Layer-Resolved Electronic Structure of Oxide Heterostructures using High Energy Photoelectron Spectroscopy

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Funding:

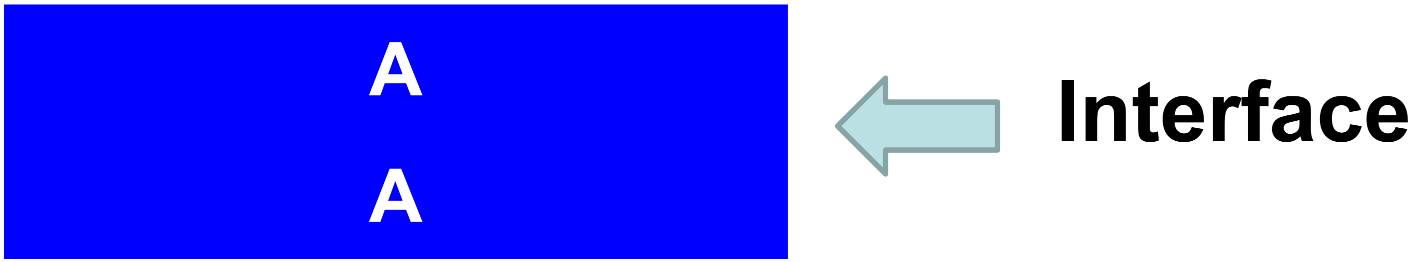
- **Nanomission, SERB, DST, Government of India**
- **Jamsetji Tata Trust**
- **CSIR Bhatnagar Fellowship**

Plan of the talk:

1. Challenges

A heterostructure is defined necessarily by the presence of an *interface*

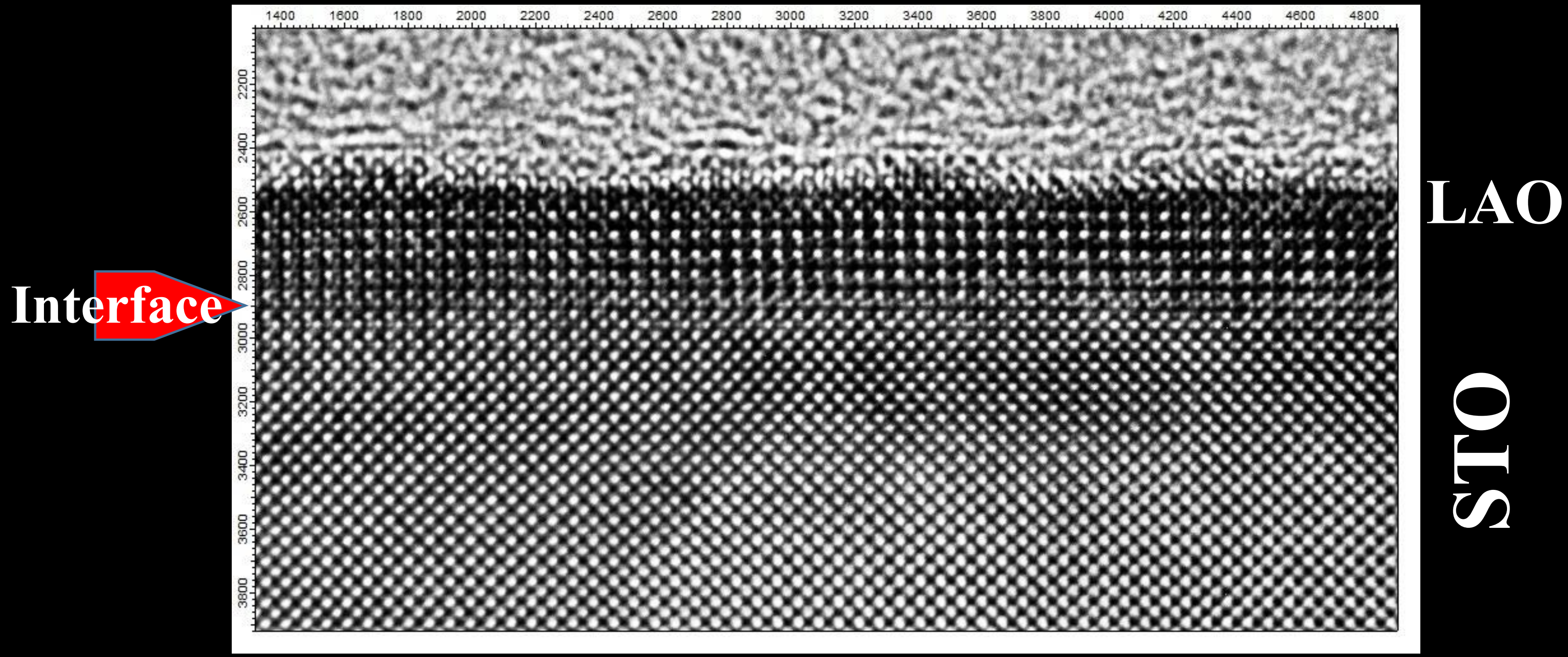
2. The technique employed
3. Our results on $LaAlO_3$-$SrTiO_3$
4. Our results on $SrTiO_3$-$LaTiO_3$ interface



$LaAlO_3$-$SrTiO_3$ (LAO-STO)

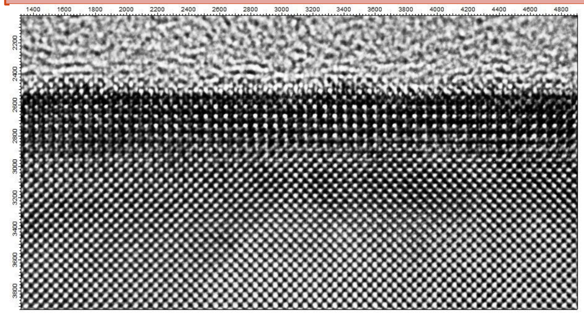
Sumanta Mukherjee et al., Phys Rev B 93, 245124 (2016)

Cross-sectional TEM



Difficulties in investigating interfaces

Interfaces are typically buried at a depth and thin



Volume averaging techniques do not have sufficient sensitivity

Need for a "microscopic" technique,
i.e. with a spatial resolution

Preferably non-invasive also!

How?

High-energy Photoemission
with <u>tunable</u> surface sensitivity

Plan of the talk:

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Plan of the talk:

1. Challenges

2. The technique employed

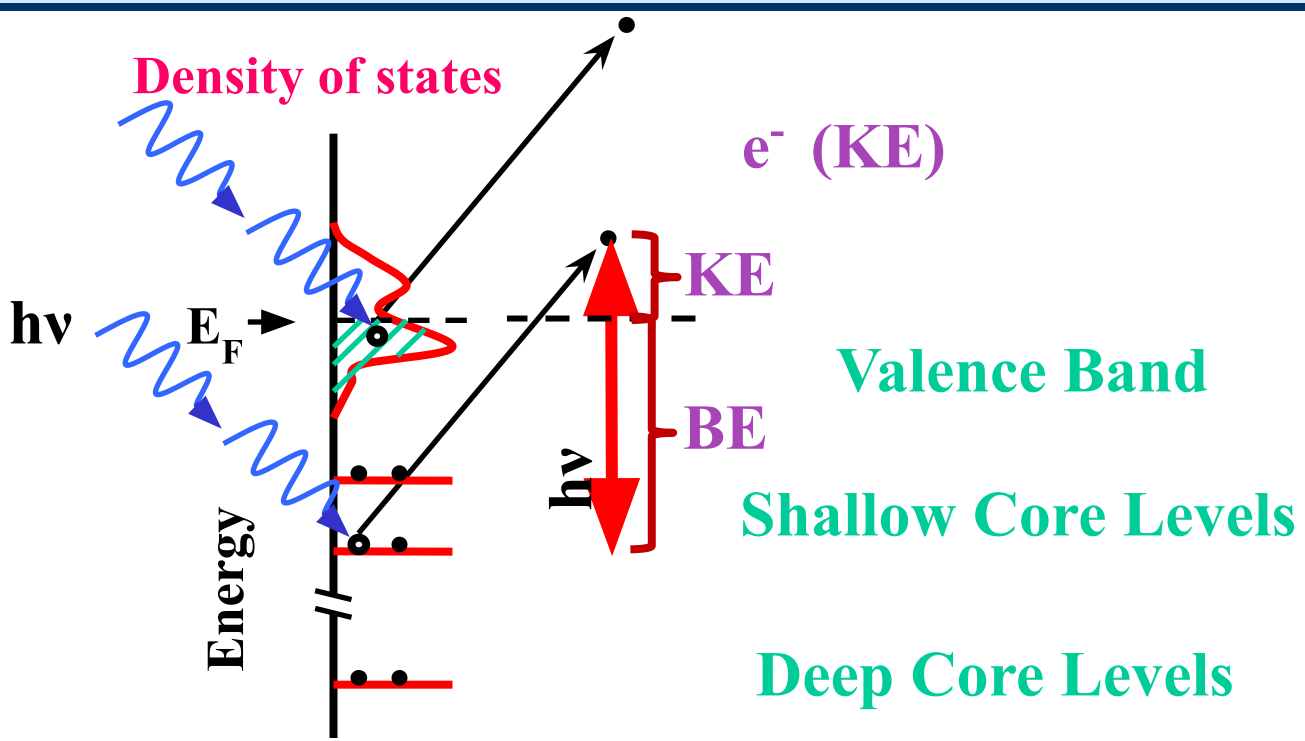
3. Our results on LAO-STO

4. Our results on $SrTiO_3$-$LaTiO_3$ interface

Laboratory and soft x-ray source:
Phys. Rev. Lett. 80, 2885 (1998);
Phys. Rev. B 59, 7473 (1999);

Synchrotron based hard x-ray source:
J. Am. Chem. Soc. 131 (2009) 470;
J. Phys. Chem. Lett. 1 (2010) 2149

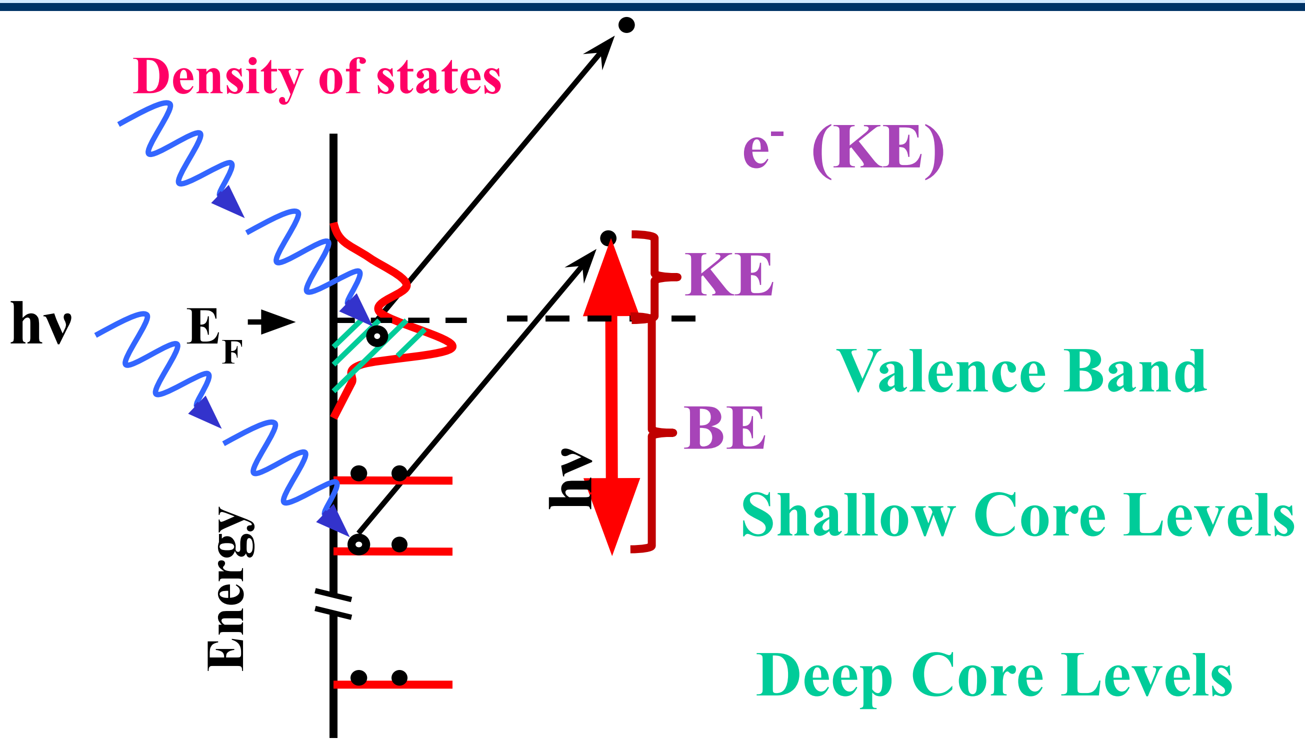
PHOTO ELECTRON SPECTROSCOPIES



Energy Conservation:

hν = KE + BE

PHOTO ELECTRON SPECTROSCOPIES



Energy Conservation:

$$h\nu = KE + BE$$

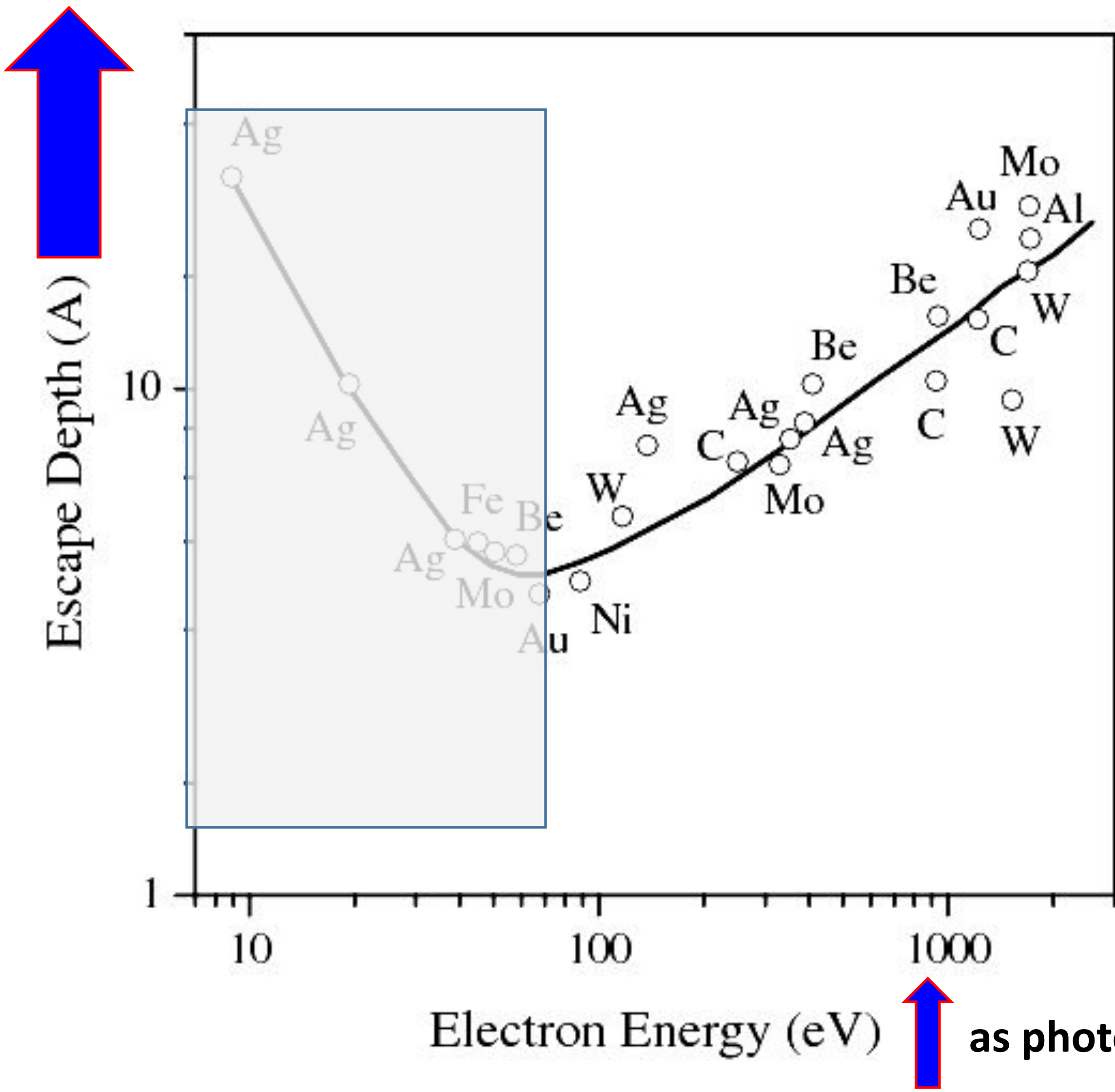
known *measure* *"BE"*

Evaluate

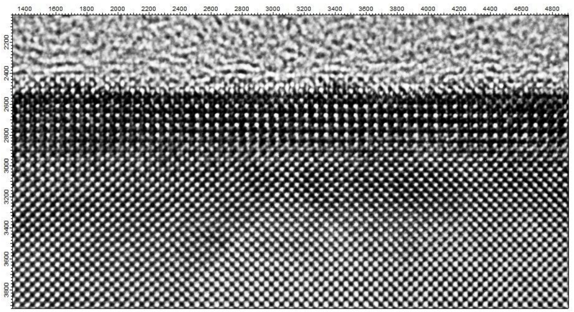
[As KE ≥ 0 ∴ BE ≤ hν]

