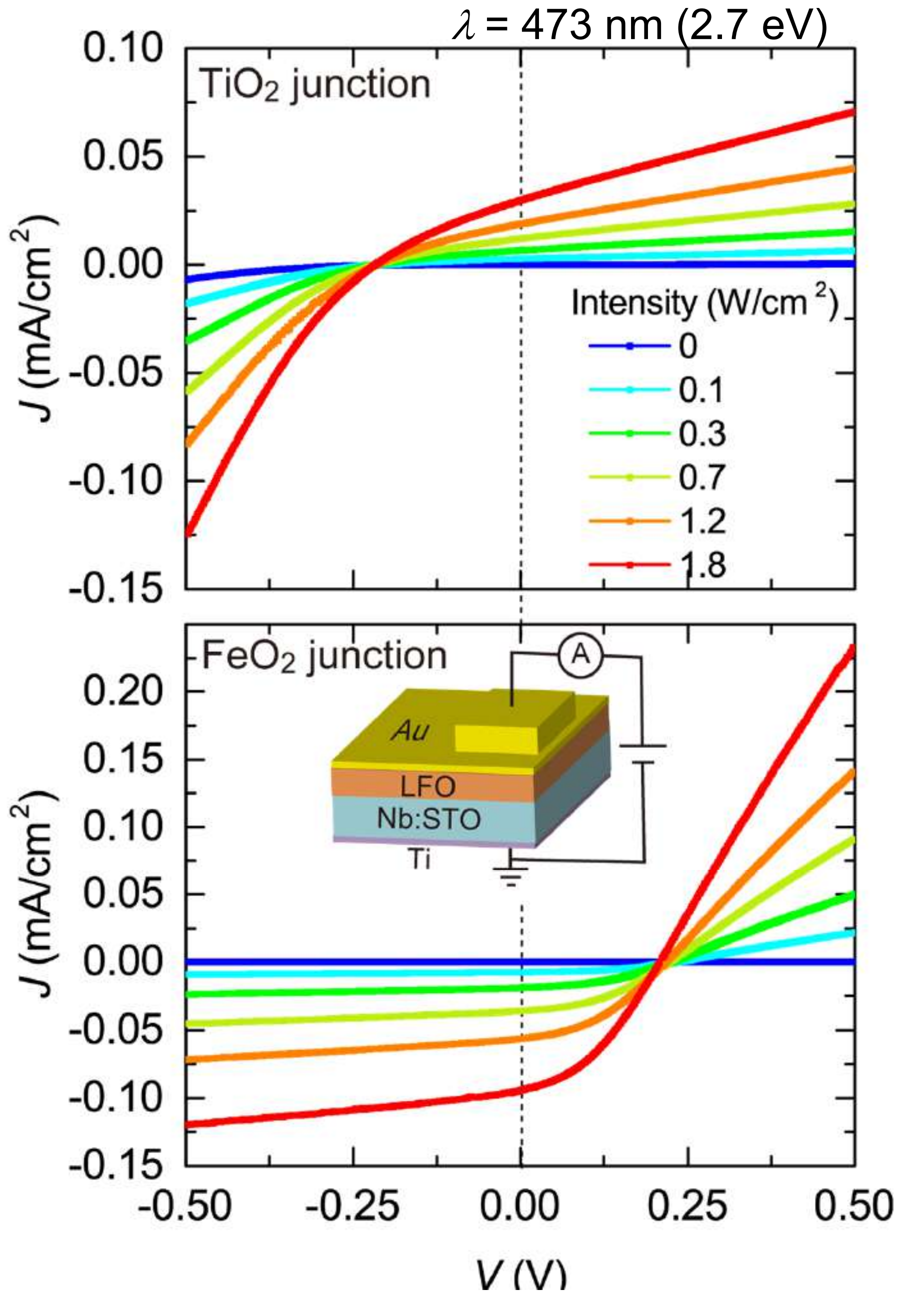


Interface is insulating irrespective of the termination

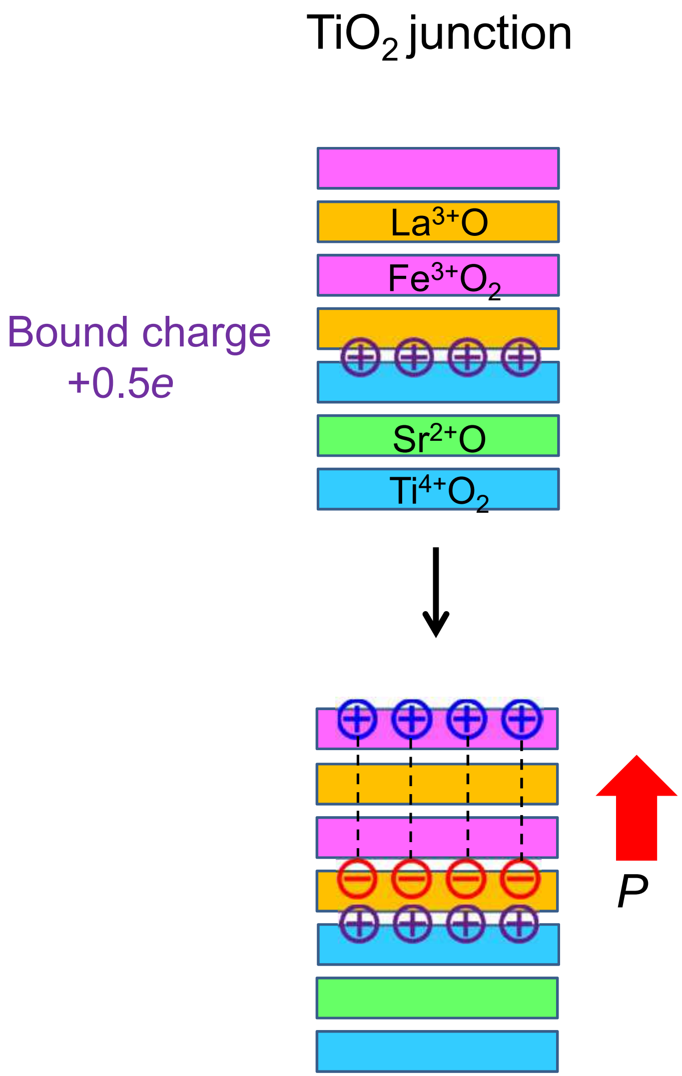
Photovoltaic effect in LFO/Nb:STO junctions

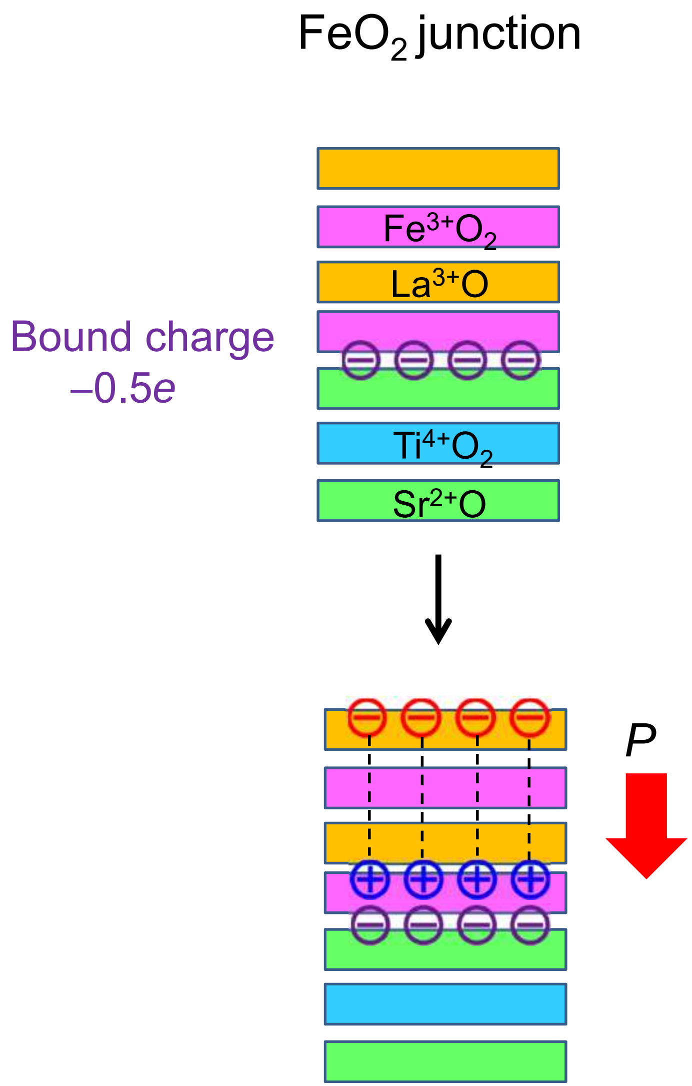
STEM-EDX



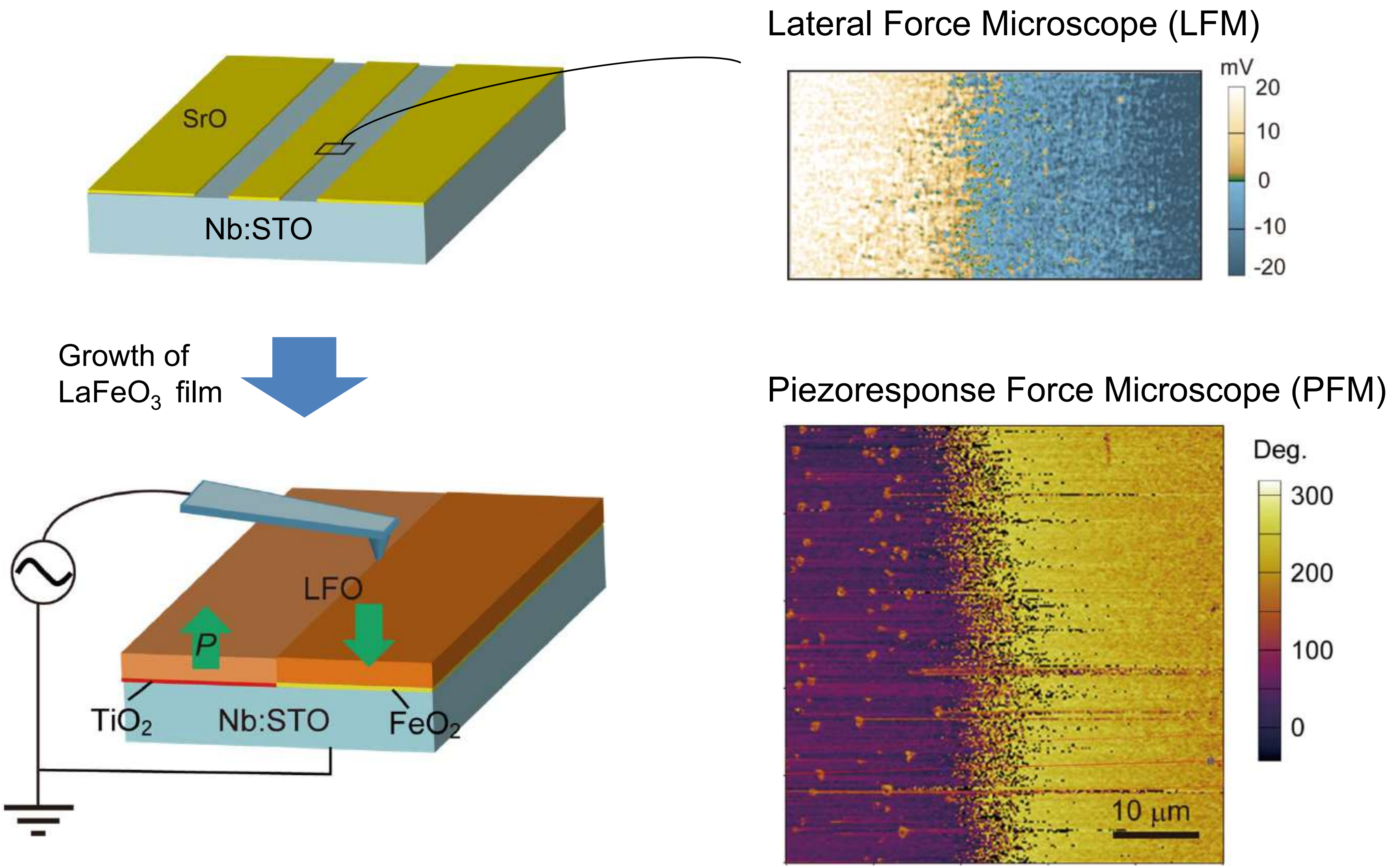


Built-in polarization





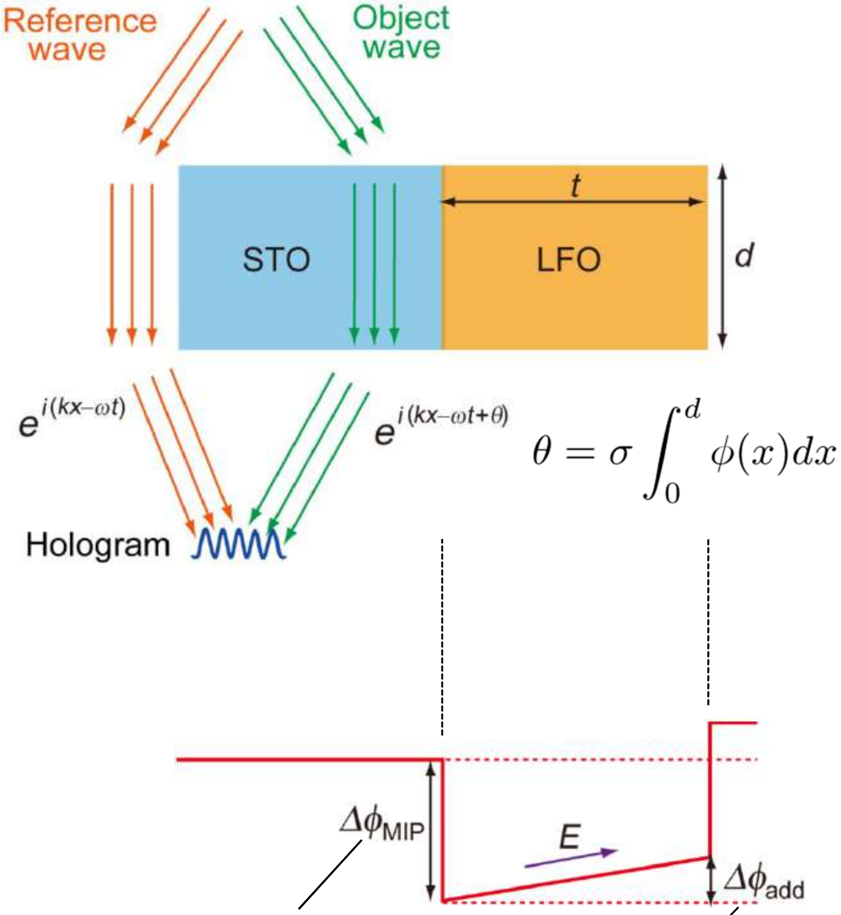
Visualization of built-in polarization by PFM



Indication of electric polarization pointing normal to the film surface.

Electron holography: direct observation of potential profile

Electron holography

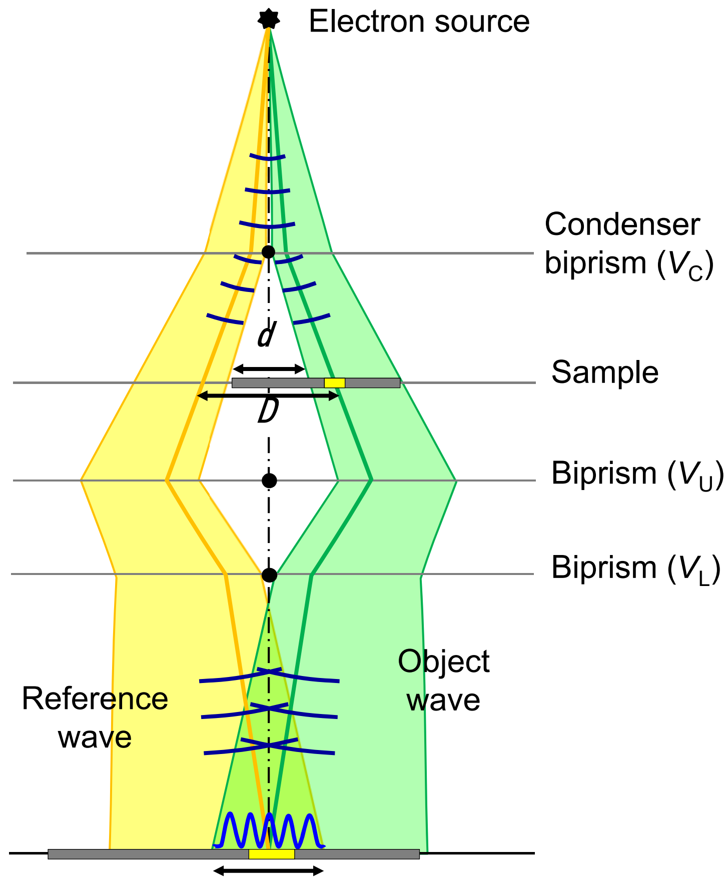


$$\theta = \sigma \int_0^d \phi(x)dx$$

Mean inner potential
(difference in the element)

Actual potential slope

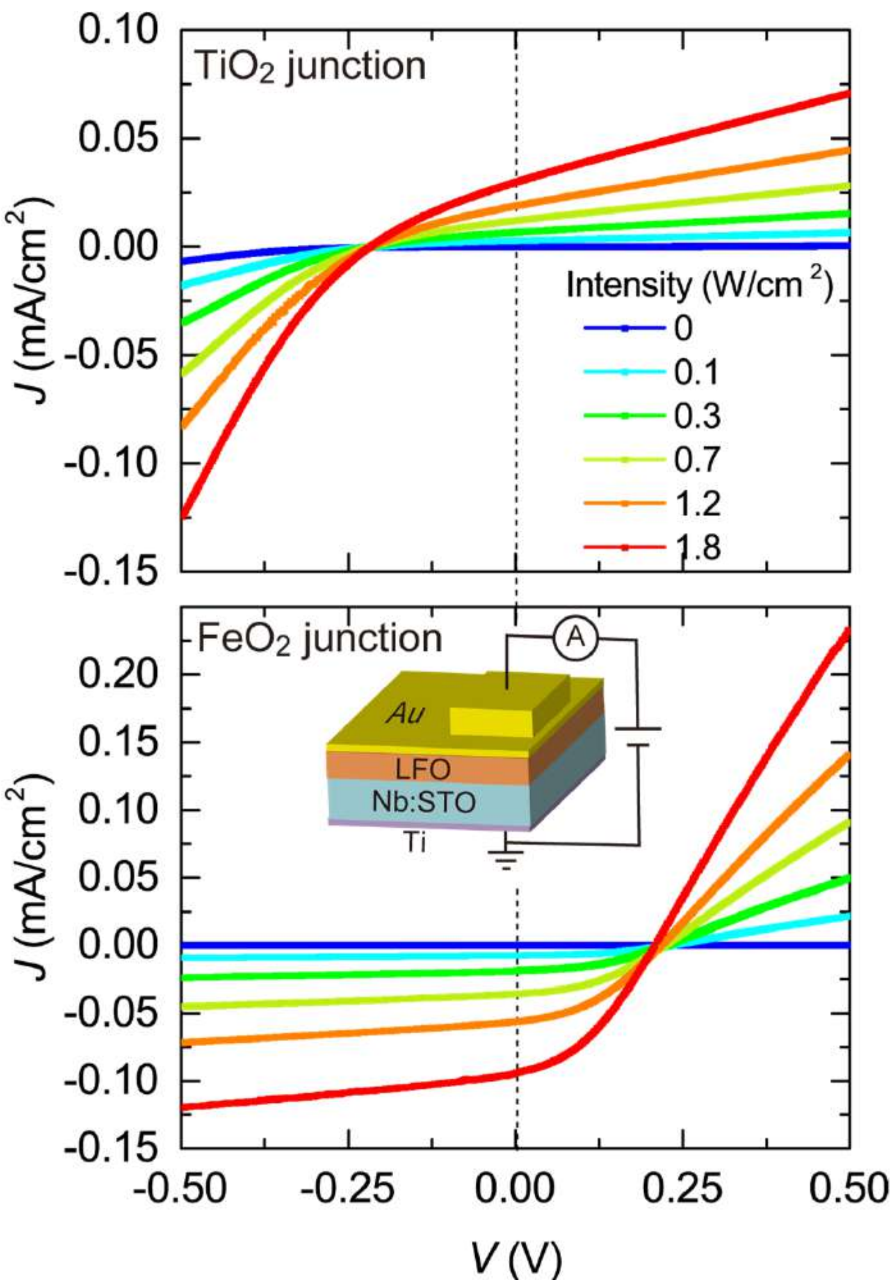
Sprit illumination holography



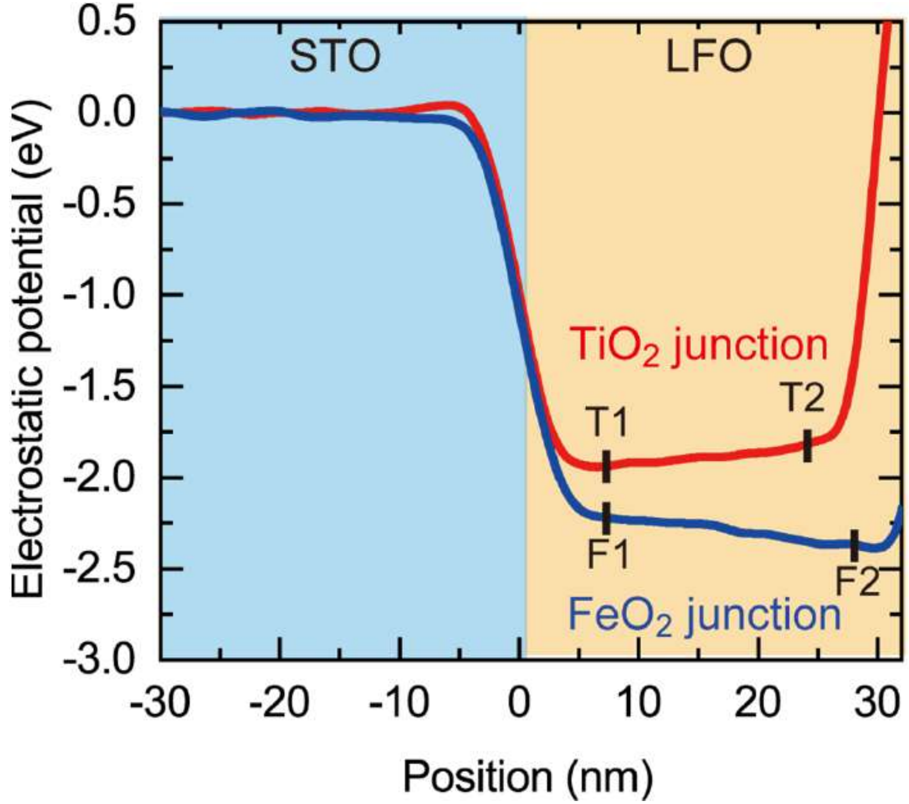
T. Tanigaki *et al.*, Appl. Phys. Lett. **101**, 043101 (2012)

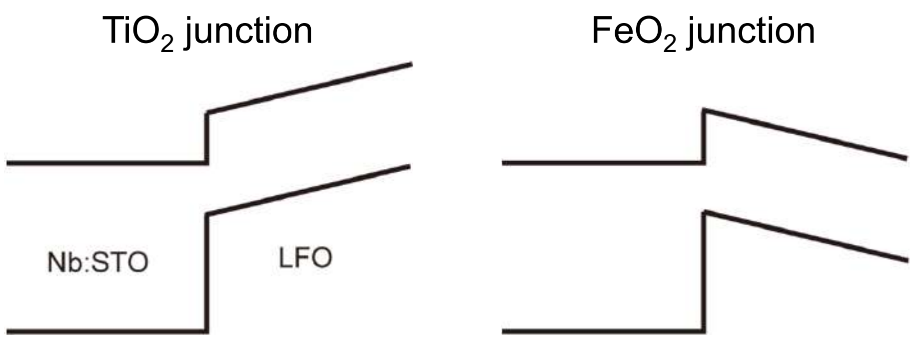
TEM: HF-3300S, Hitachi High-Technologies Co.