Also as BE ≥0 ∴ KE ≤ hν

Technique used:
Photoelectron spectroscopy



as photon energy

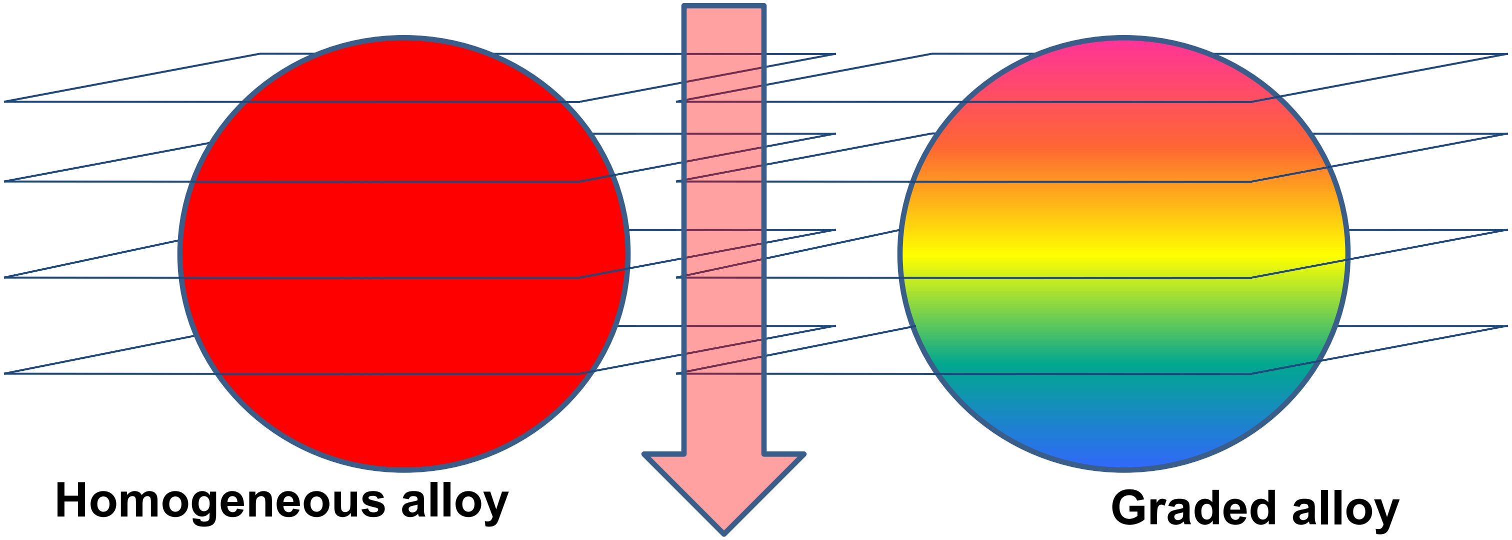


Electron (kinetic) energy

= photon energy – "BE"

Vary **Fixed**

Photon-energy dependent photoelectron spectroscopy



Increase the probing depth

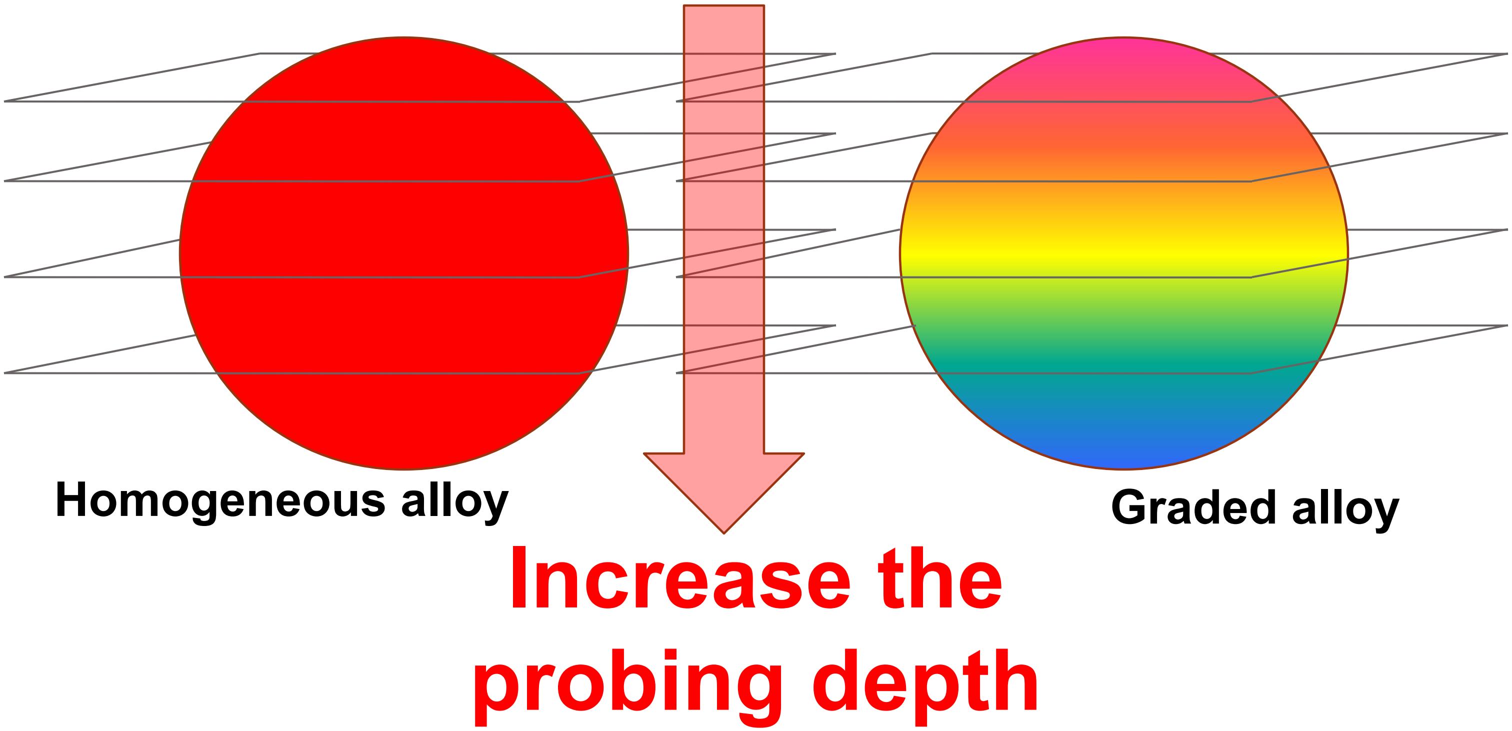
Phys. Rev. Lett. 80, 2885 (1998);
Phys. Rev. B 59, 7473 (1999);
Europhys. Lett. 55, 246 (2001);
J. Appl. Phys. 90, 2504 (2001);
J. Am. Chem. Soc. 131, 470 (2009);
J. Phys. Chem. Lett. 1, 2149 (2010)

Chem. Mater. 25, 1222 (2013)

Do we have the sensitivity?

Really?!

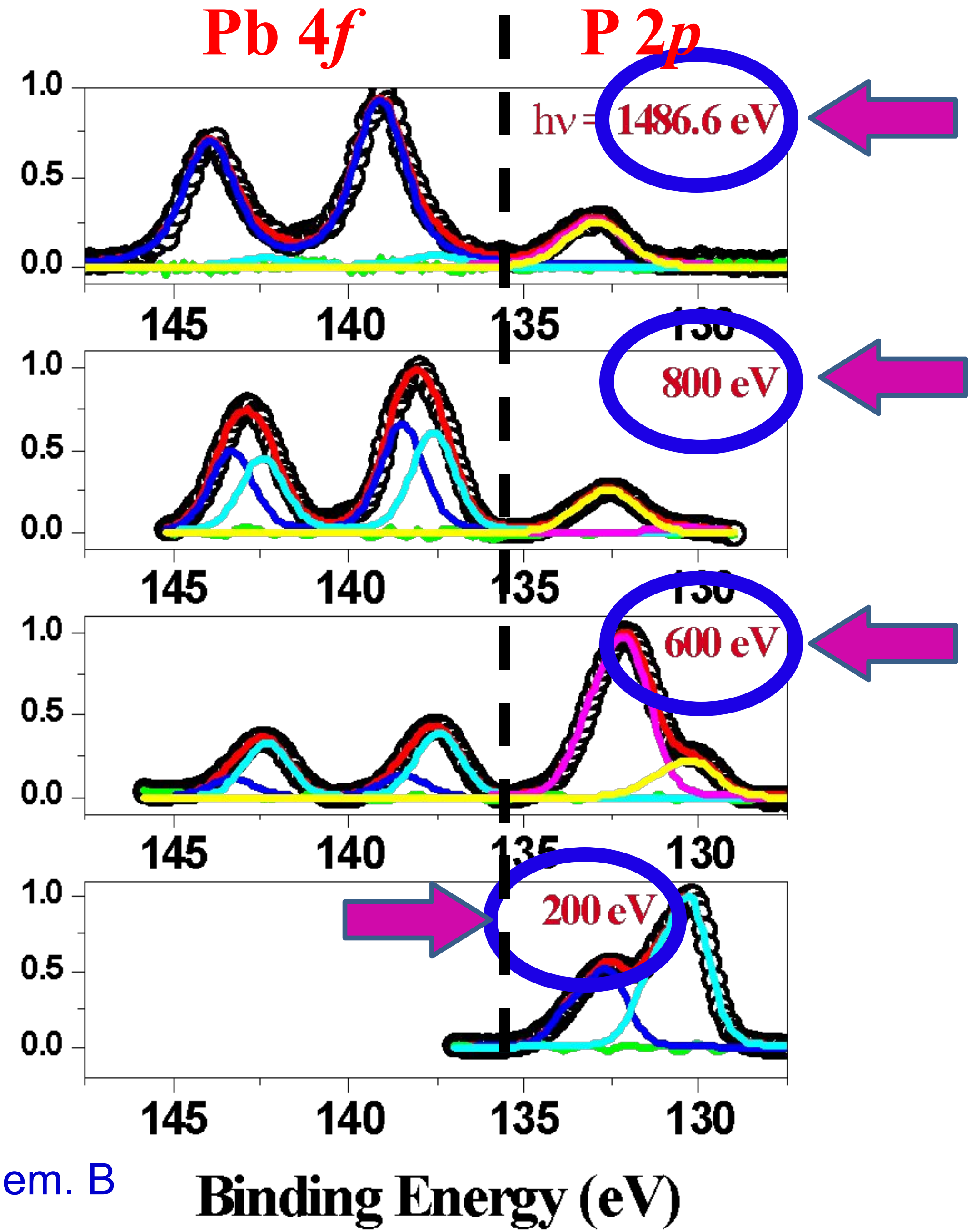
Photon-energy dependent photoelectron spectroscopy



Do we have enough sensitivity?

Do spectra really change with changing probing depth?

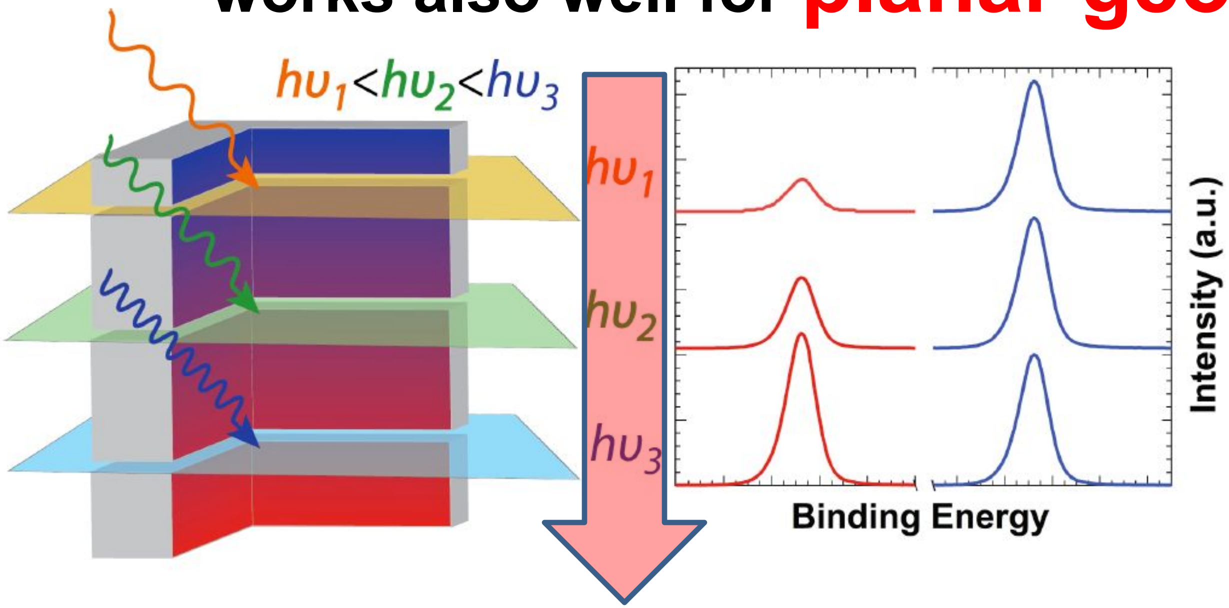
PbSe
QD's



Sapra et al., J. Phys. Chem. B **110**, 15244 (2006).

Photon-energy dependent photoelectron spectroscopy

works also well for **planar geometry**



Increase the probing depth

Chem. Mater. 25, 1222 (2013);
JESRP 200, 332 ((2015) ;
&
Ed. J. Woicik, 2016

Mukherjee et al.,
Phys. Rev. B 91, 085311 (2015)

on Magnetic Tunnel Junctions

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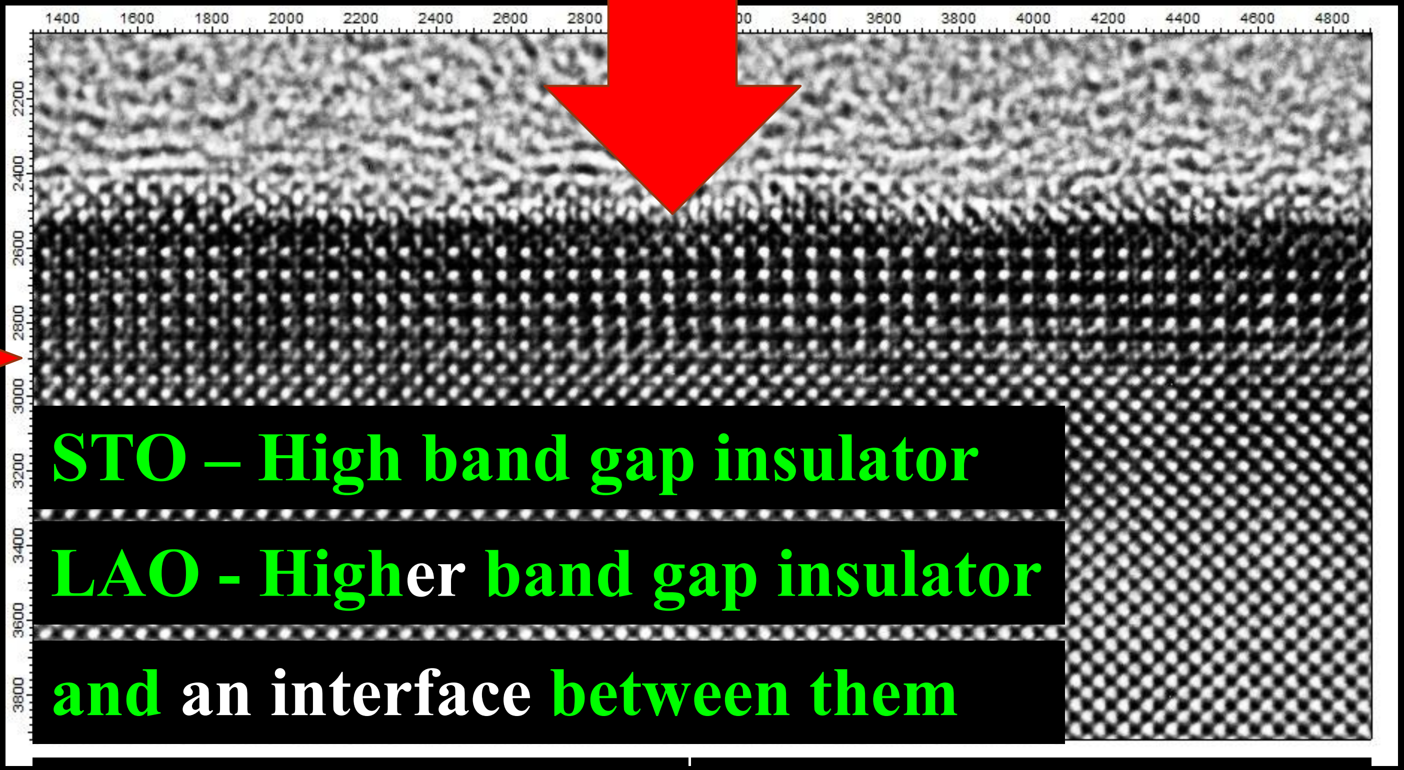
$LaAlO_3$-$SrTiO_3$ (LAO-STO)

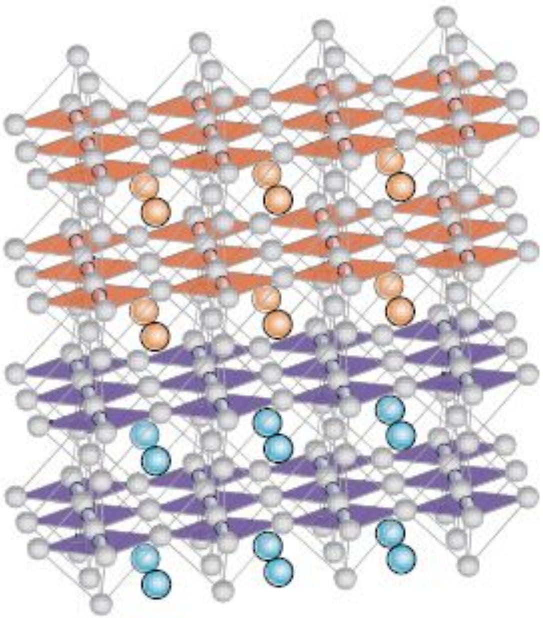
Cross-sectional TEM



High mobility metal Superconductivity

Magnetism

High mobility electron gas at the interface of two insulators



Negatively charged layers (AlO_2)

Positively charged layers (LaO)

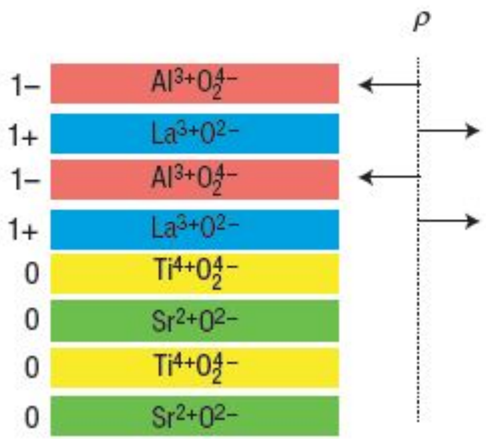
Charge-neutral layers (STO)

A. Ohtomo *et al*, *Nature*, 427, 423, (2004)

Introduction

A 2-D Electron Gas:

Polar discontinuity at the hetero-interface (of polar and non-polar material) results in two dimensional electron gas (2DEG) to avoid polar catastrophe.