Electron holography: direct observation of potential profile

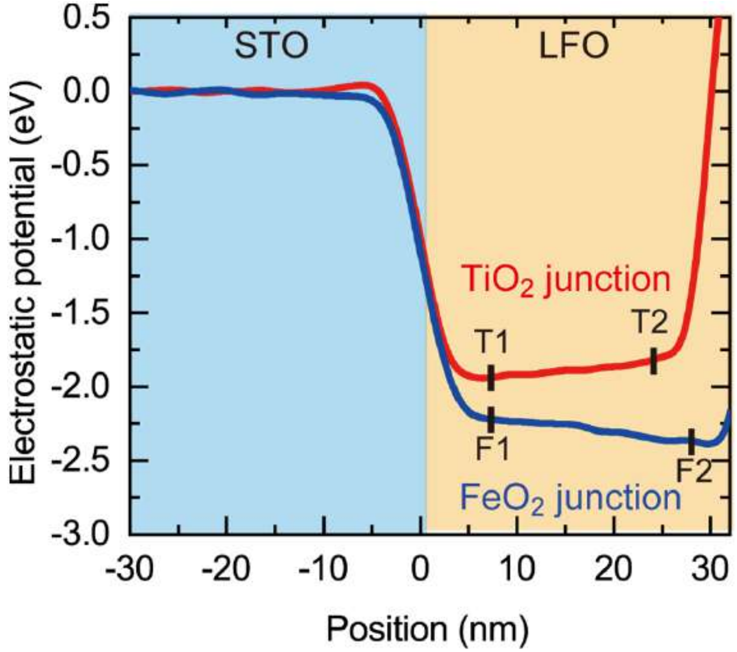


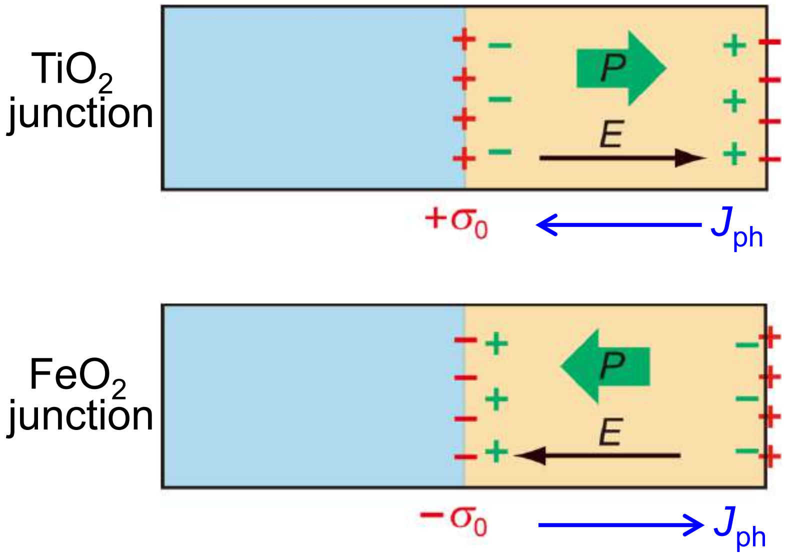
Current in opposite direction





Estimation of induced electric polarization





$$\sigma_0 - P = \varepsilon_0 E$$

$$\sigma_0 = 0.5e/u.c. = 53\ \mu\text{C}/\text{cm}^2$$

$$P = P_s + P_d$$

P_s : spontaneous P

P_d : dielectric P

$$P_d = \chi E = \varepsilon_0(\varepsilon_r - 1)E$$

$E = -58$ kV/cm : TiO_2 junction

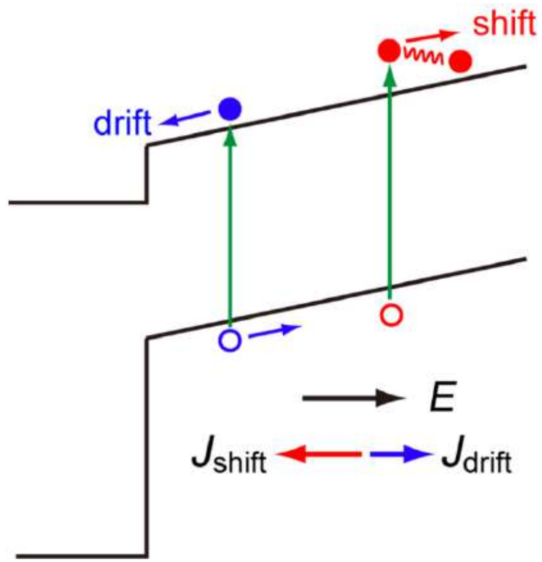
$E = +81$ kV/cm : FeO_2 junction

$$\longrightarrow P_d = 0.17\ \mu\text{C}/\text{cm}^2$$

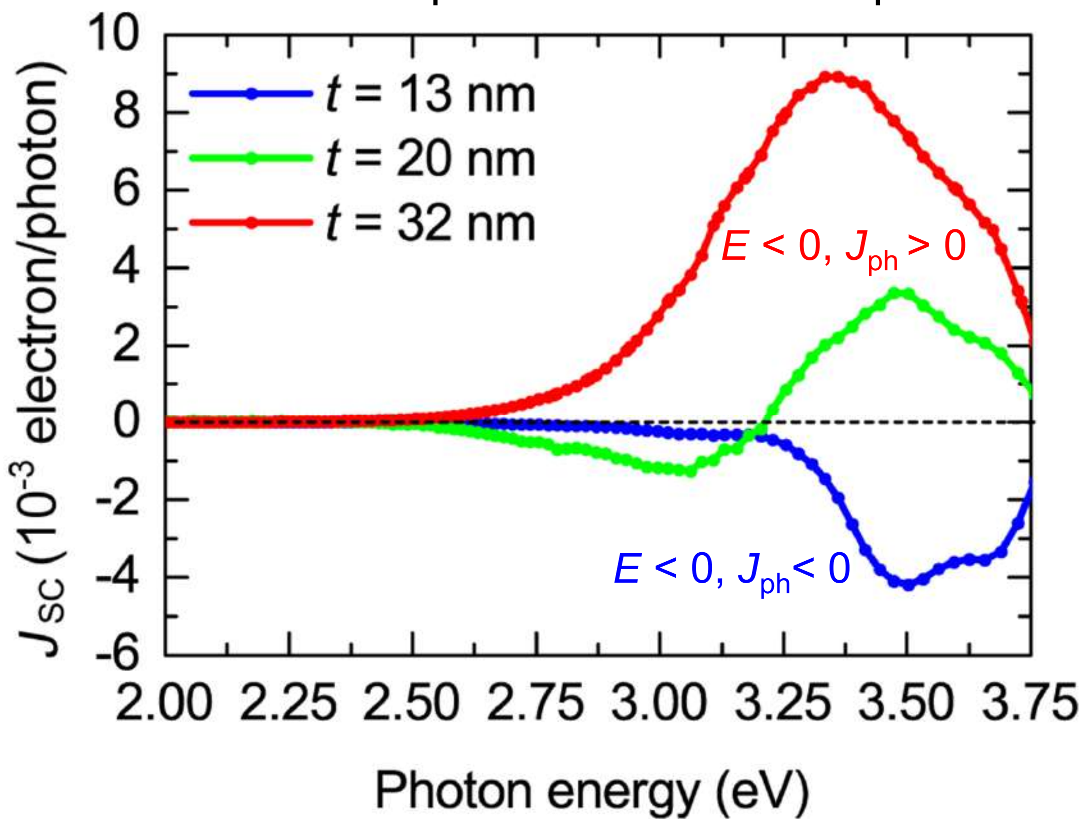
$$P_s = 53\ \mu\text{C}/\text{cm}^2$$

Origin of photocurrent in LFO/Nb:STO junctions

M. Nakamura *et al*. Phys. Rev. Lett. 116 156801 (2016)



Thickness dependence of action spectra

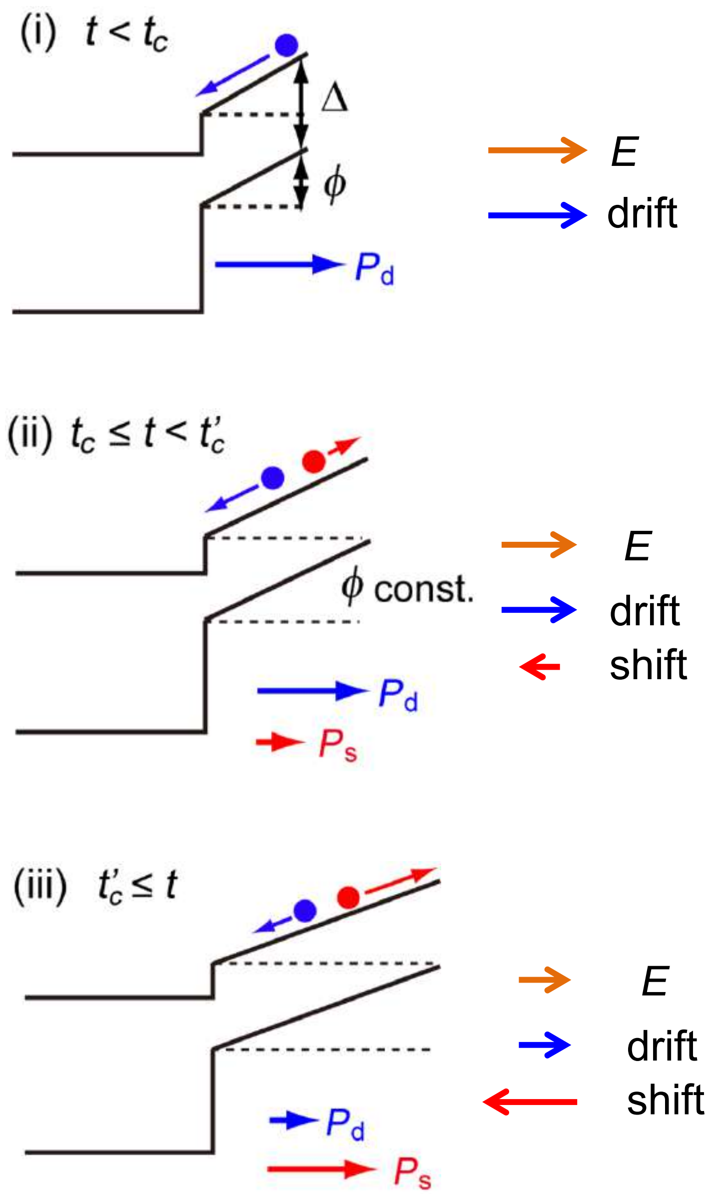


$J_{drift} \propto E_{int} \propto P_d$ $\qquad J_{shift} \sim P_s$

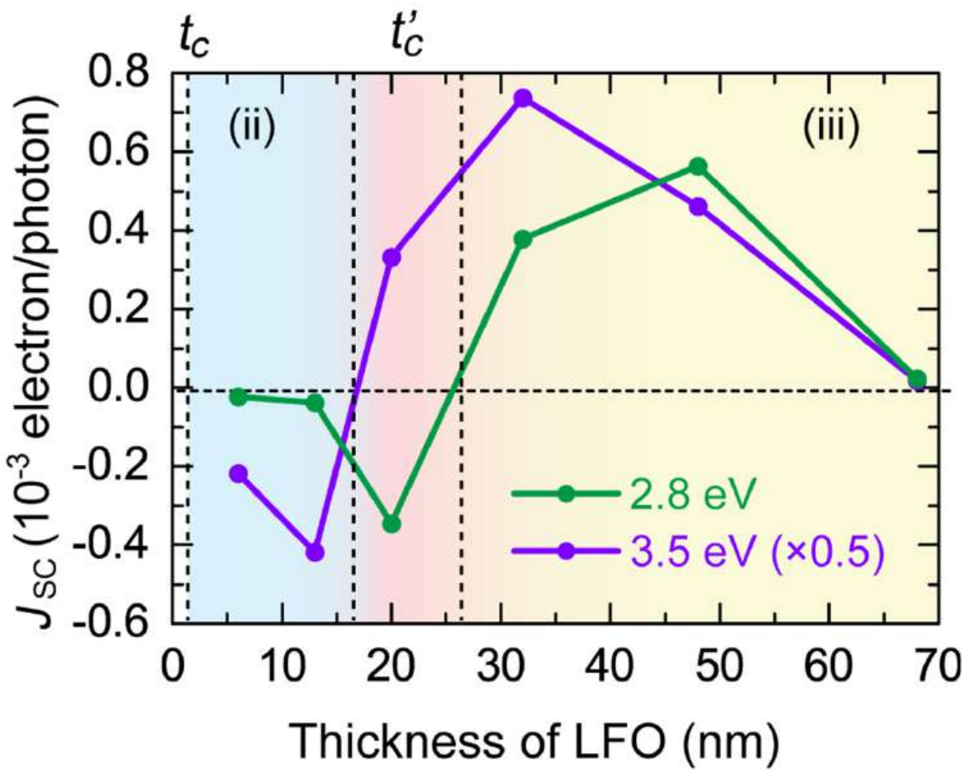
t = 13 nm : drift current is dominant

t = 32 nm : shift current is dominant

Evolution of polarization and photocurrent



Thickness dependence of J_{SC}



$t = t_c$ polar catastrophe (1.4 nm (3 u.c.))