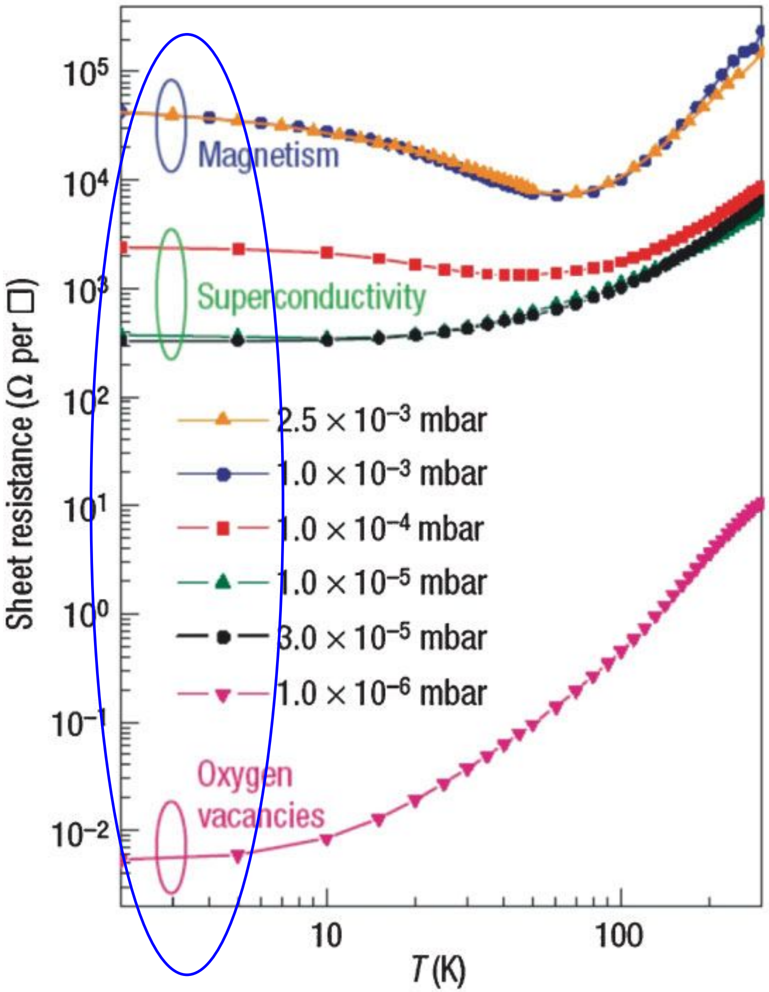
1. N Nakagawa et al. Nature Materials 5, 204-209 (2006)
2. C. Cen et al. Nature Materials 7, 298-302 (2008)

Open issues:

1. **Is polar catastrophe the complete story?**
2. **Role of oxygen vacancies?**
3. **Is there any atomic intermixing across STO-LAO interface?**
4. **What is the thickness and the location of the electron gas?**
5. **Origin of Magnetism and Superconductivity?**

Is polar catastrophe the complete story?

Origin:



- **Tunable Carrier Concentration** **(10^{12} to 10^{17} cm^{-2})**

Polar break-down: ~ 3 x 10^{14} cm^{-2}

- **Oxygen deficiency**

- **Intermixing of La and Sr**

A. Brinkman *et al Adv. Mater.* **21**, 1665**(2009)**
A. Fert *et al. Phys. Rev. Lett.* **98**, 216803 **(2007)**
P. R. Willmott *et al. Phys. Rev. Lett*. **99**, 155502 (**2007**)

How 2-dimensional is 2DEG?

Tens of nm! Cannot be an interface.

Where is it?

Distribution:

Polar catastrophe model: 0.5 nm

H. Hwang *et al. Science* **427**, 423 (2004)

From superconductivity (~150 mK): 10 nm

N. Reyren *et al. Science* **317**, 1196 (2007)

Infra-red ellipsometry: 12 nm

J. Mannhart *et al. Phys. Rev. Lett.*. **104**, 156807 (2010)

CTAFM measurements: 7-25 nm

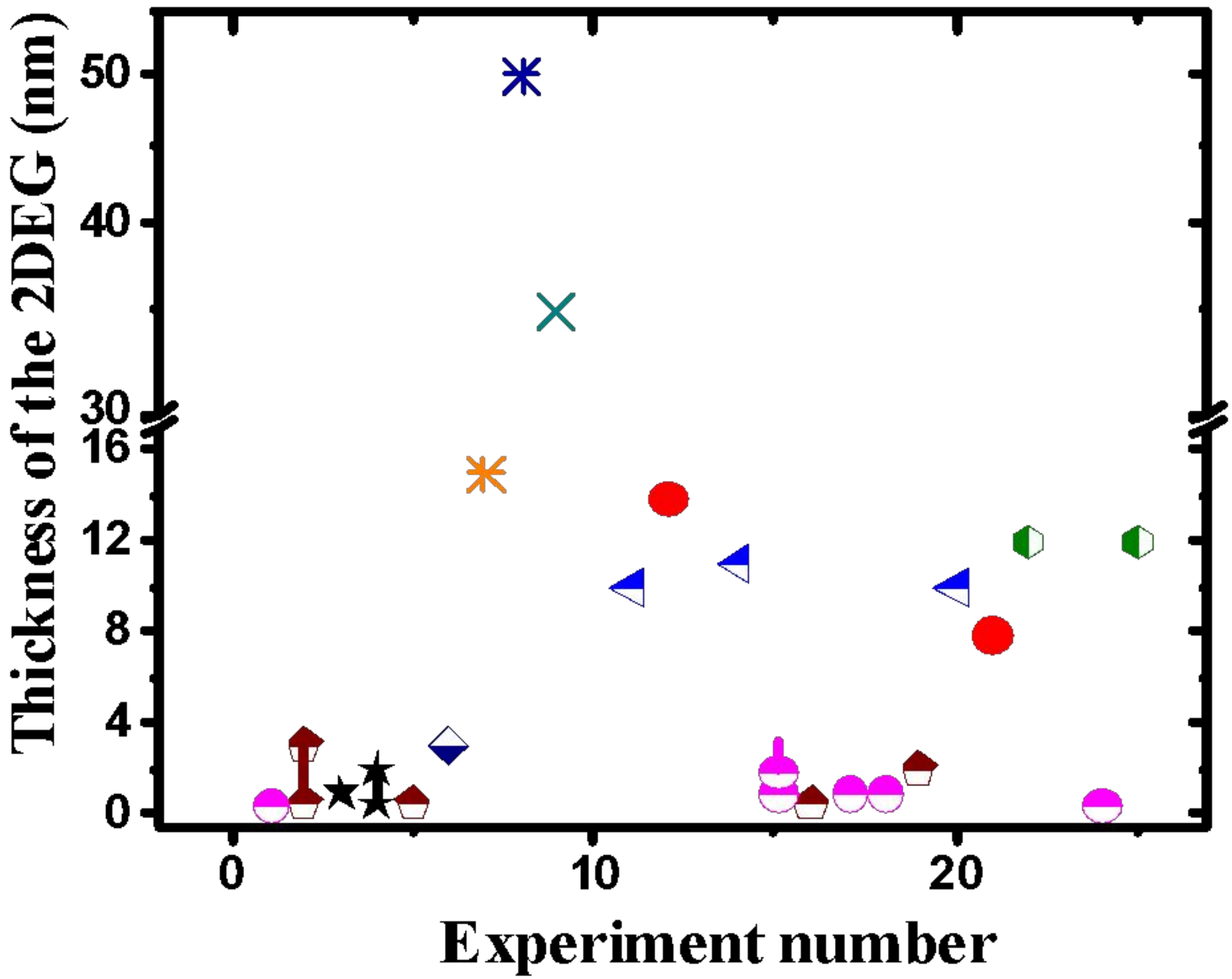
M. Balestic *et al. Nature Mater* **7**, 621 (2008)

Calculation based on formation of oxygen defects: ≥ μm

W. Siemons *et al*, *Phys. Rev. Lett*. **98**, 196802 (2007)

How 2-dimensional is 2DEG?

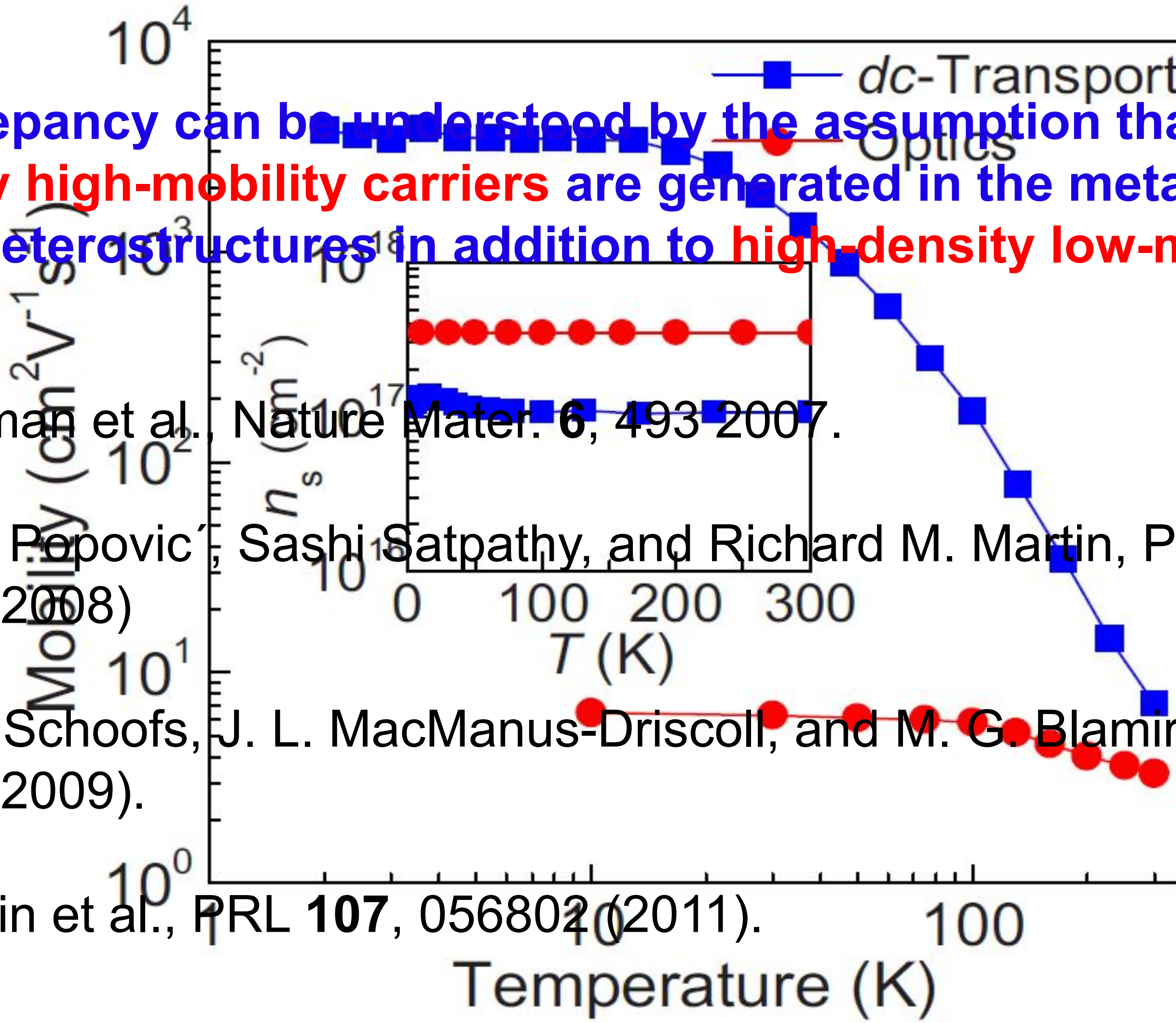
Distribution:



Color+symbol codes represent same types of experiments by different groups

Nature of the conducting carriers

Multiple conducting carriers generated in $LaAlO_3$ /$SrTiO_3$ heterostructures,
S. S. A. Seo et al., Appl. Phys. Lett. **95**, 082107 2009

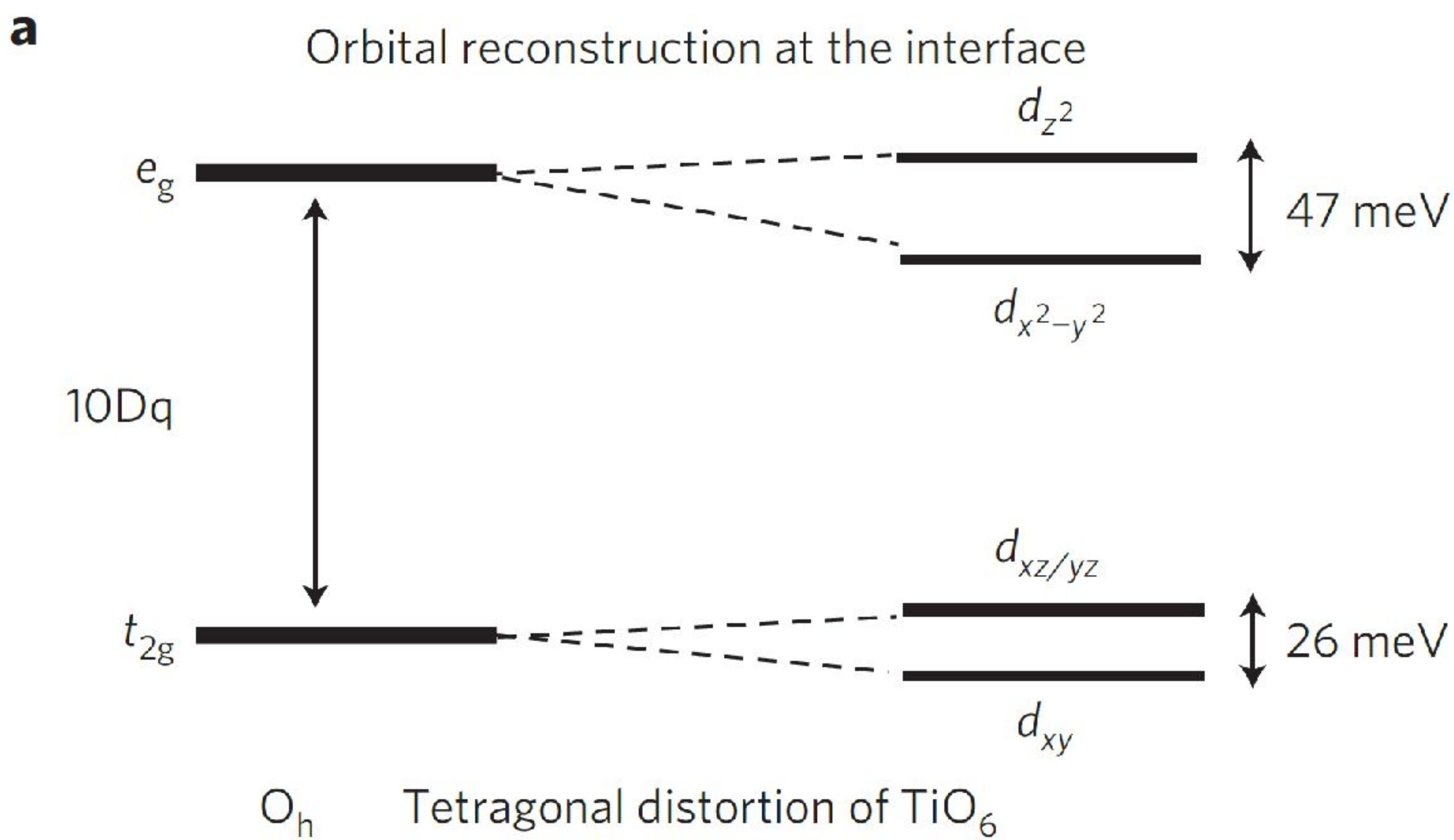


"The discrepancy can be understood by the assumption that low-density high-mobility carriers are generated in the metallic LAO/STO heterostructures in addition to high-density low-mobility carriers."

1. A. Brinkman et al., Nature Mater. **6**, 493 2007.
2. Zoran S. Popovic´, Sashi Satpathy, and Richard M. Martin, PRL 101, 256801 (2008)
3. T. Fix, F. Schoofs, J. L. MacManus-Driscoll, and M. G. Blamire, PRL **103**, 166802 (2009).
4. D. A. Dikin et al., PRL **107**, 056802 (2011).

Lift of degeneracy and different extent of confinements

With Carrier concentration ~ 3 x 10^{14} cm^{-2}



Open issues:

Is polar catastrophe the complete story?

Carrier concentration ~10^{12}-10^{17} cm^{-2} as against ~$3*10^{14}$ cm^{-2}

Role of oxygen vacancies? Intermixing across STO-LAO interface?

The location, thickness and nature of the electron gas?

At the interface (~0.5 nm thick)?

Extension in to the substrate (~10 nm thick)?

Multiple carrier types?

Strongly/weakly correlated?

First, we probed the core levels

Bengaluru:

Sumanta Mukherjee

Banabir Pal

Debraj Choudhury

Sumanta Mukherjee et al.,
Phys Rev B 93, 245124 (2016)

Indranil Sarkar

Wolfgang Drube (PETRA)

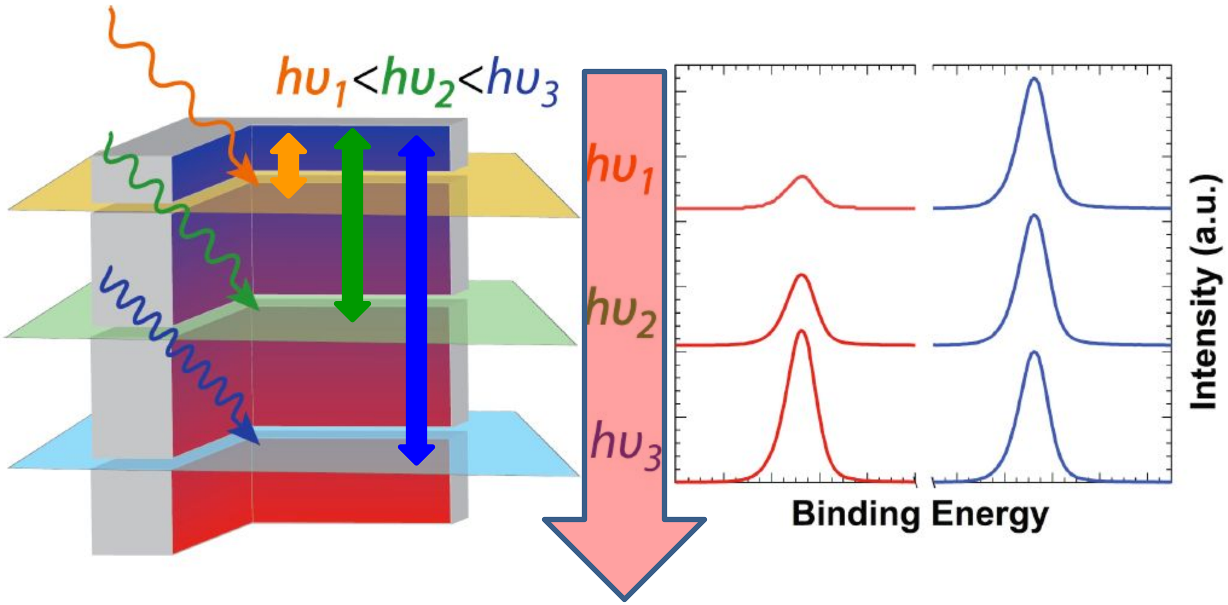
Mihaela Gorgoi (BESSY)

Olof Karis (Uppsala)

Hide Takagi (MPI, Stuttgart)

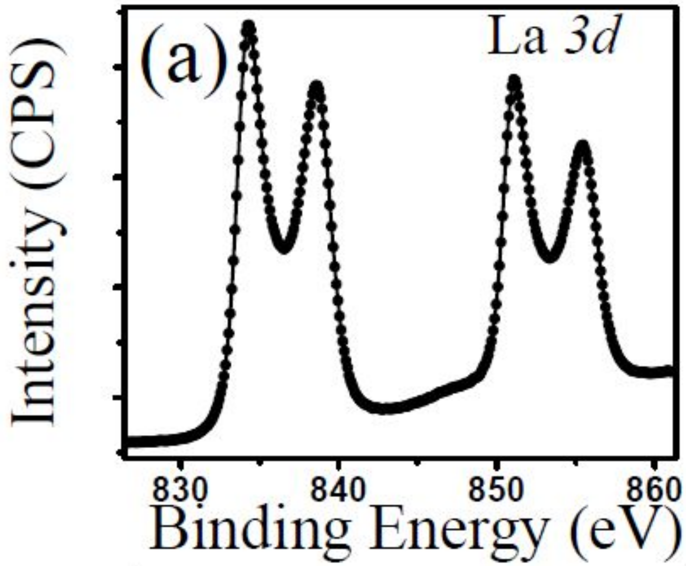
Jobu Matsuno (Riken)

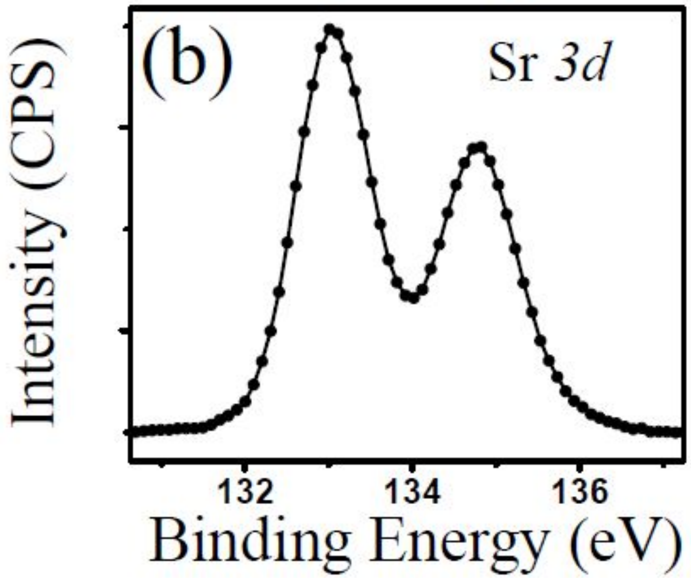
Photon-energy dependent photoelectron spectroscopy

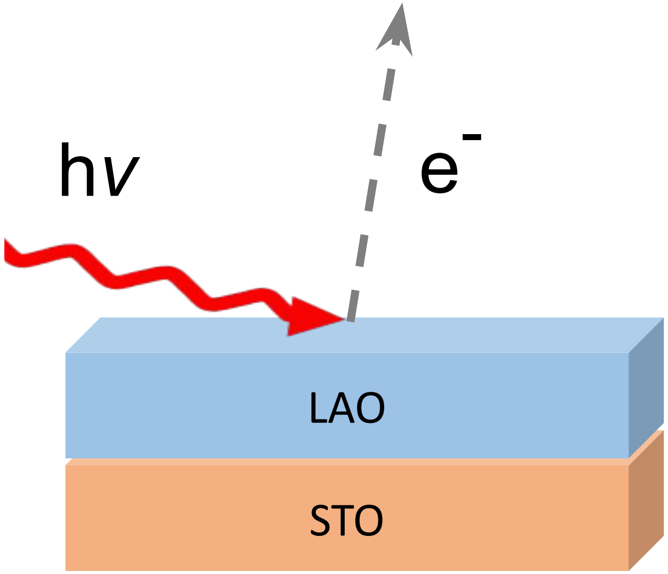


Increase the probing depth

Analysis of La/Sr photoemission intensities

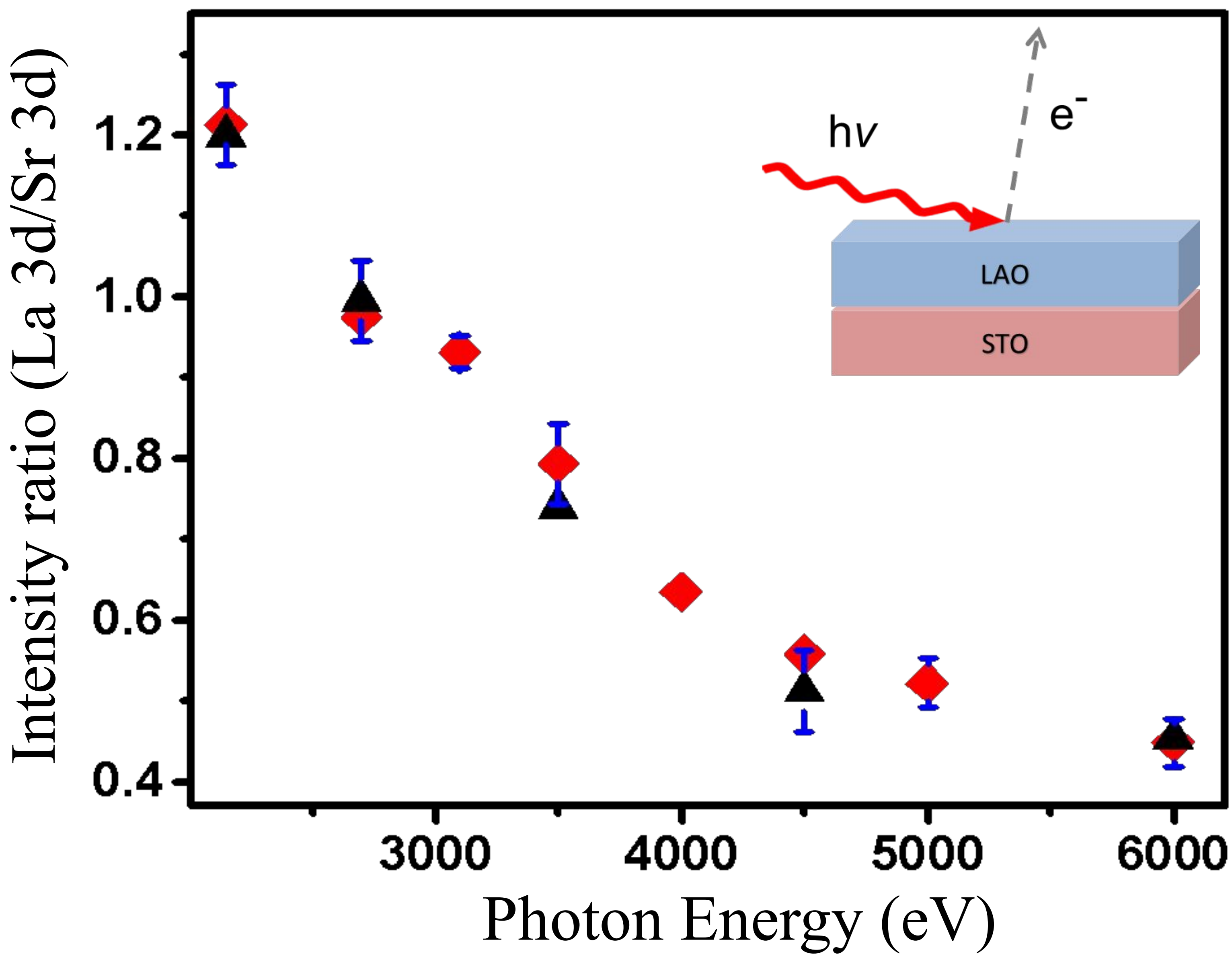




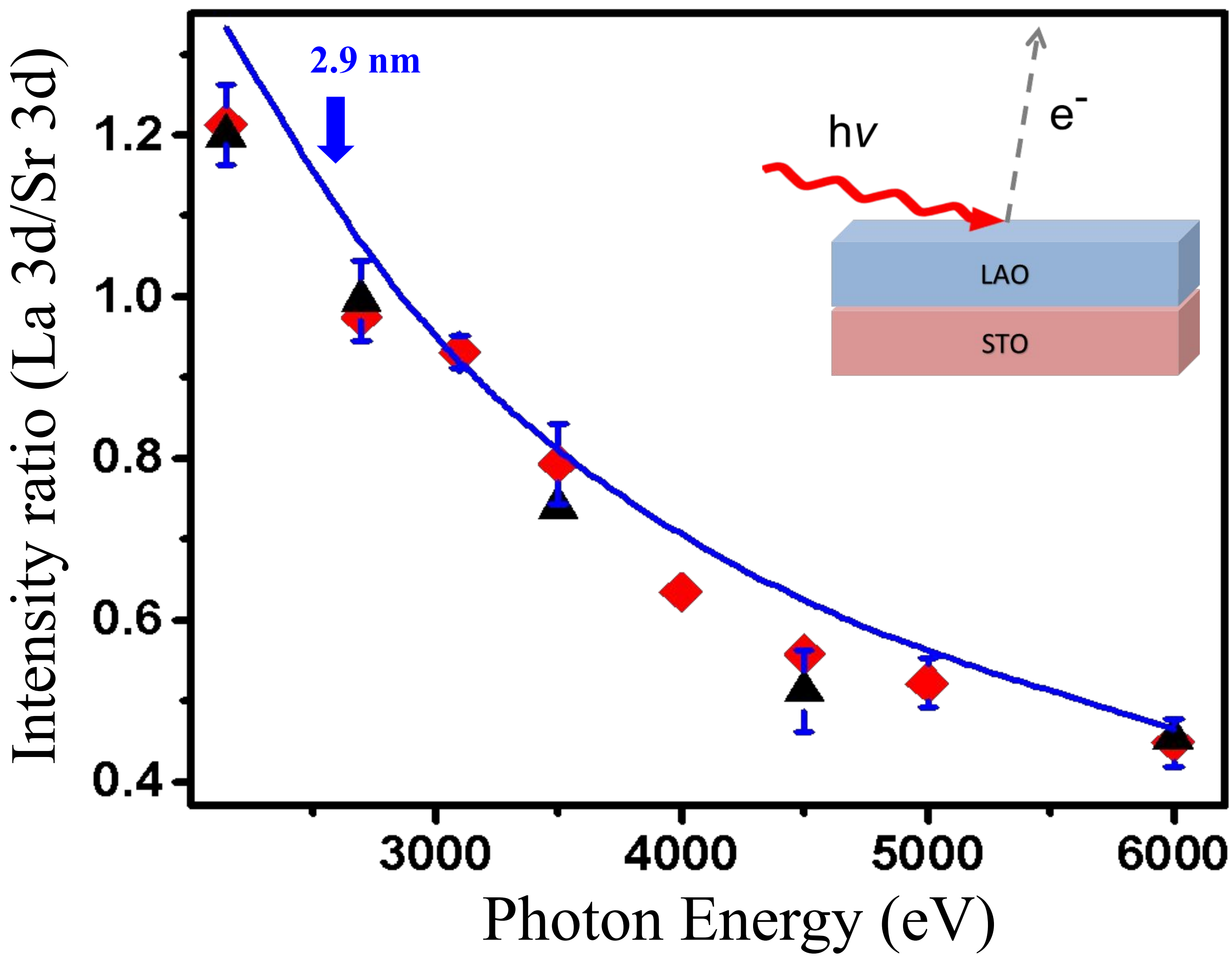


With hv ⇑,
La/Sr ⇓.