$t = t'_c$ sign reversal in J_{SC} (17 ~ 25 nm)

$J_{drift} \propto E_{int} \propto P_d$ $J_{shift} \sim P_s + P_d$

Relation between shift current and polarization

<u>Polarization</u>

$$P_s = P_{ion} + \boxed{P_{elec}}$$

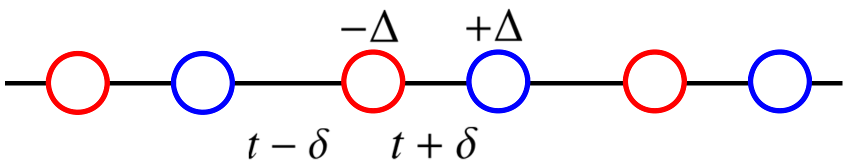
$$P_{elec} = \frac{e}{2\pi}\int_{BZ} dk\, A_{nn}(k)$$

<u>Shift current</u>

$$\bar{R}_{cv} = \int_{BZ} dk\,(\partial_k \phi_{cv} + A_{cc} - A_{vv})$$

$$\propto P_c - P_v$$

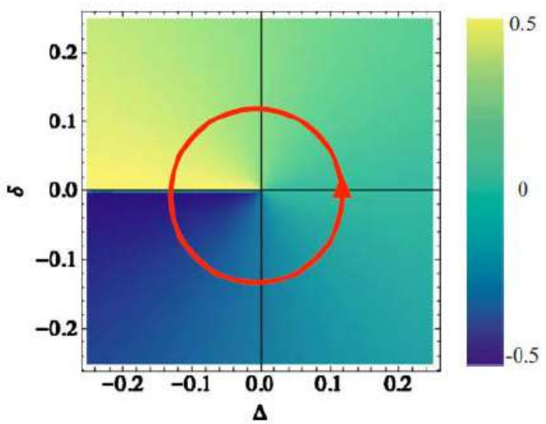
Rice-Mele model



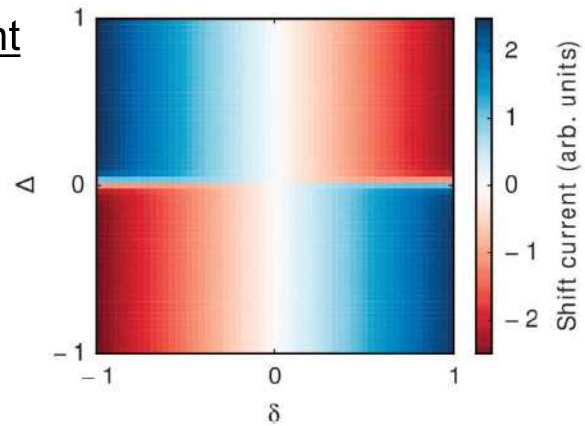
$$\hat{H} = \sum_i \left[\Delta(-1)^i c_i^\dagger c_i + \left(t + (-1)^i \delta\right) c_i^\dagger c_{i+1} + h.c.\right]$$

$\Delta \neq 0, \delta \neq 0 \longrightarrow$ Inversion symmetry broken

<u>Polarization</u>



<u>Shift current</u>



D. Vanderbilt *et al.*, Phys. Rev. B **48**, 4442 (1993)

S. Onoda *et al.*, Phys. Rev. Lett. **93**, 167602 (2004)

D. Xiao *et al.*, Rev. Mod. Phys. **82**, 1959 (2010)

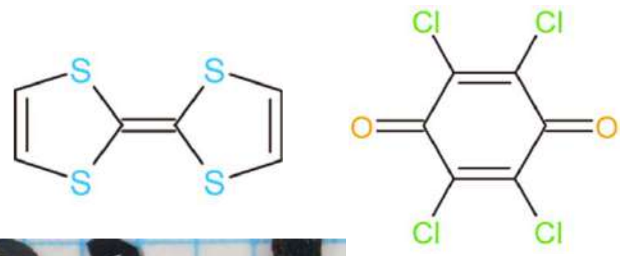
T. Morimoto and N. Nagaosa, Sci. Adv. **2** (2016)

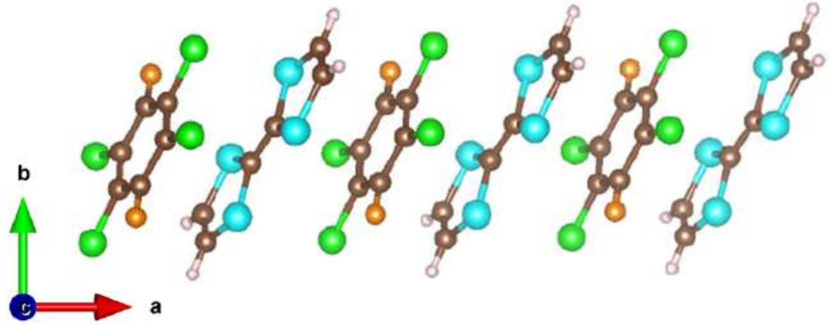
L. Z. Tan *et al.*, Npj Comp. Mater. **2**, 16026 (2016)

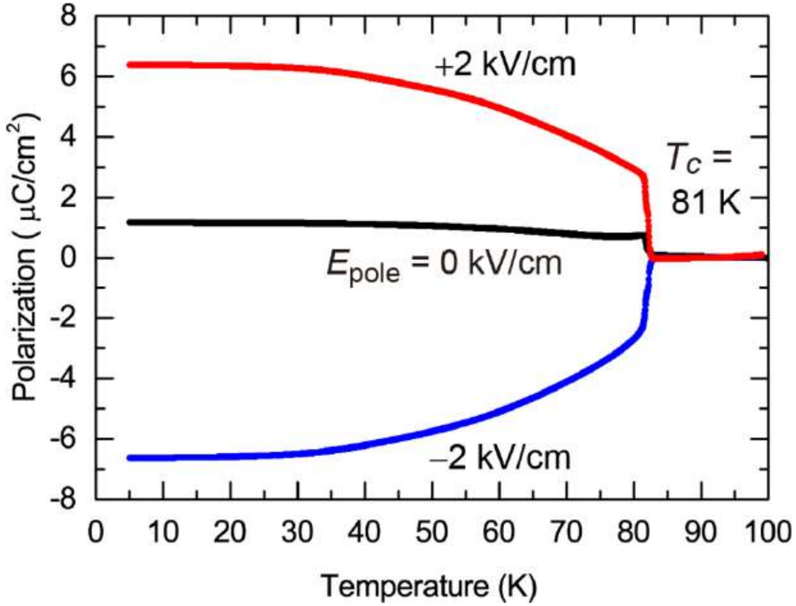
B. M. Fregoso *et al.*, ArXiv: 1701.00172

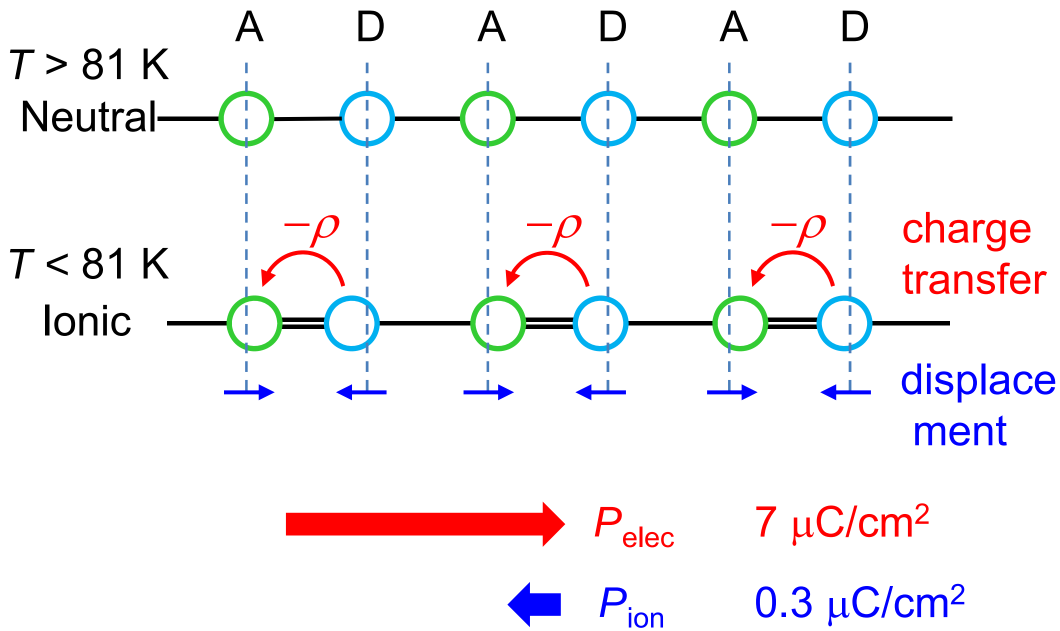
Organic charge-transfer complex TTF-CA

TTF (Donor) *p*-CA (Acceptor)