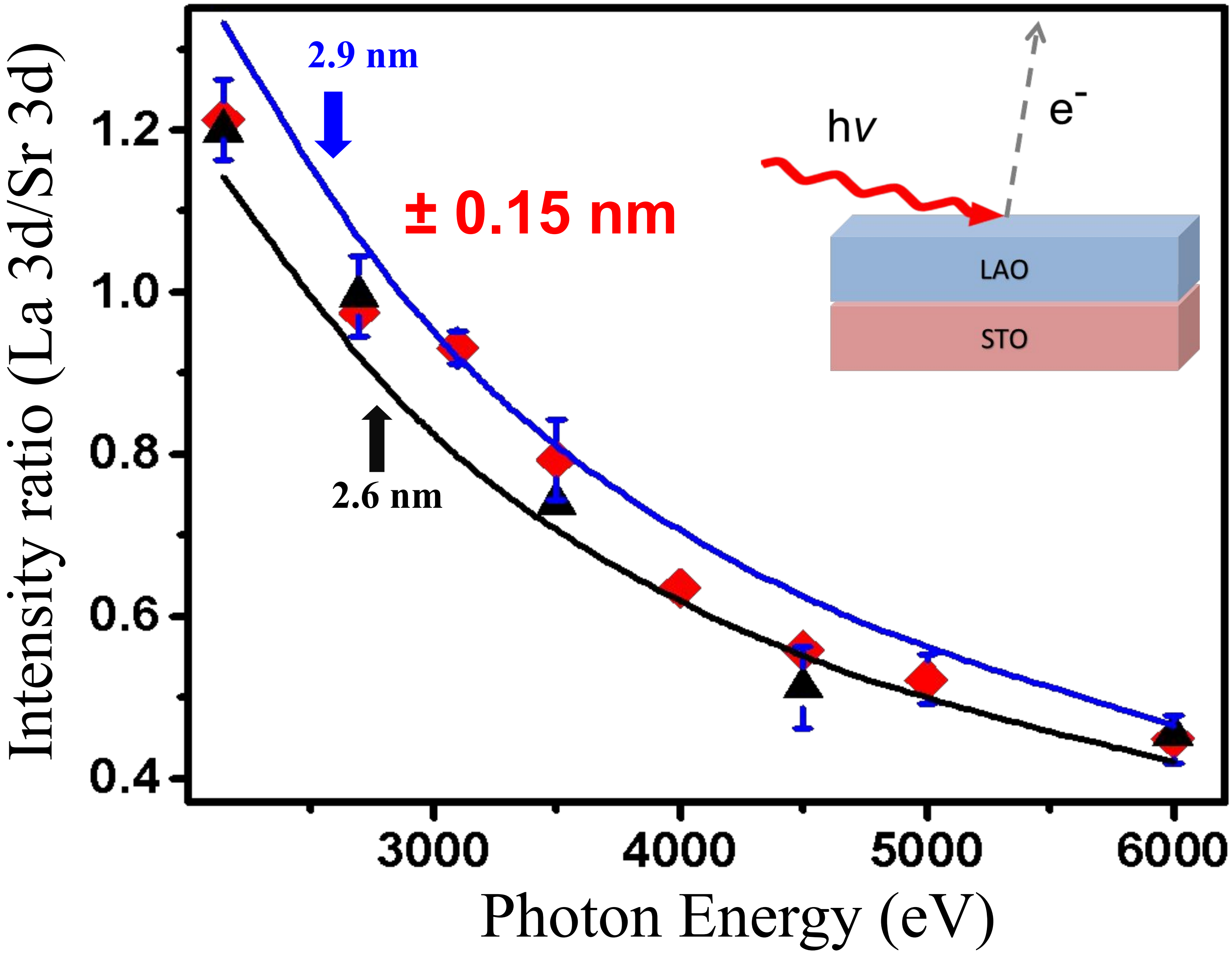
Simulation of La/Sr ratio for different thickness of LAO layer



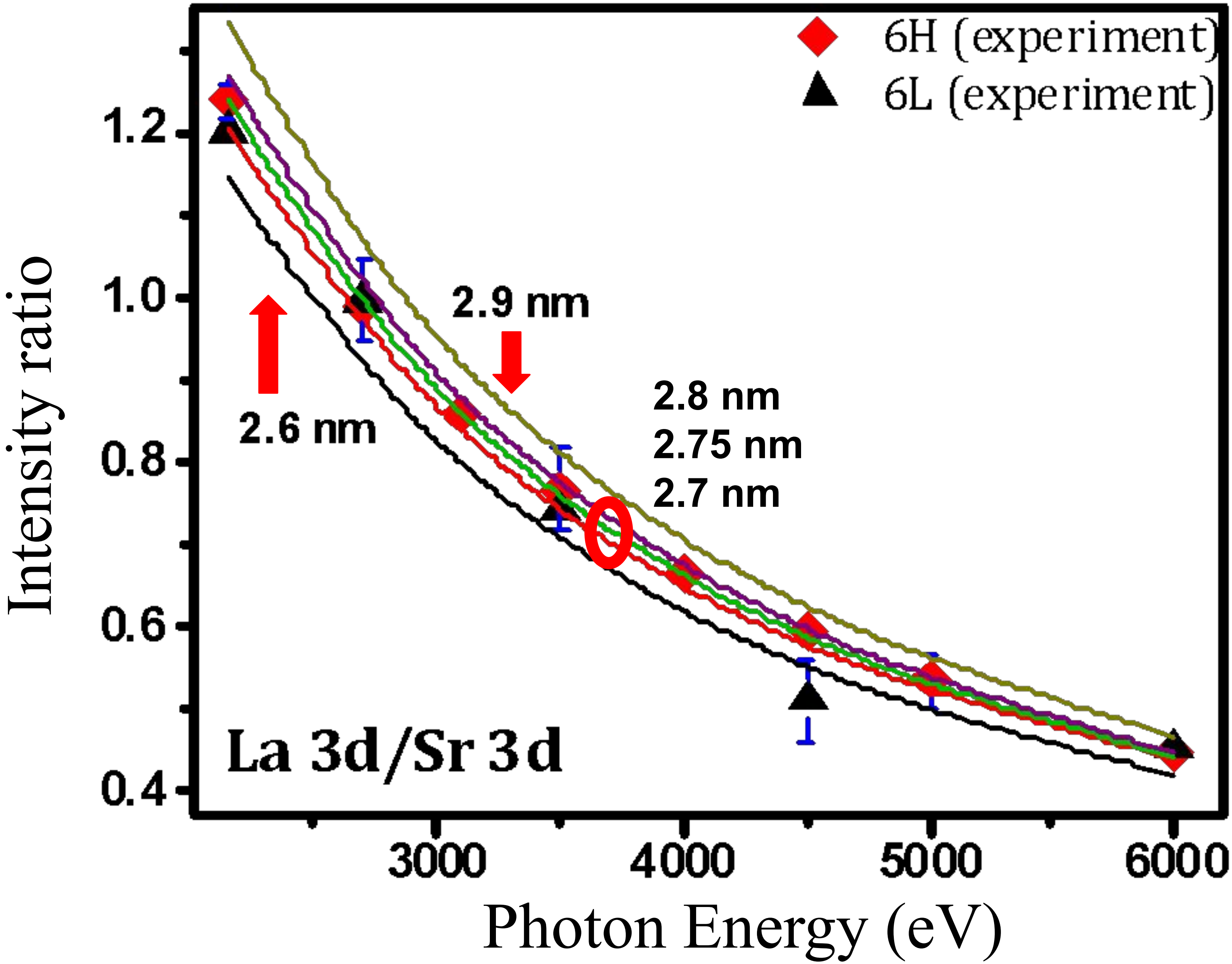
Simulation of La/Sr ratio for different thickness of LAO layer



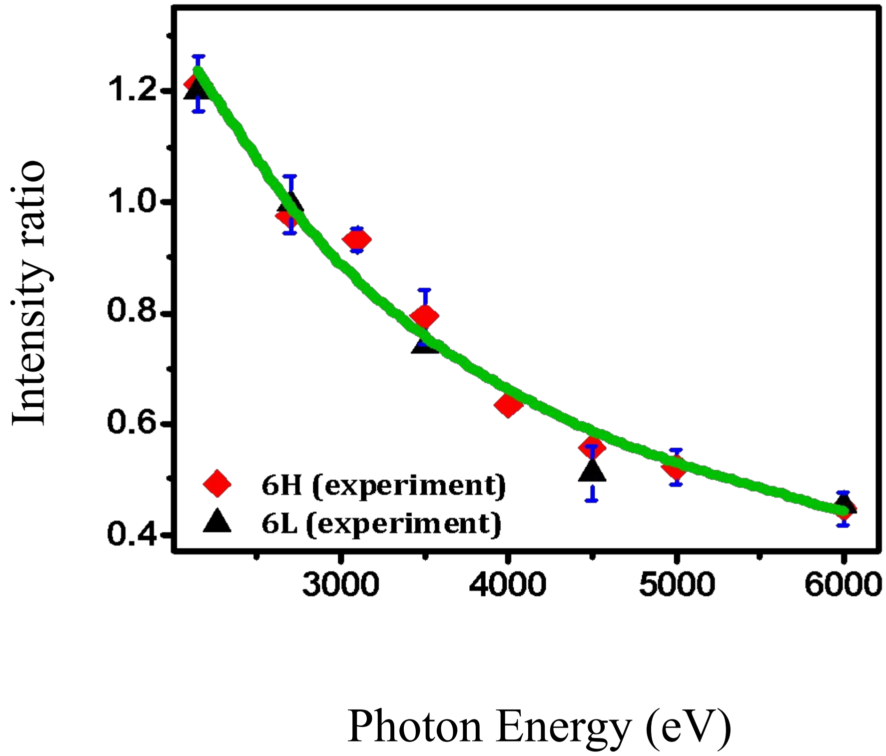
Simulation of La/Sr ratio for different thickness of LAO layer



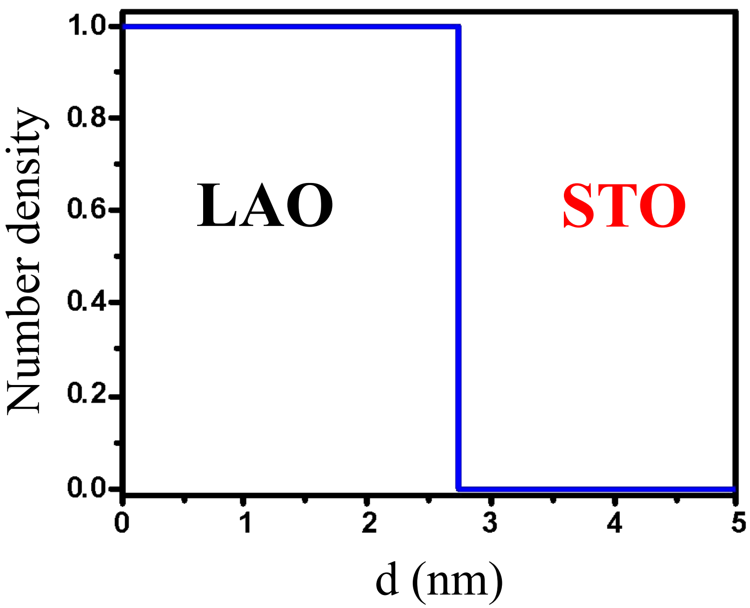
Fitting of La/Sr ratio for different thickness of LAO layer



Fitting of La/Sr ratio



Sharp Interface

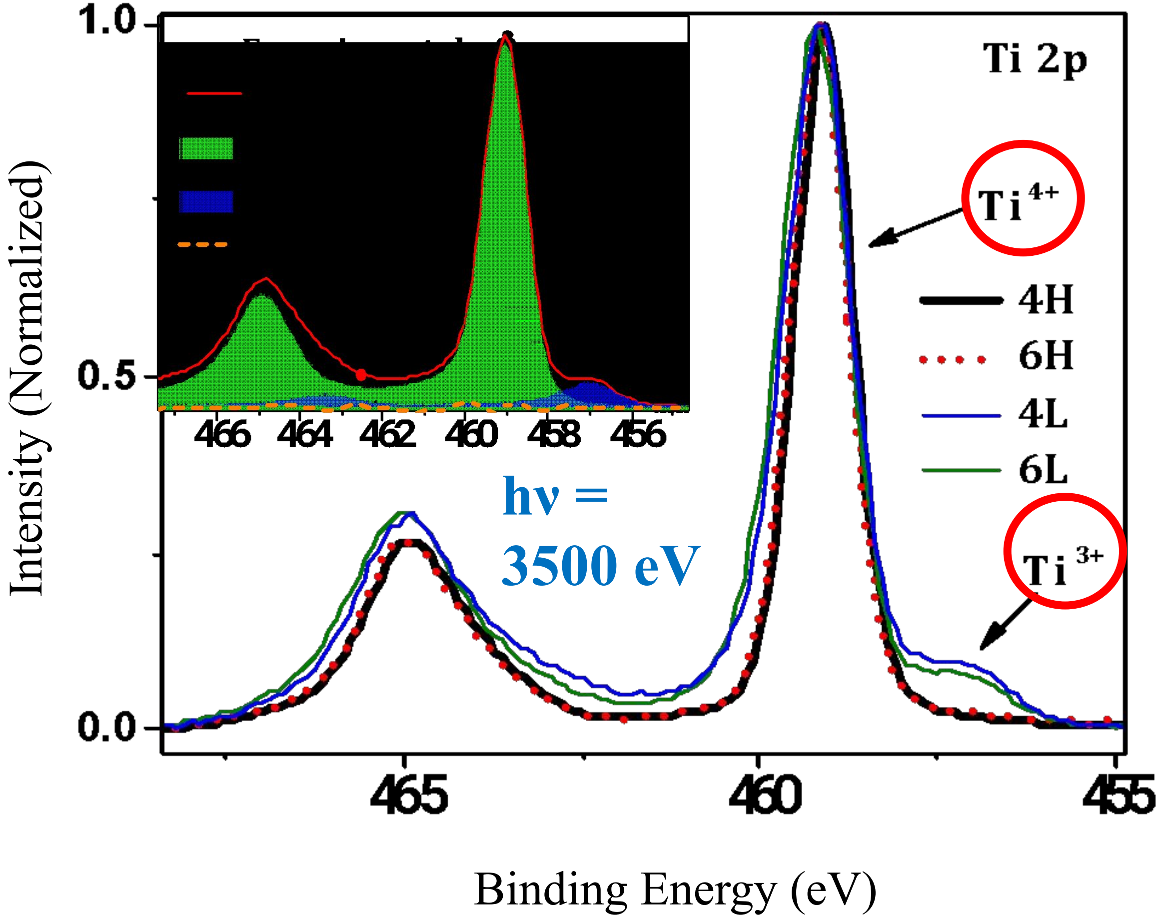


LAO thickness = 2.75 nm

❖ **Minimal (< ~1 uc) mixing between La and Sr**

Ti 2p photoemission from 4 samples

Disclaimer: We can only probe LAO-STO in the relatively high charge carrier density (> 5 . 10^{13} cm^{-2}) limit.



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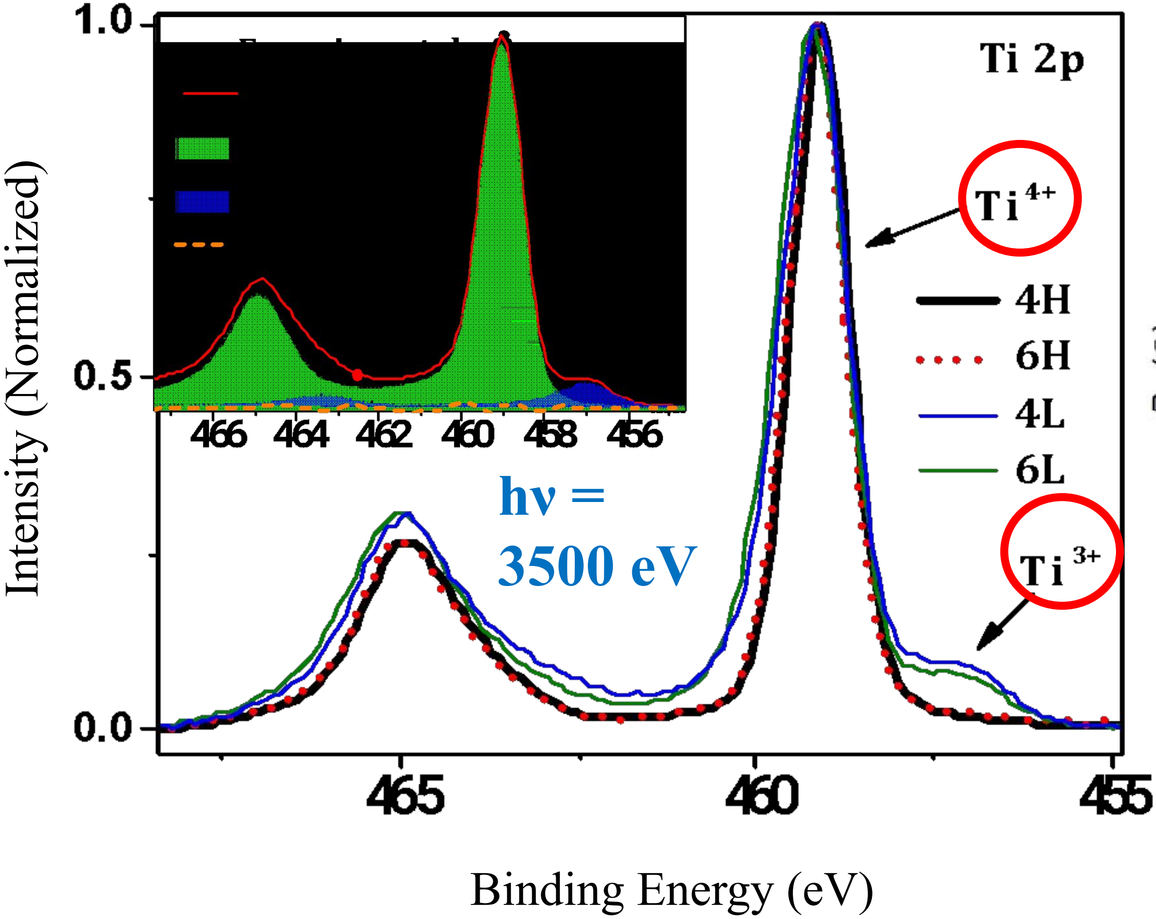
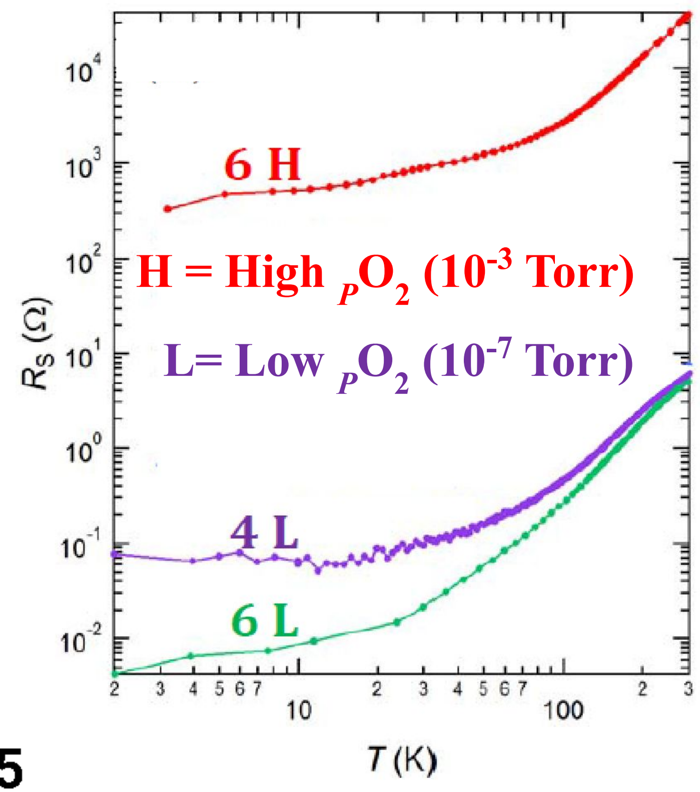
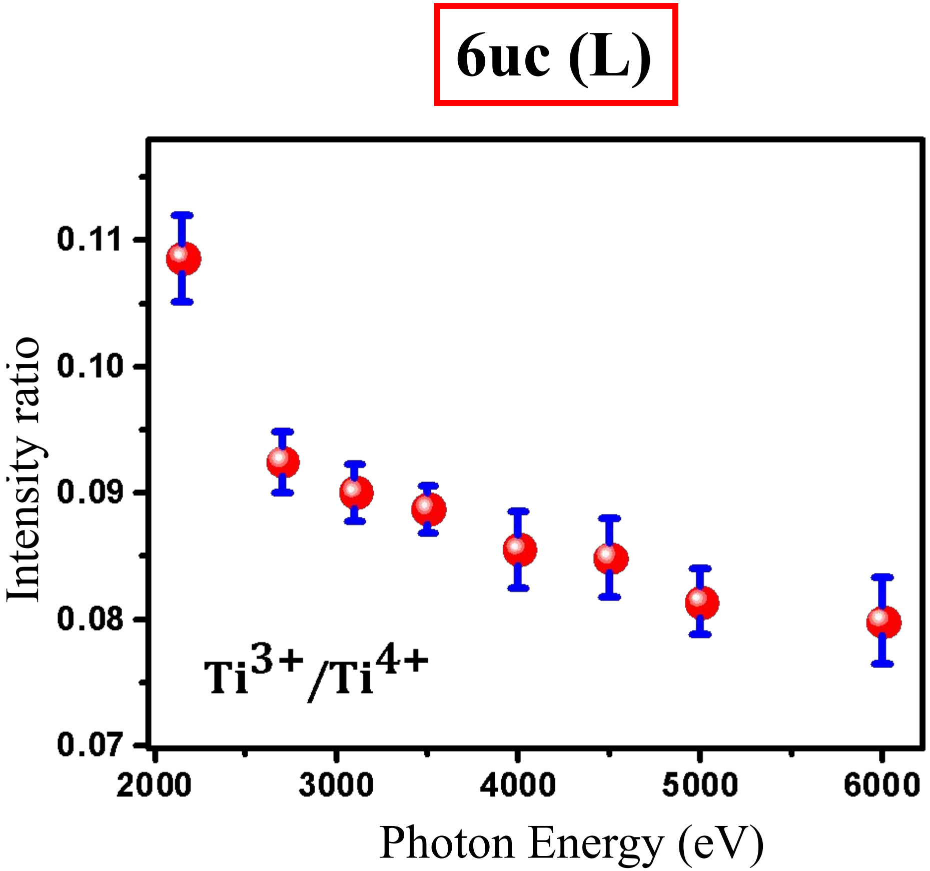
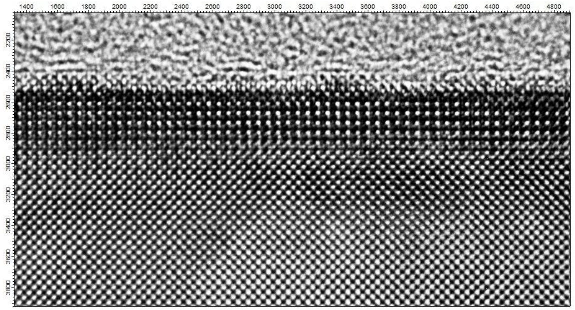




Ti 2p spectra from low pressure (L) samples





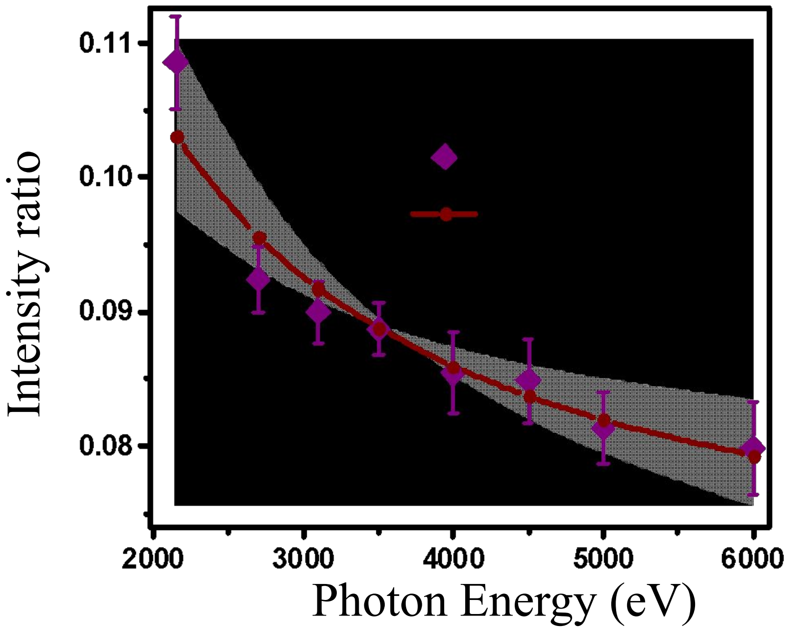
Ti^{3+} is closer to the interface

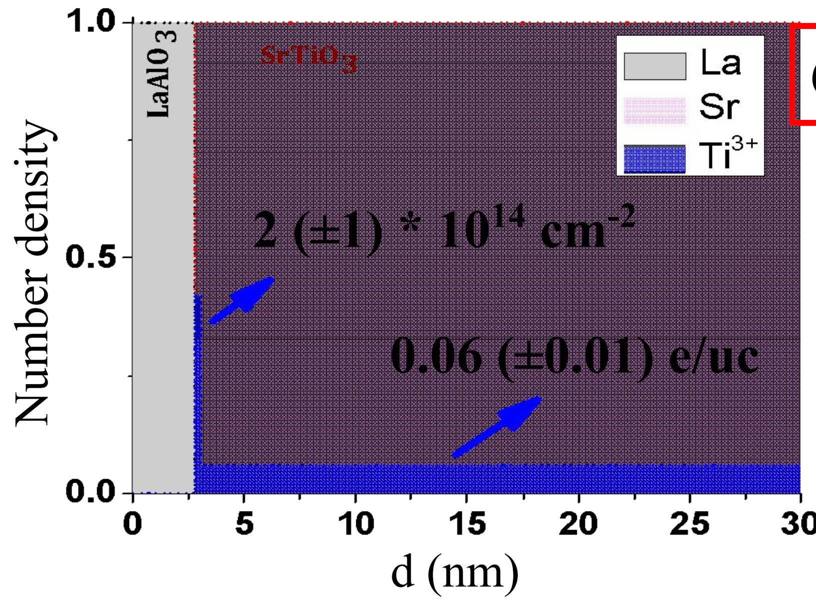
Fitting of Ti 2p spectra (With one distribution of Ti^{3+})

6uc (L)

Does not fit the experimental ratio

Best Fit





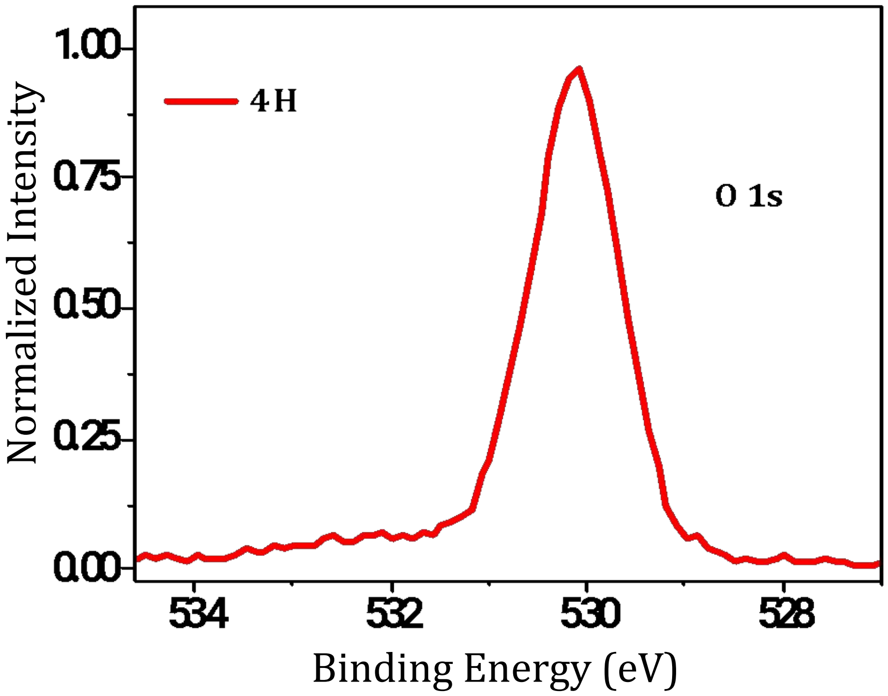
6uc (L)

What is the origin of the electron distributions?

Polar break-down, Band Bending, Doping??

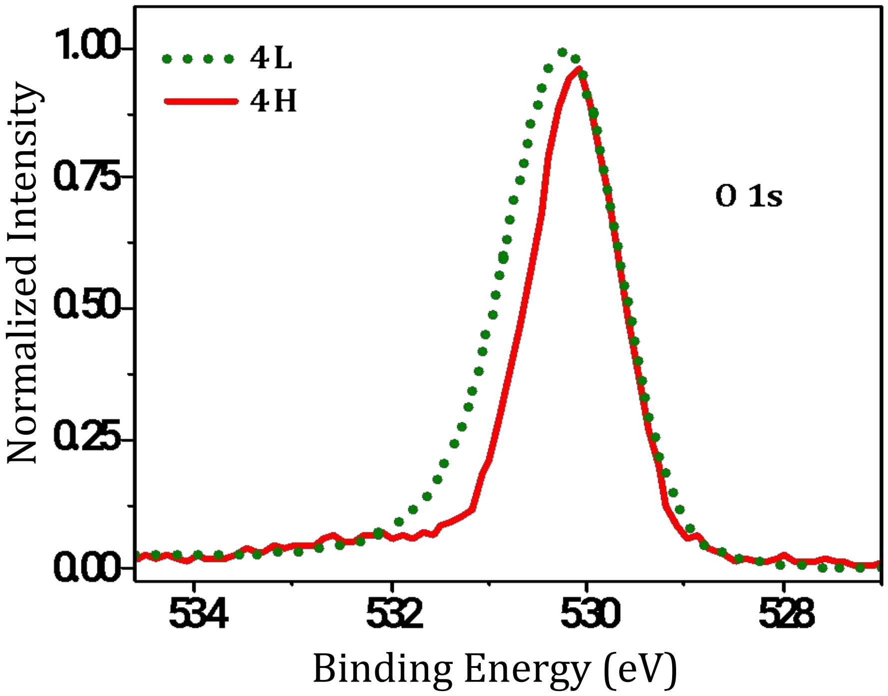
What is the oxygen vacancy doing? Where is it?

O 1s spectra



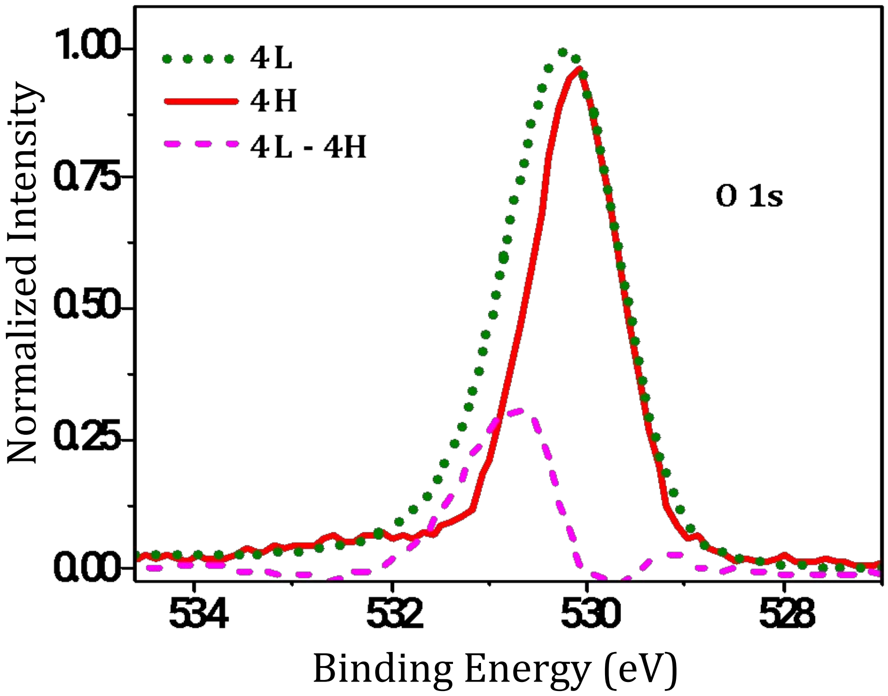
1.00
0.75
0.50
0.25
0.00
Normalized Intensity
4H
O 1s
534
532
530
528
Binding Energy (eV)

O 1s spectra



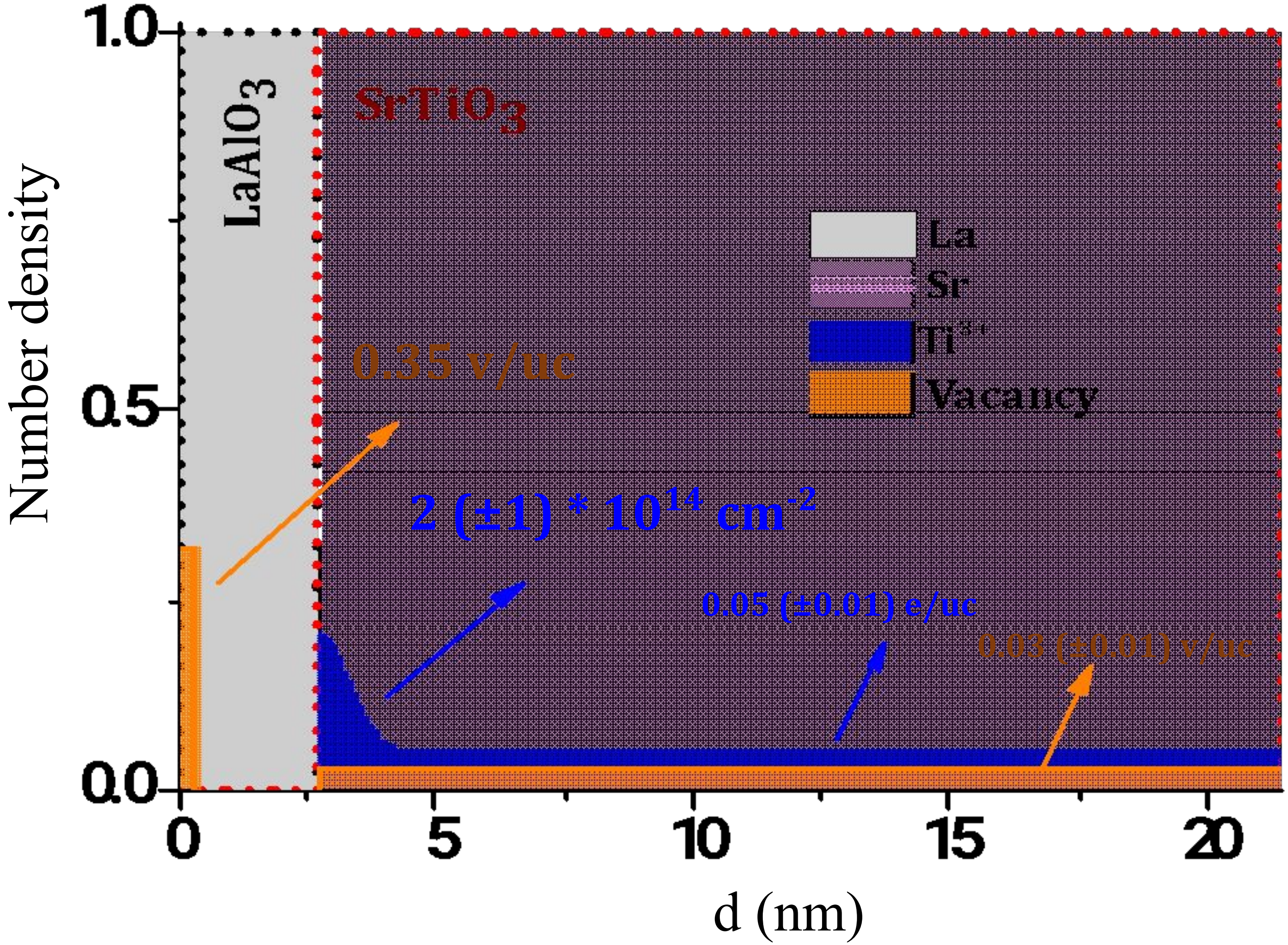
4L
4H
O 1s
Normalized Intensity
1.00
0.75
0.50
0.25
0.00
534
532
530
528
Binding Energy (eV)