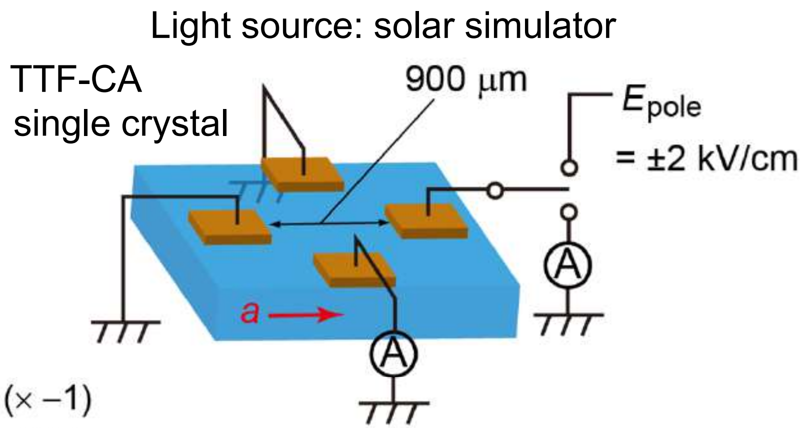




Not *"ionic"* but *"electronic"* ferroelectric

K. Kobayashi *et al*. Phys. Rev. Lett. **108**, 237601 (2012)

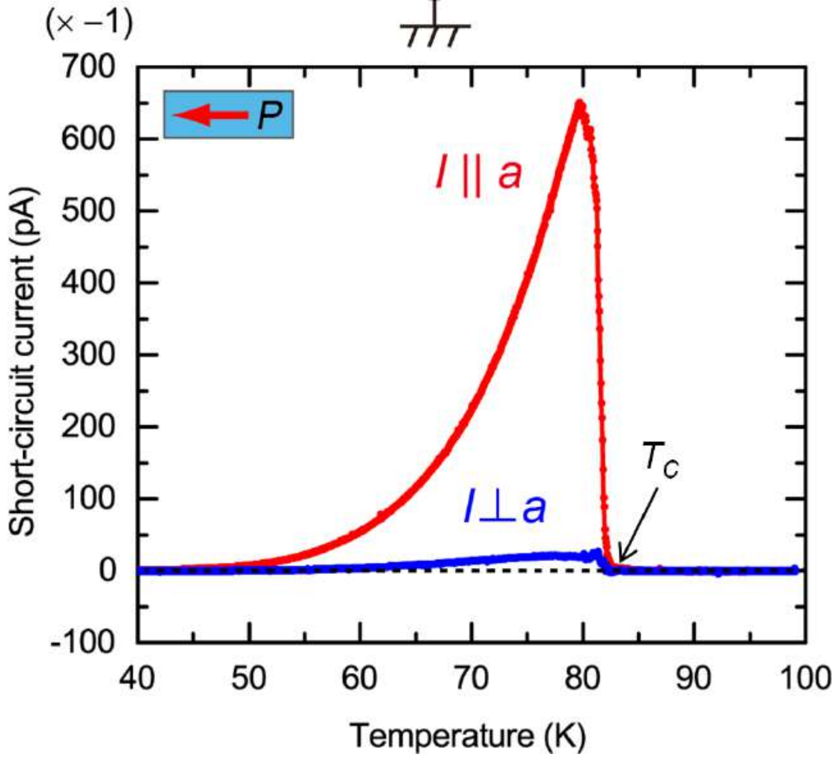
Photovoltaic property of TTF-CA

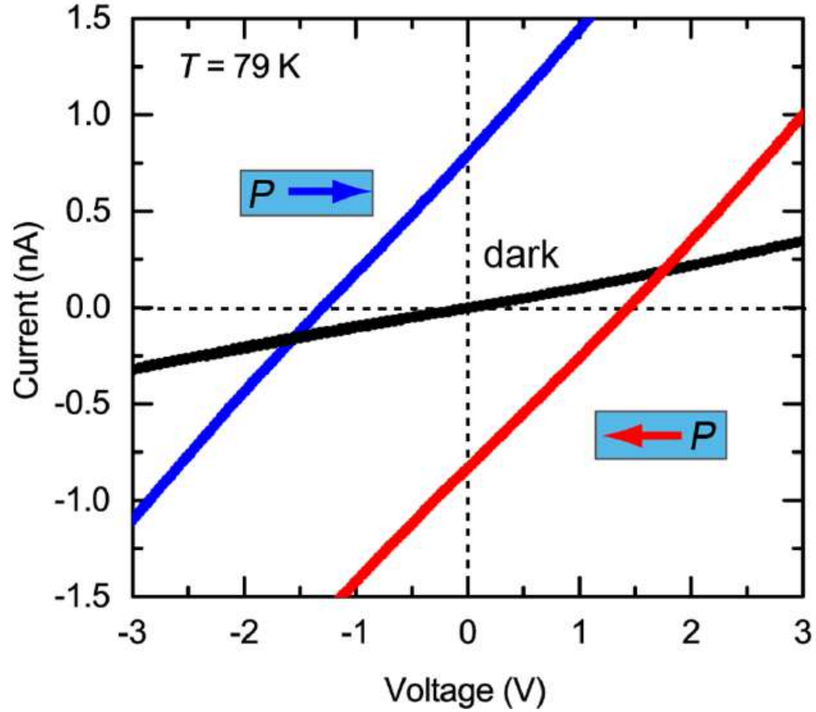


TTF-CA J_{SC} = 1.6 μA/cm^2 (0.1 W/cm^2)

c.f.) $BiFeO_3$ 0.4 μA/cm^2
($h\nu = 3.06$ eV, 40 W/cm^2)
Nat. Commun. 2, 256 (2011)