O 1s spectra

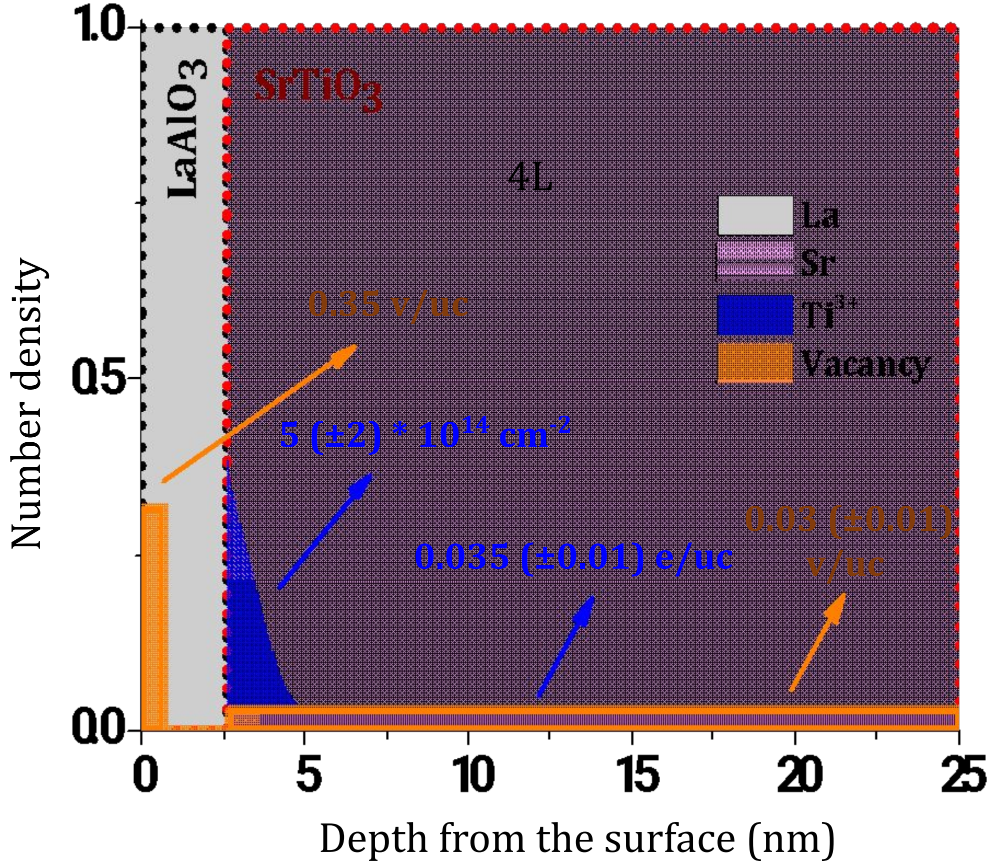


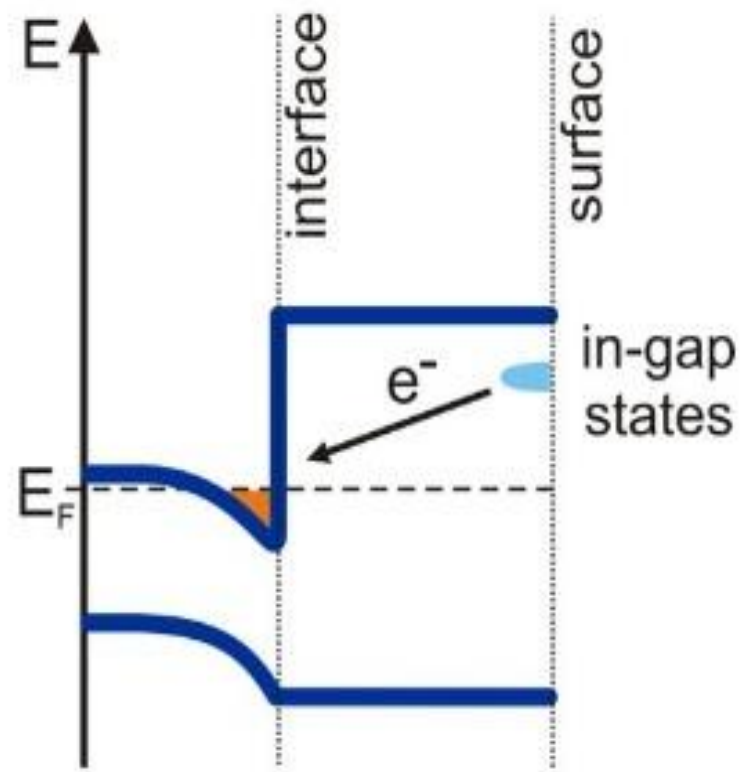
4L
4H
4L - 4H
O 1s
Normalized Intensity
1.00
0.75
0.50
0.25
0.00
534
532
530
528
Binding Energy (eV)

The interface structure: 6uc (L)



The interface structure: 4uc (L)





The deeper distribution is related to oxygen vacancies

Transfer of electrons from surface oxygen 2p band and band bending at the interface is possibly the origin of the interface carriers

Bristowe et al., PRB **83, 205405 (2011)**
Li et al., PRB **84, 245307 (2011)**

Electronic structure: $LaAlO_3$-$SrTiO_3$ Valence band

Bengaluru:

Sumanta Mukherjee

Banabir Pal

Indranil Sarkar

Wolfgang Drube

Ambroise van Roekeghem

Silke Biermann

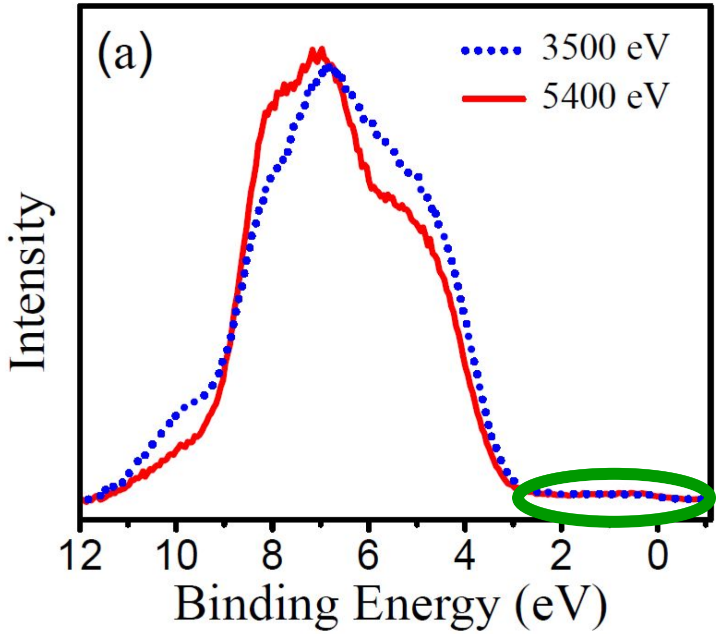
Hide Takagi

Jobu Matsuno

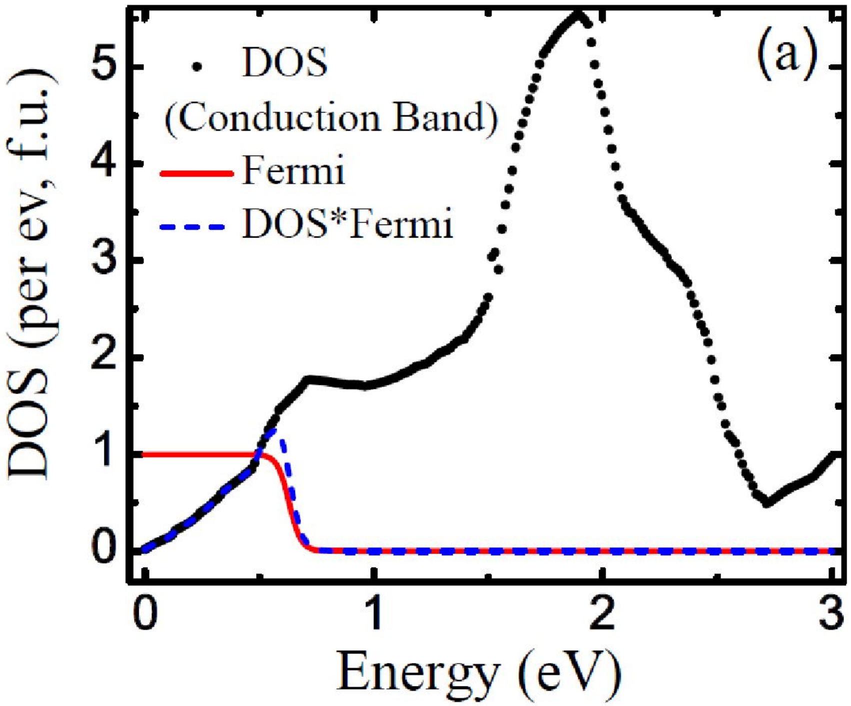
Sumanta Mukherjee et al.,
EPL 123, 47003 (2018).

How correlated each of these electron distributions are?

Valence Band Study

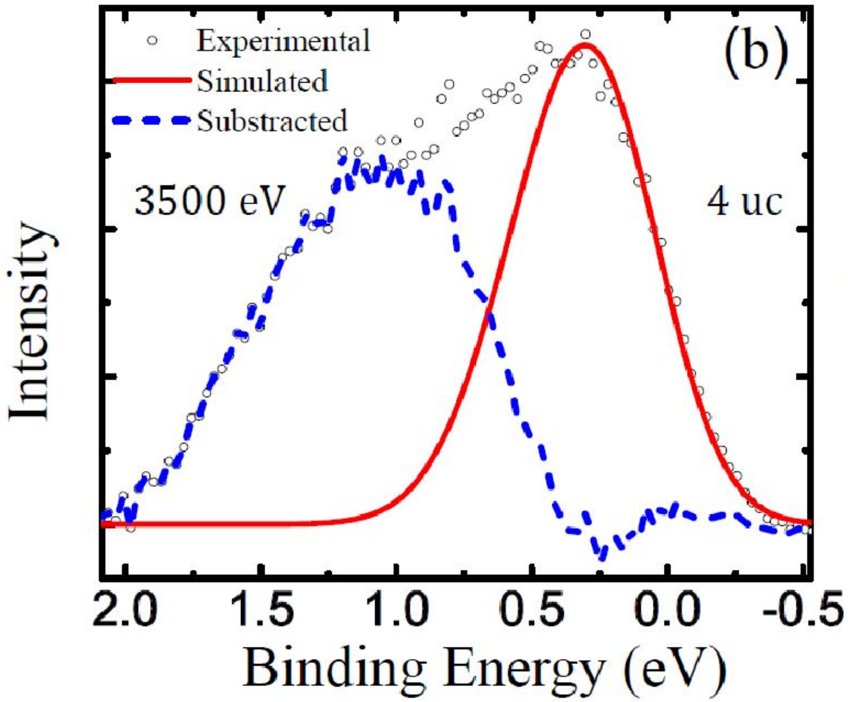


(a)
3500 eV
5400 eV
Intensity
12
10
8
6
4
2
0
Binding Energy (eV)



Shanthi and Sarma, PRB **57** (1998) 2153

Large spectral weight in the second (“incoherent”) peak!



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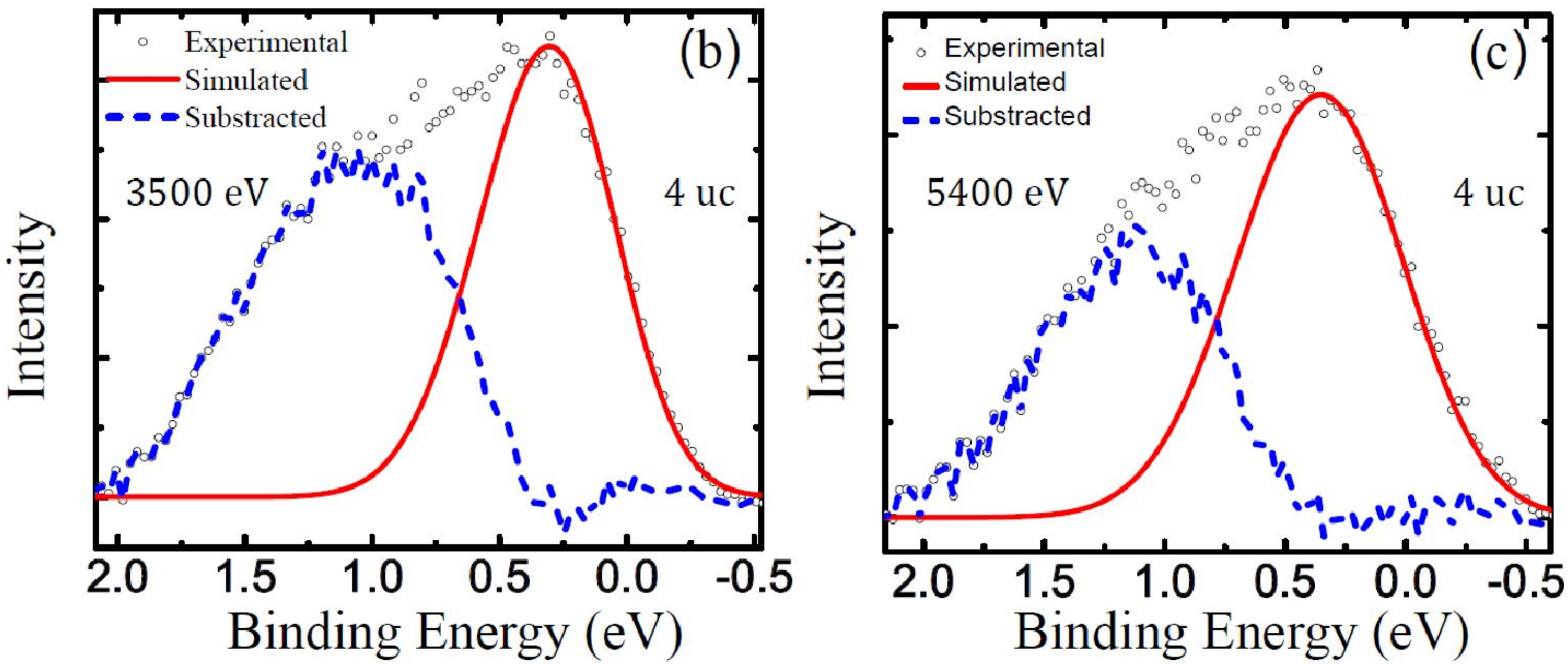

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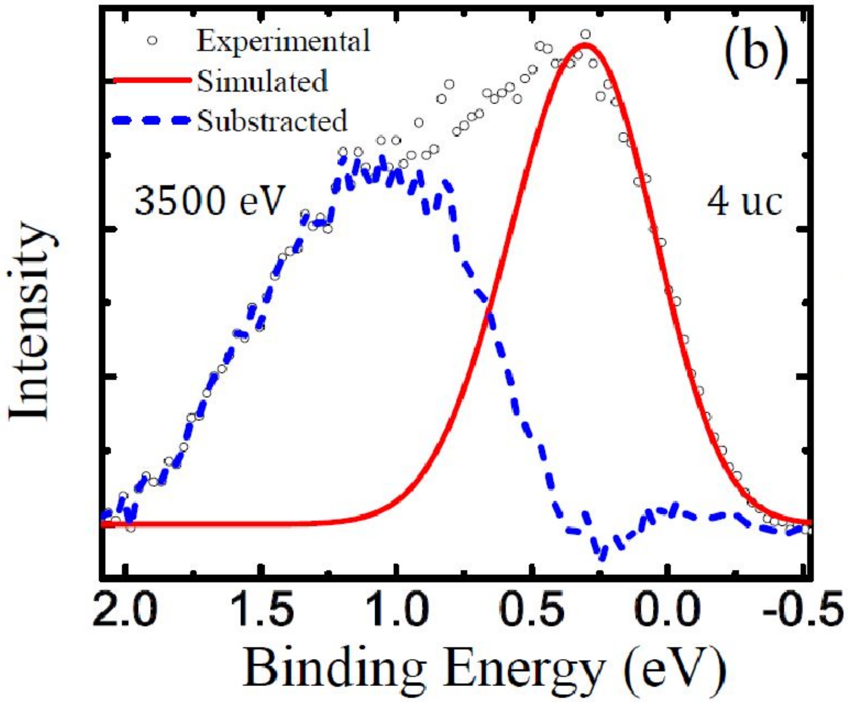
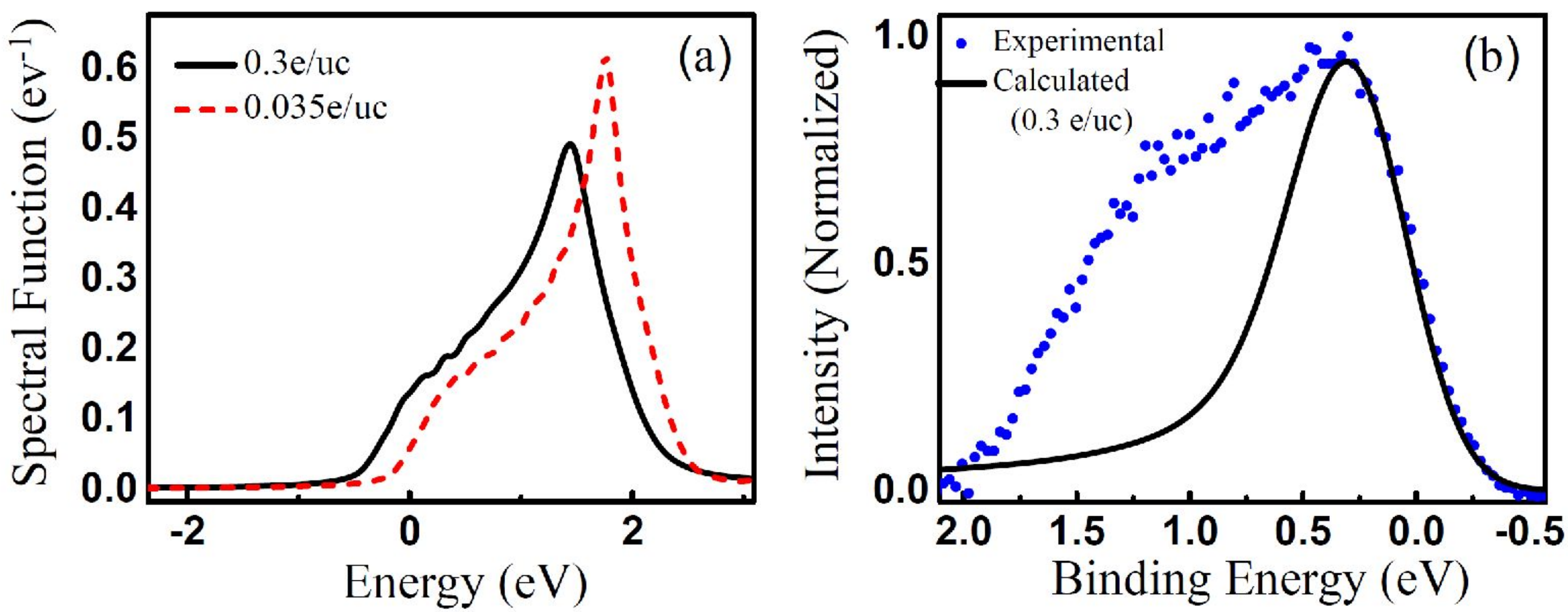


Spectral function of lightly doped $SrTiO_3$ calculated within screened exchange dynamical mean field theory



(i) Correlation induced lower Hubbard signature - X

ii) Plasmonic replica – X

ii) Oxygen vacancy induced states – Maybe (PRB 57 (1998) 2153)

v) Polaronic feature – Maybe

A large fraction of the doped electrons are localized!