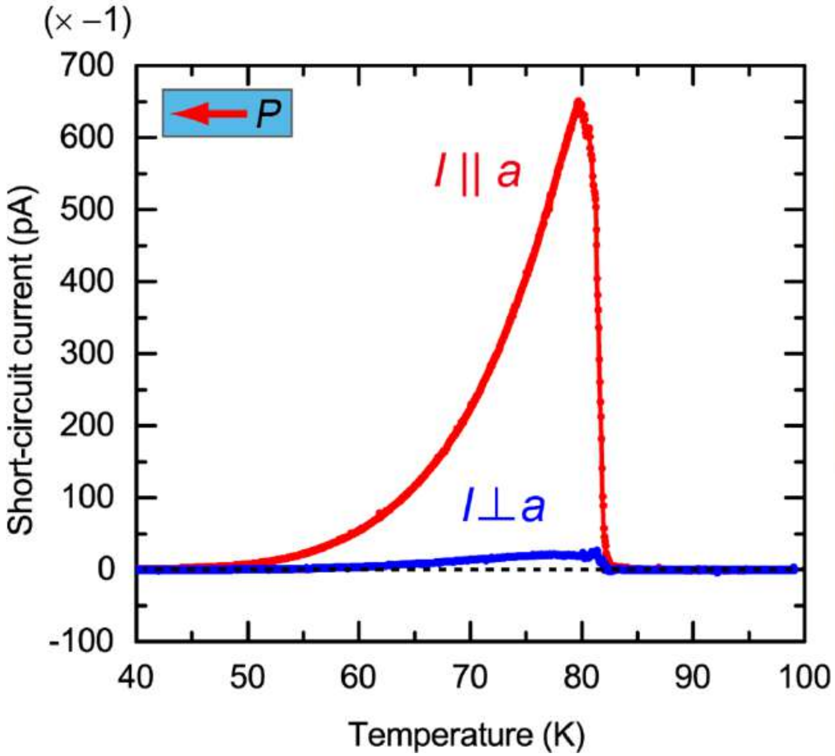
→ more than 1000 times larger

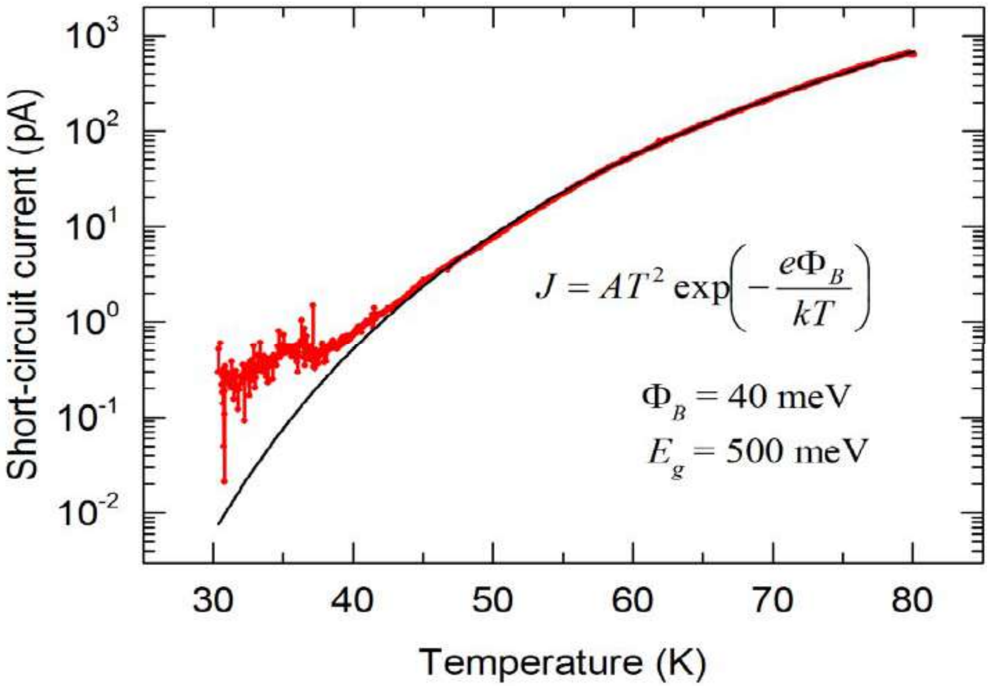


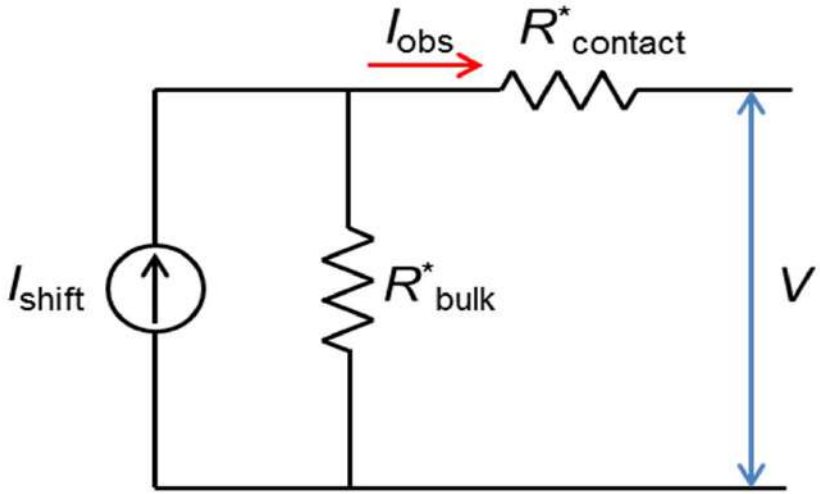


M. Nakamura *et al*. Nat. Commun. **8**, 281 (2017)

Schottky barrier at electrodes





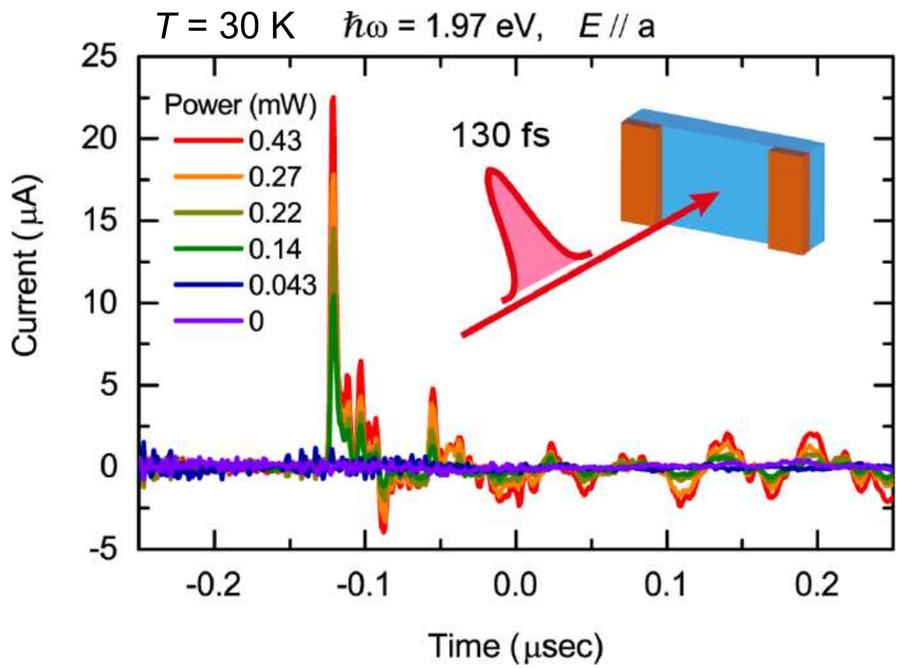


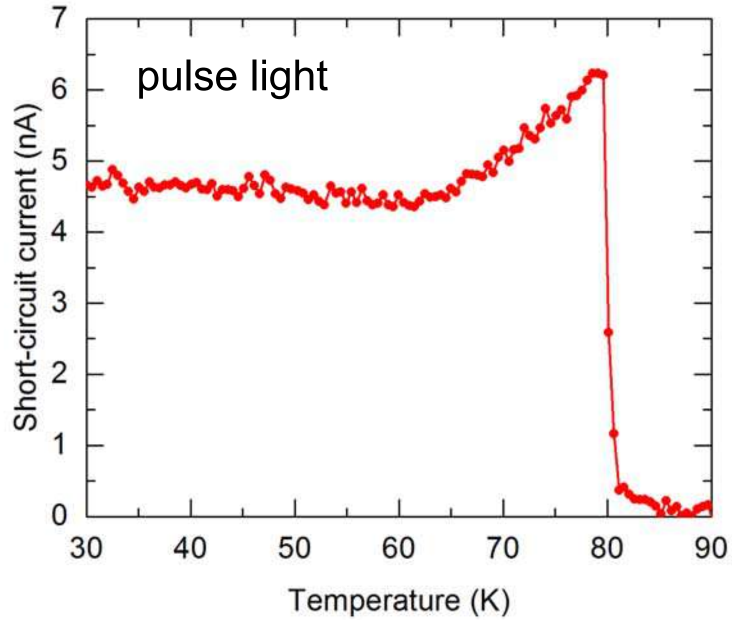
Electrode: Carbon paint

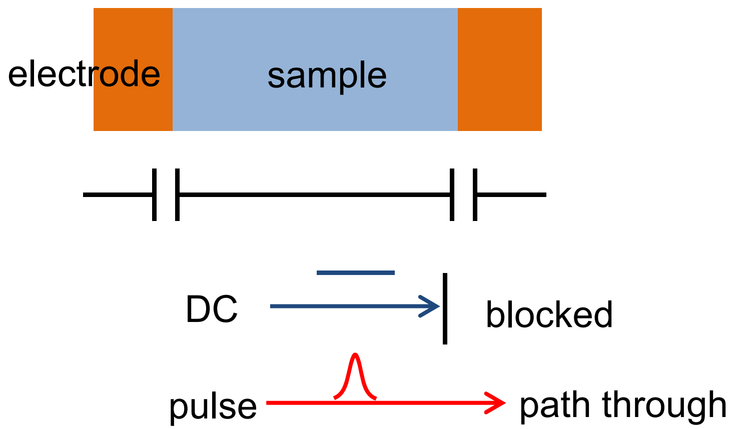
High volatility prevents evaporation of metals

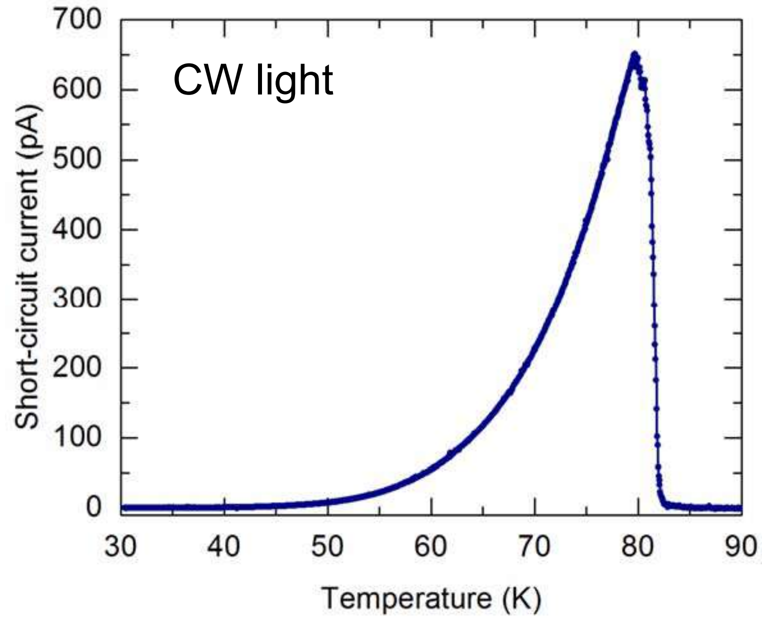
M. Nakamura *et al*. Nat. Commun. **8**, 281 (2017)

Shift current induced by pulse light





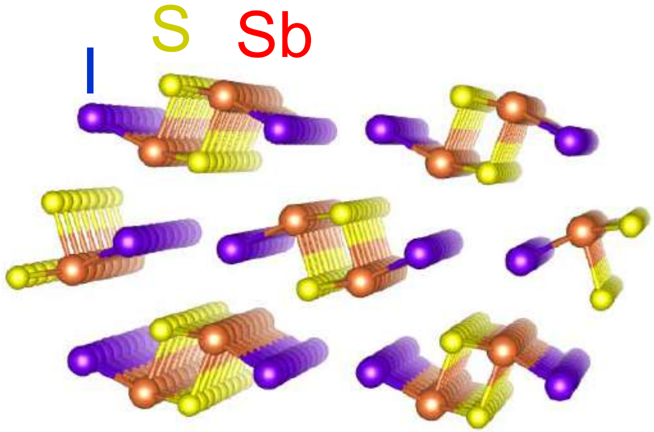


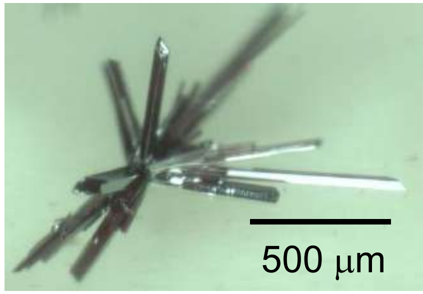


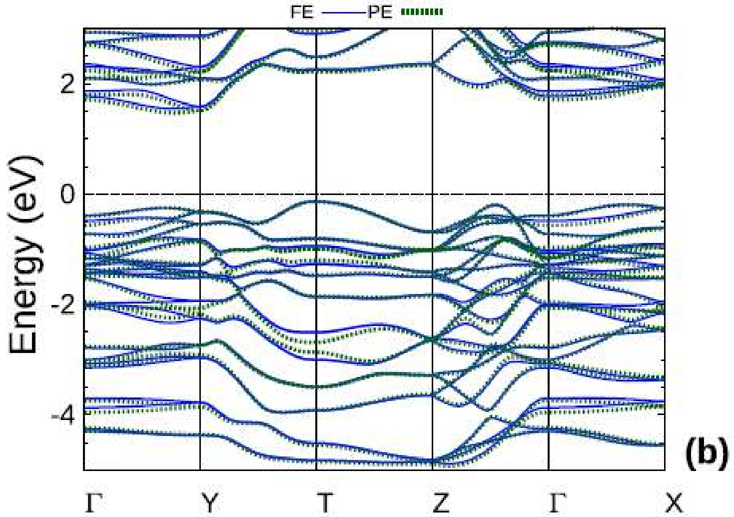
M. Nakamura *et al*. Nat. Commun. **8**, 281 (2017)

A prototypical ferroelectric semiconductor SbSI

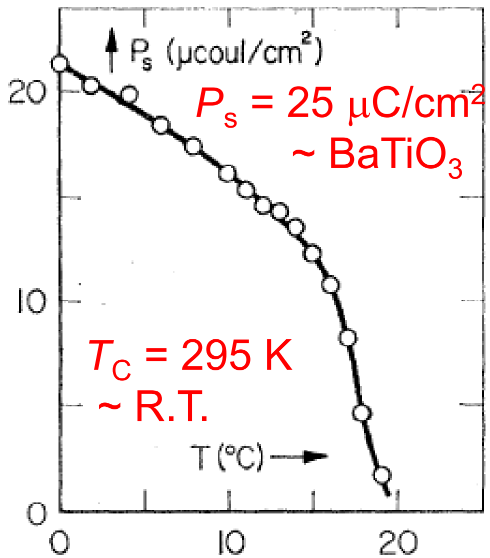
D. Amoroso and S. Picozzi Phys. Rev. B (2016)

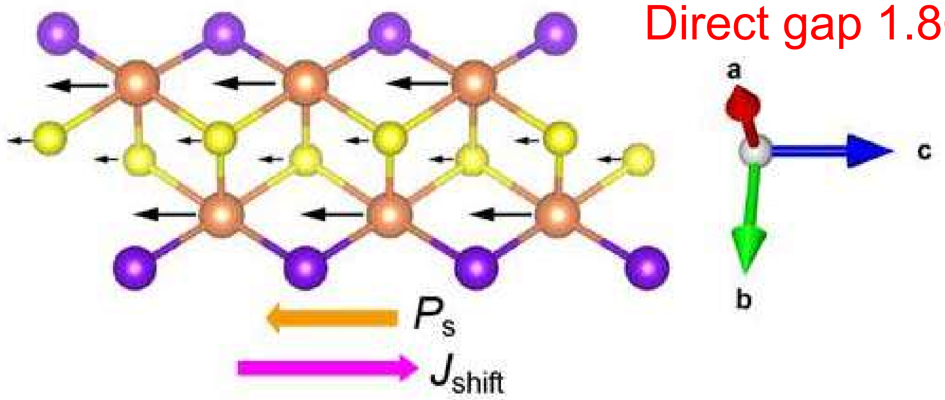






Indirect gap 1.6~1.8 eV
Direct gap 1.8~2.0 eV

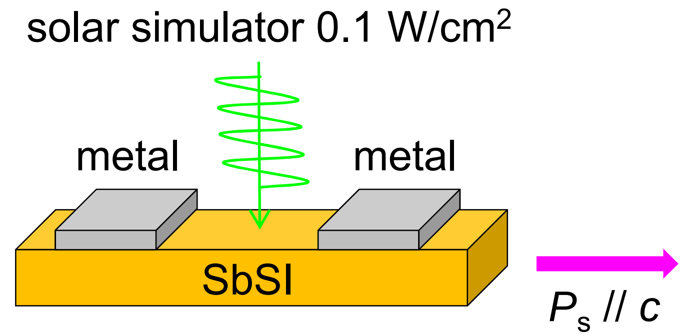


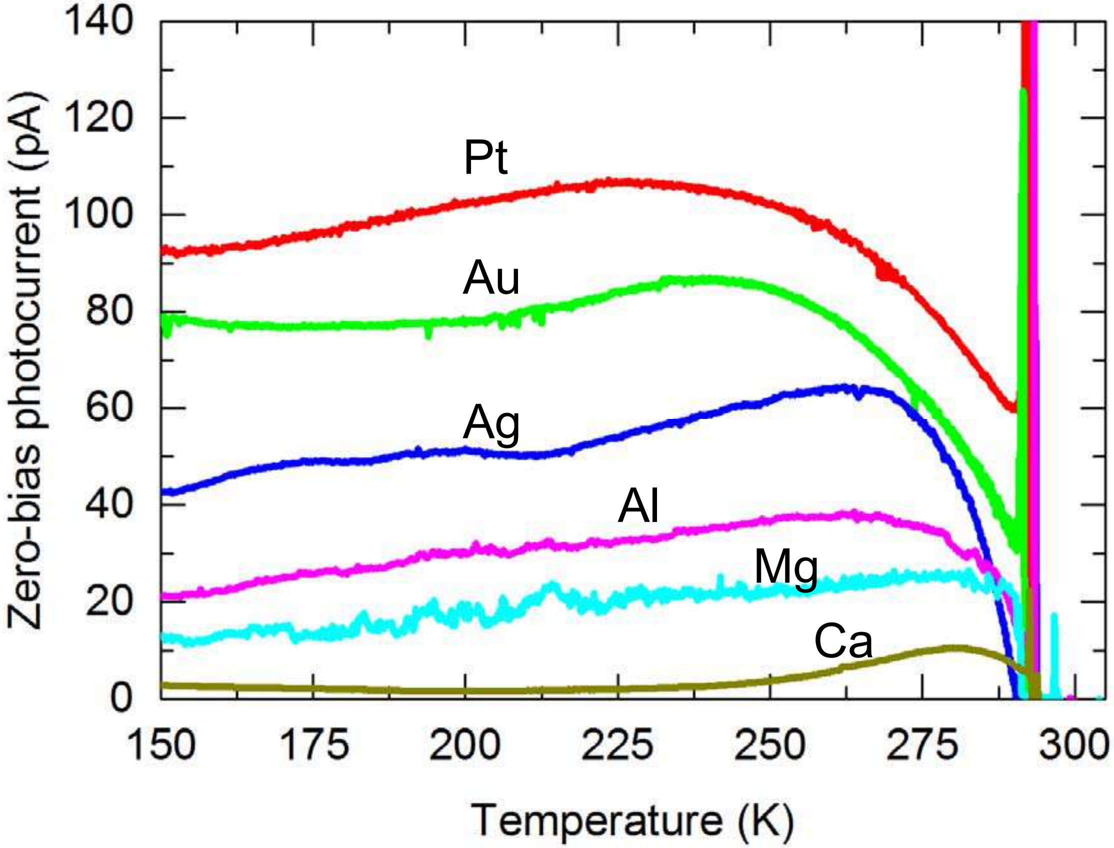


FE: E. Fatuzzo *et al*. Phys. Rev. (1962)
PV Effect: Fridkin APL (1967)

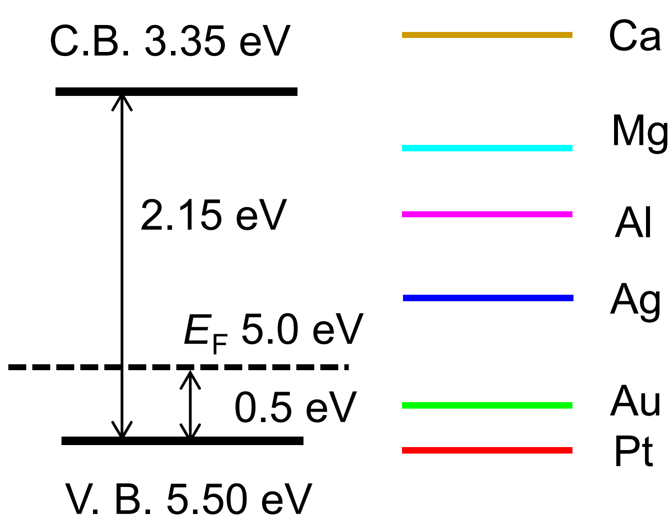
Shift Current: N. Ogawa *et al.*
Phys. Rev. B **96**, 241203(R) (2017)
THz dynamics: M. Sotome, N. Ogawa, N. Nagaosa *et al.*
PNAS **116**, 1929 (2019)

Electrode dependence of photocurrent in SbSI





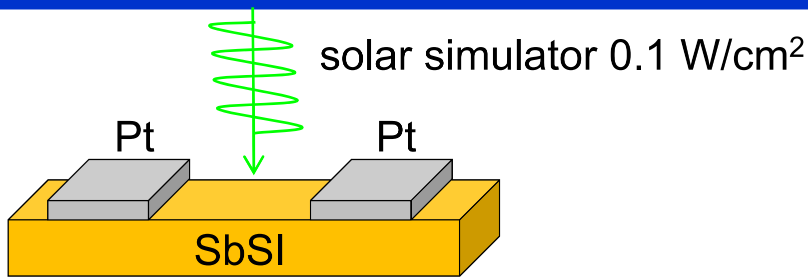
Band diagram of SbSI

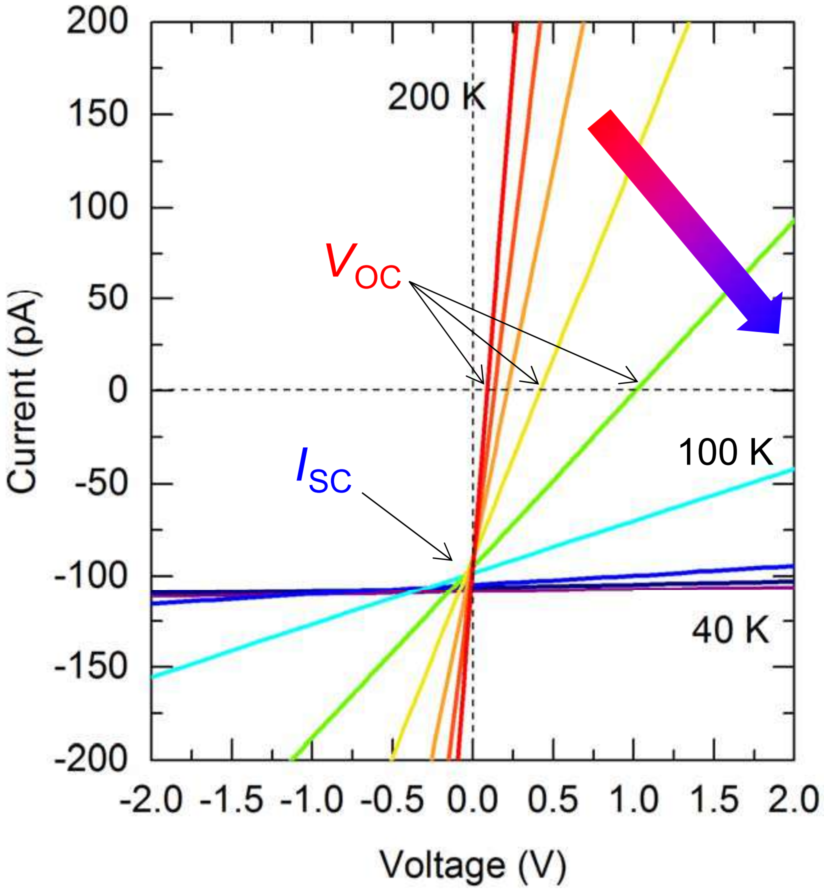


M. Nakamura, MK *et al*., Appl. Phys. Lett. **113**, 232901 (2018)

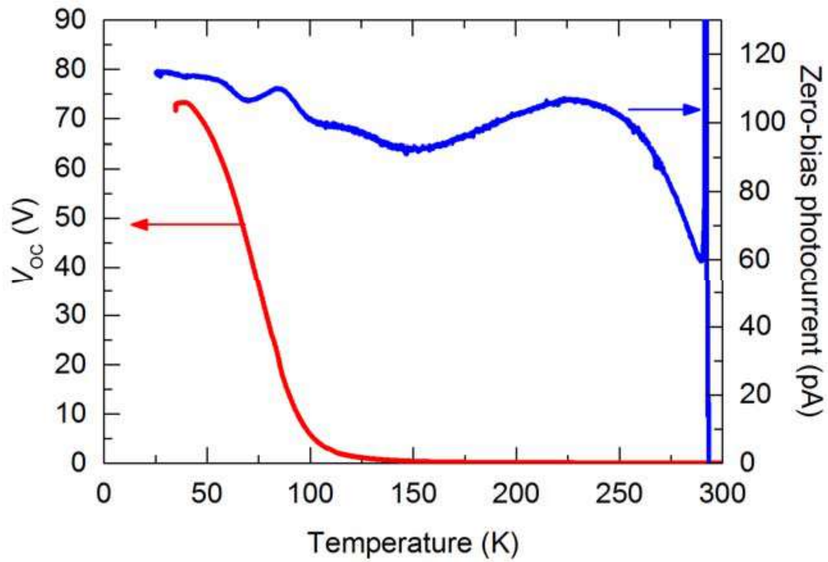
R. Nie *et al*. Adv. Energy Mater. (2017)

Photovoltaic properties of SbSI with Pt electrodes

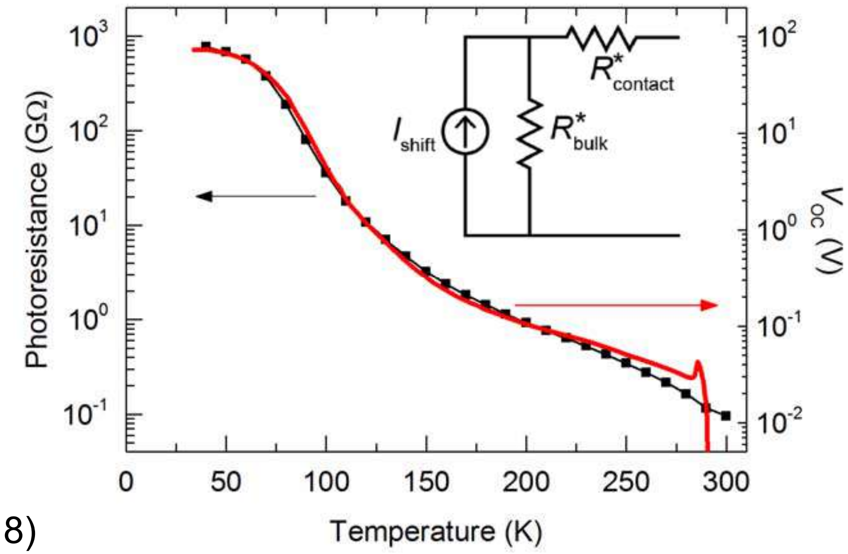




Temperature dependence of I_{SC} and V_{OC}

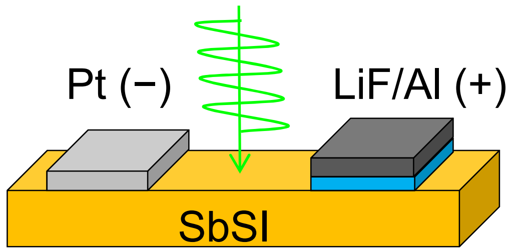


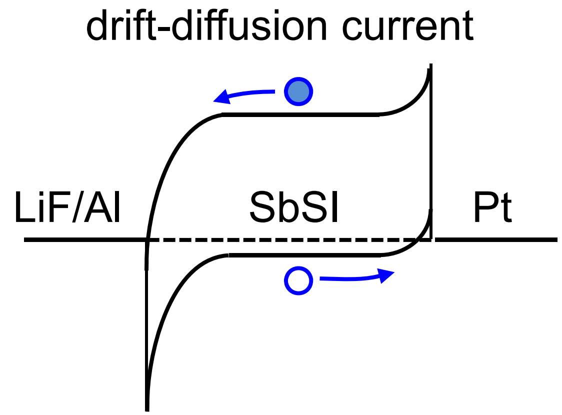
Resistance under photo irradiation

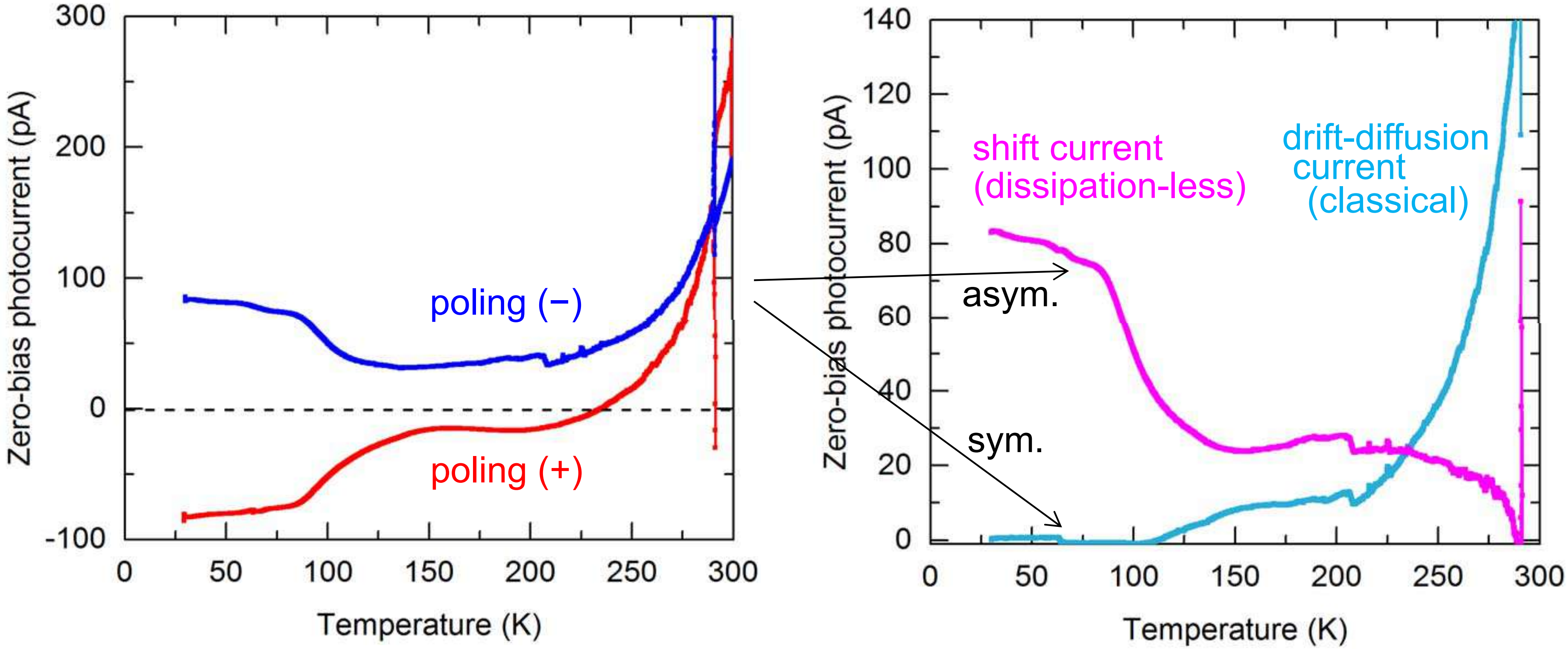


M. Nakamura, MK *et al*., Appl. Phys. Lett. **113**, 232901 (2018)

Photocurrent in asymmetric electrode structure

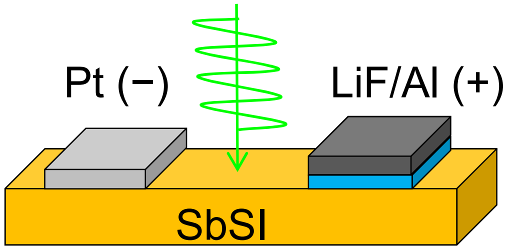


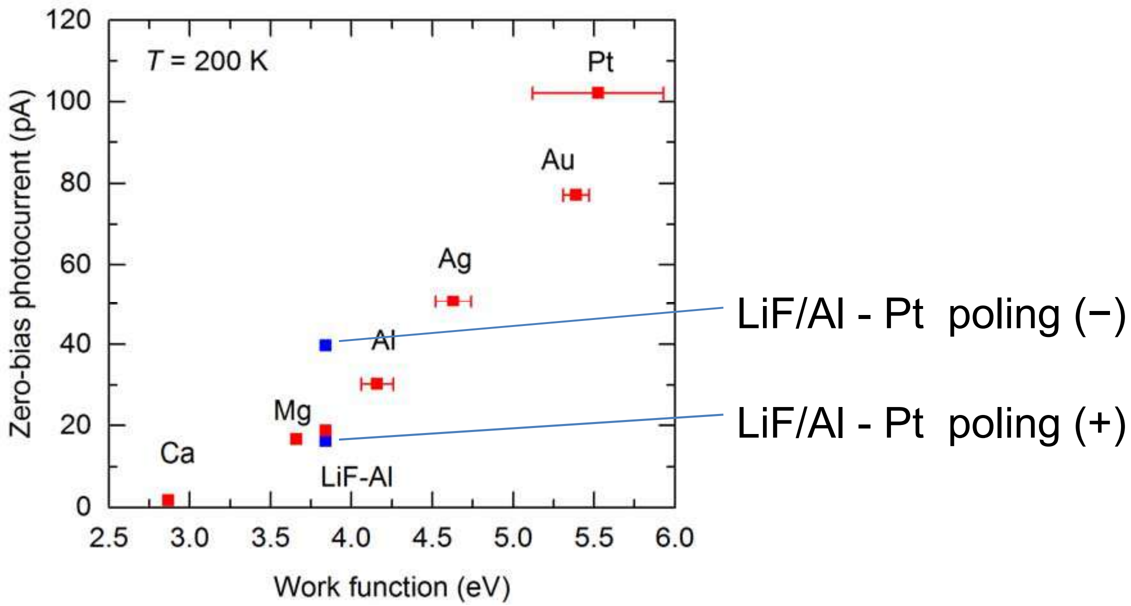


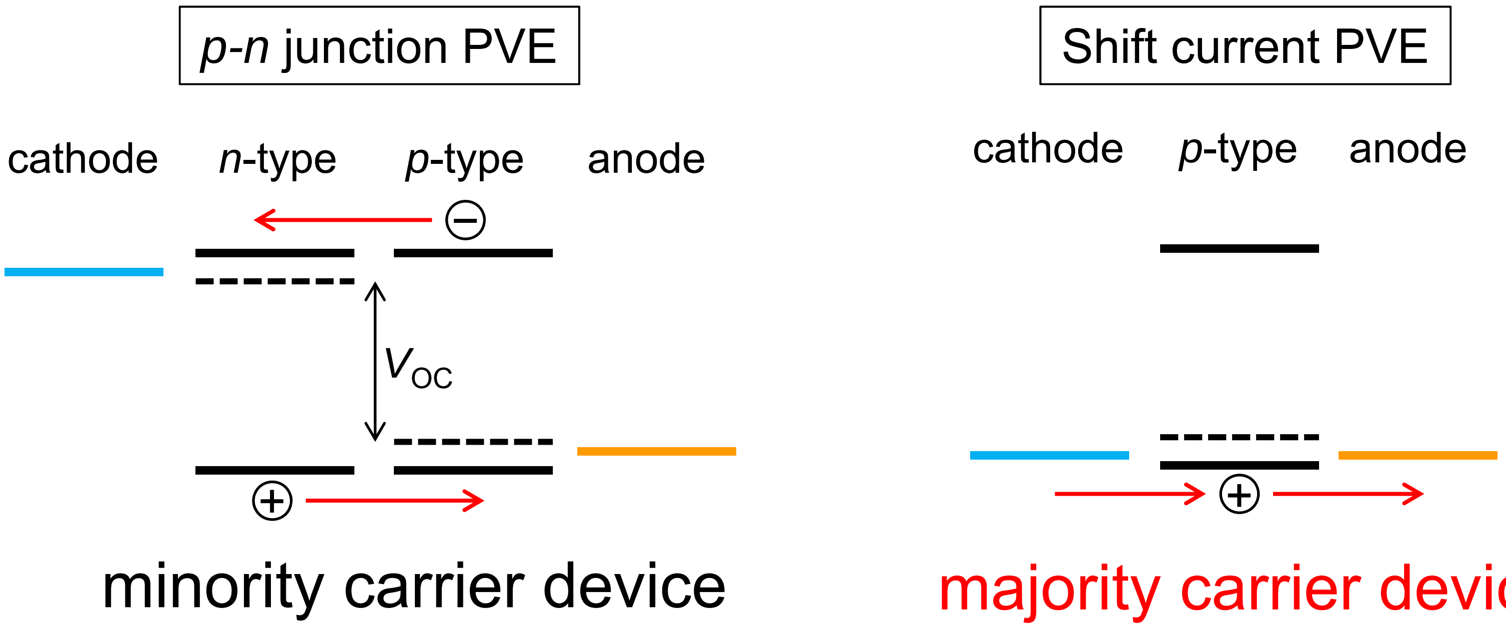


Evidence of majority carrier device

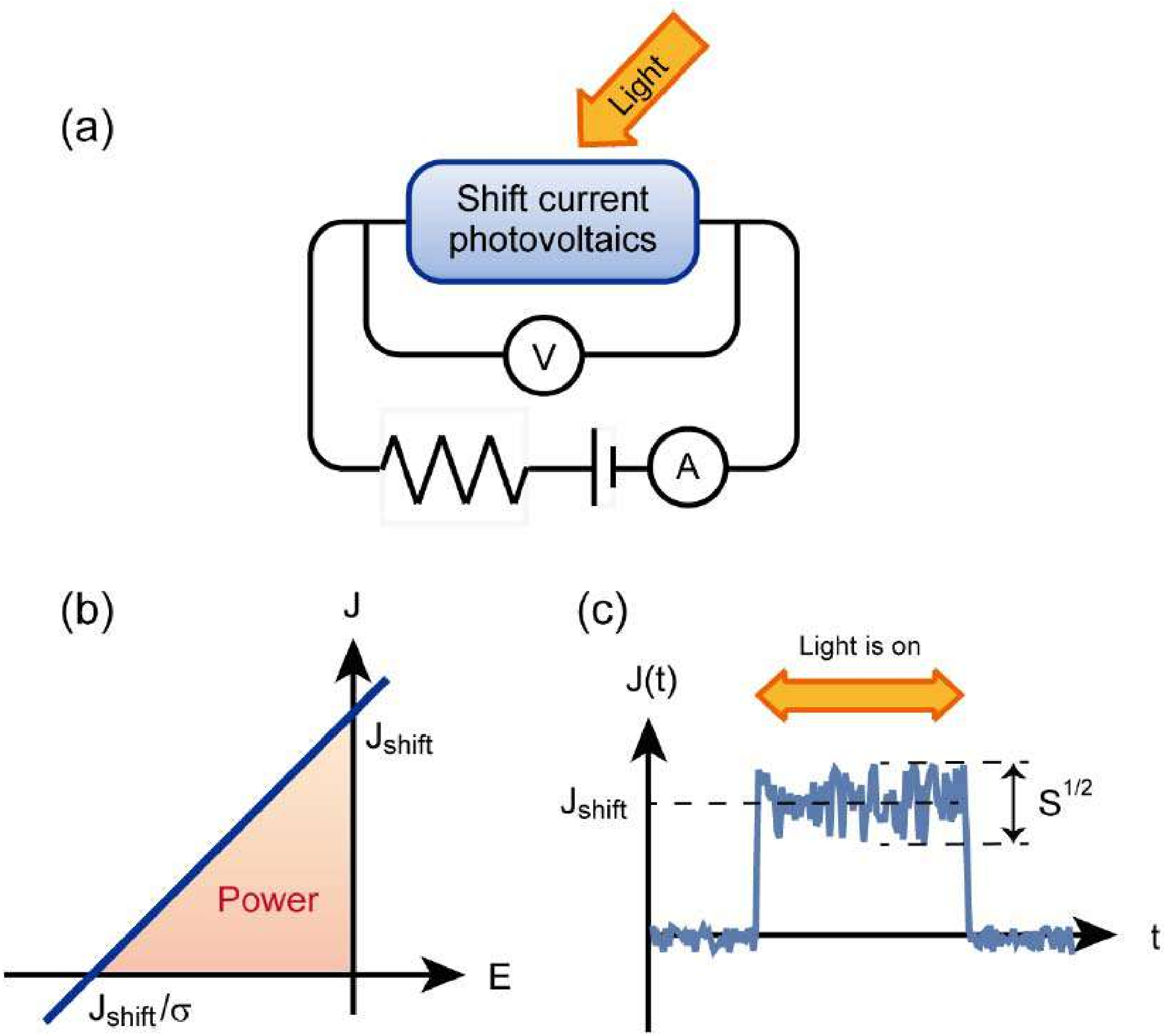
M. Nakamura, MK *et al.*,
Appl. Phys. Lett. **113**, 232901 (2018)







What about low noise photo-detector

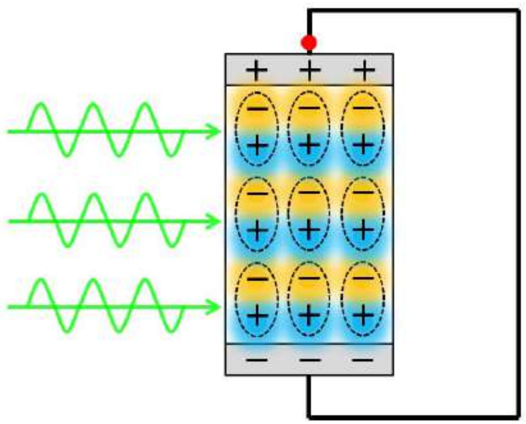


T. Morimoto, M. Nakamura, M. Kawasaki, N. Nagaosa, PRL **121** 267401 (2018)

Summary & perspective

Shift current photo voltaic effect

Quantum mechanical motion of carriers
Polarization by not ions but electrons is the issue
Majority carrier device action
Quantitative agreement with Floquet theory



Things to do

Finding new materials with large effect
Thin film / heterostructures growth
Quantum mechanical nature to be verified