Hard X-ray Photoelectron Spectroscopy (HAXPES) Study of

$LaTiO_3$-$SrTiO_3$ interface

Mott insulator   Band insulator

$LaAlO_3$-$SrTiO_3$ interface

Band insulator   Band insulator

Bangalore:

Banabir Pal

Shyamashis Das,

Sumanta Mukherjee

Yanwei Cao,

M. Kareev,

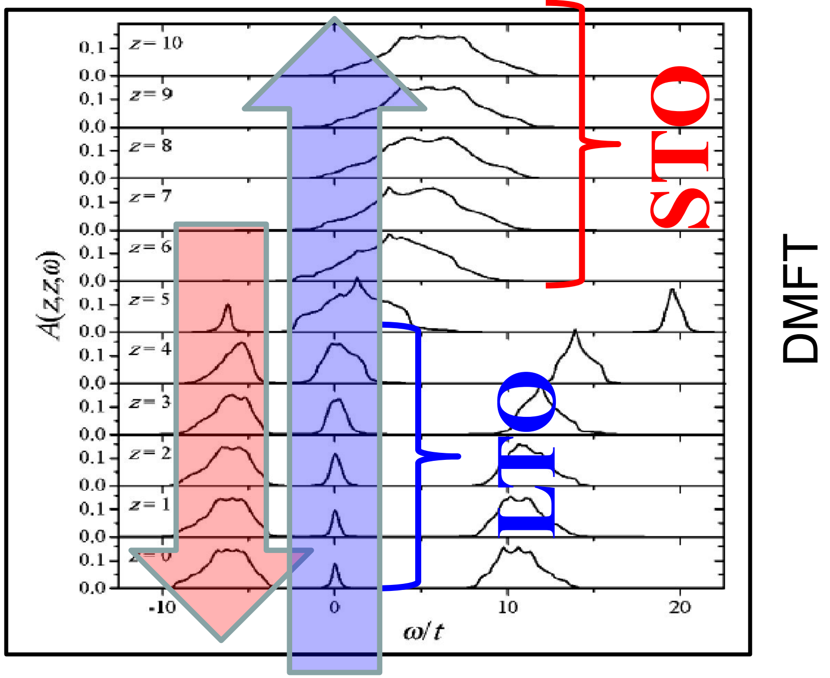
Jak Chakhalian (U. of Arkansas)

Indranil Sarkar

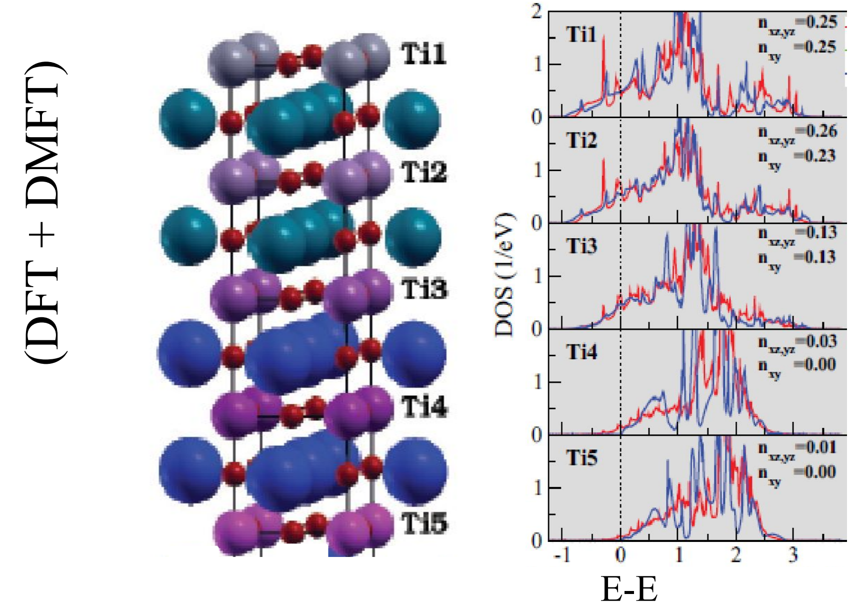
Wolfgang Drube (PETRA)

Unpublished

Diversity of theoretical expectations



S. Okamoto and A. J. Millis, Phys. Rev. B **70**, 241104(R) (2004)



F. Lechermann *et. al.* Phys. Rev. B **87** 241101 (2013)

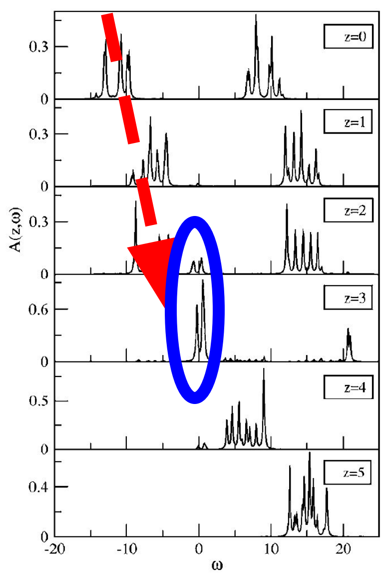


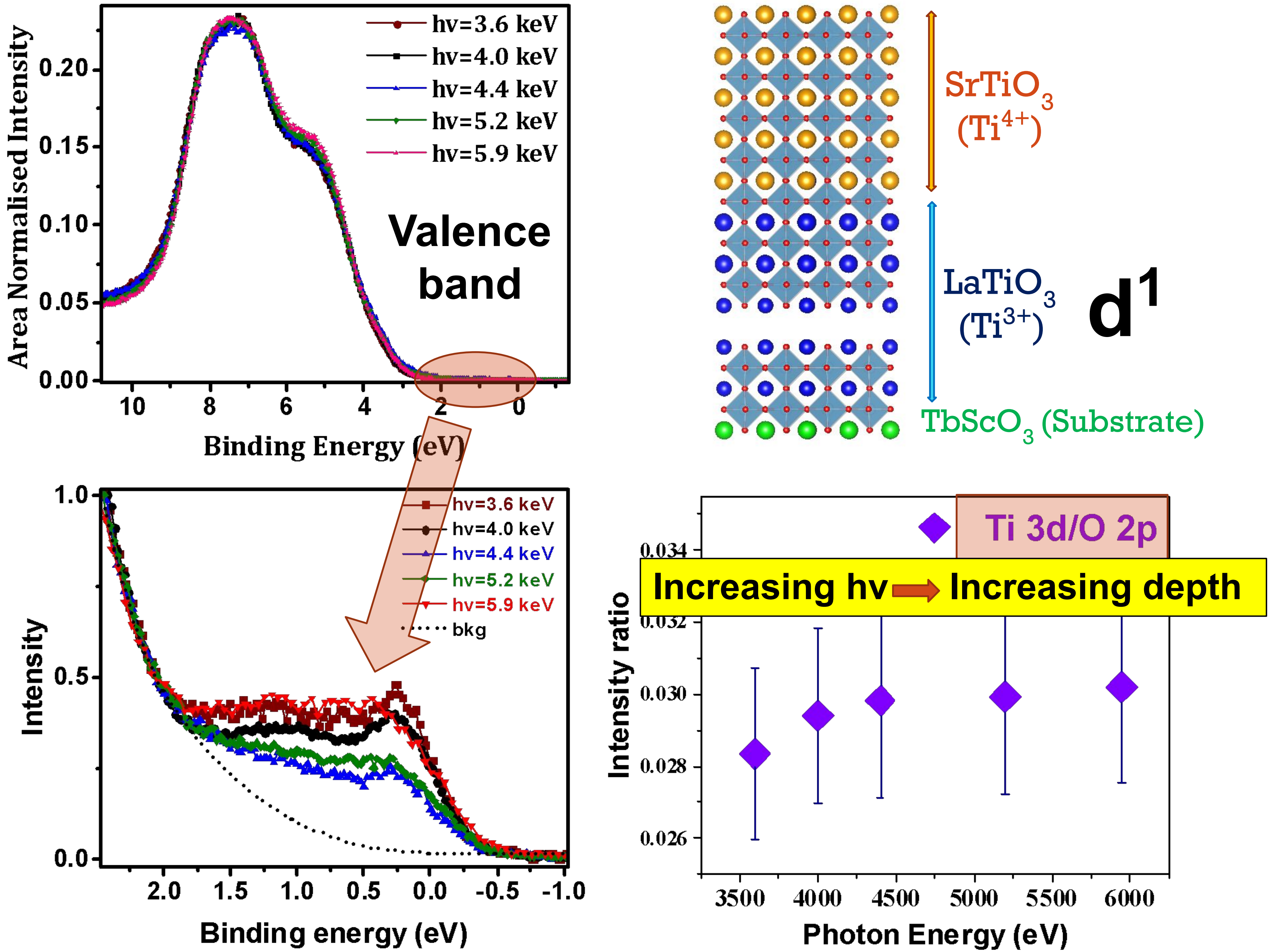
FIG. 3. Position dependent local density of states along the 16-site heterostructure for $U=20t$ and $\epsilon=3$.

S. S. Kancharla and E. Dagotto Phys. Rev. B **74**, 195427 (2006)

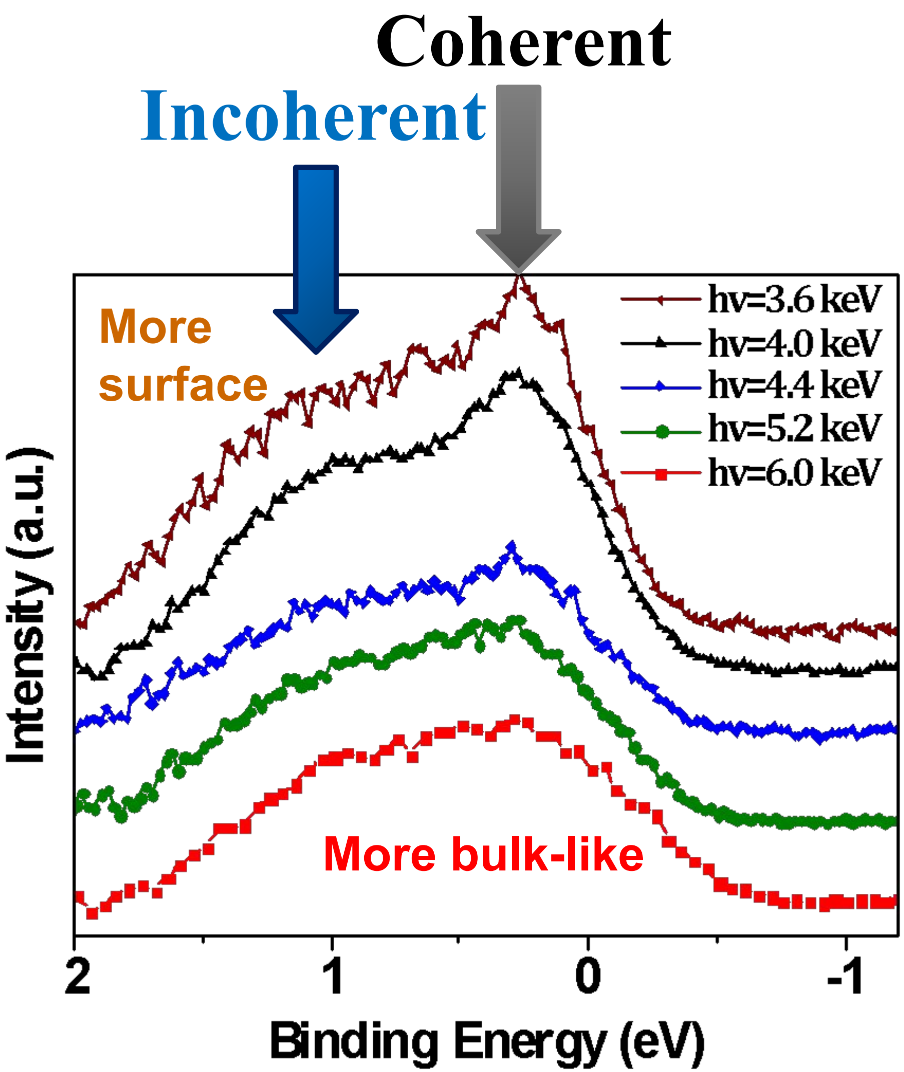
PRL **99,** 016802 (2007) PHYSICAL REVIEW LETTERS week ending 6 JULY 2007

Correlation-Driven Charge Order at the Interface between a Mott and a Band Insulator

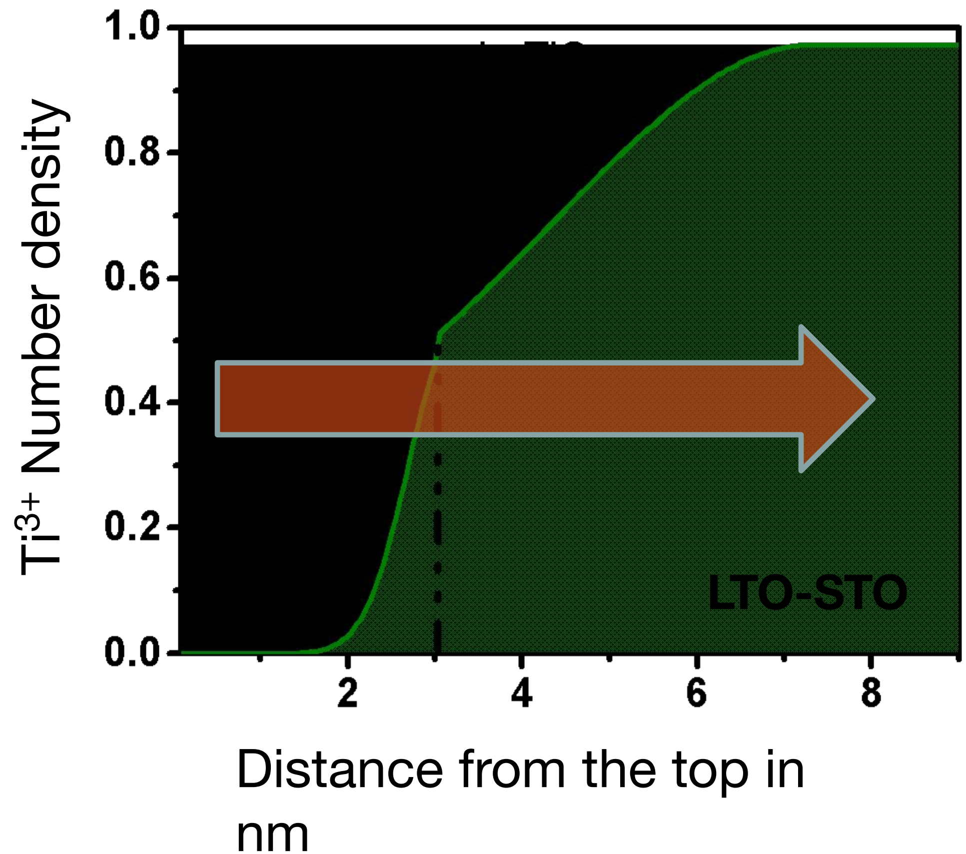
Rossitza Pentcheva[1,*] and Warren E. Pickett[2]



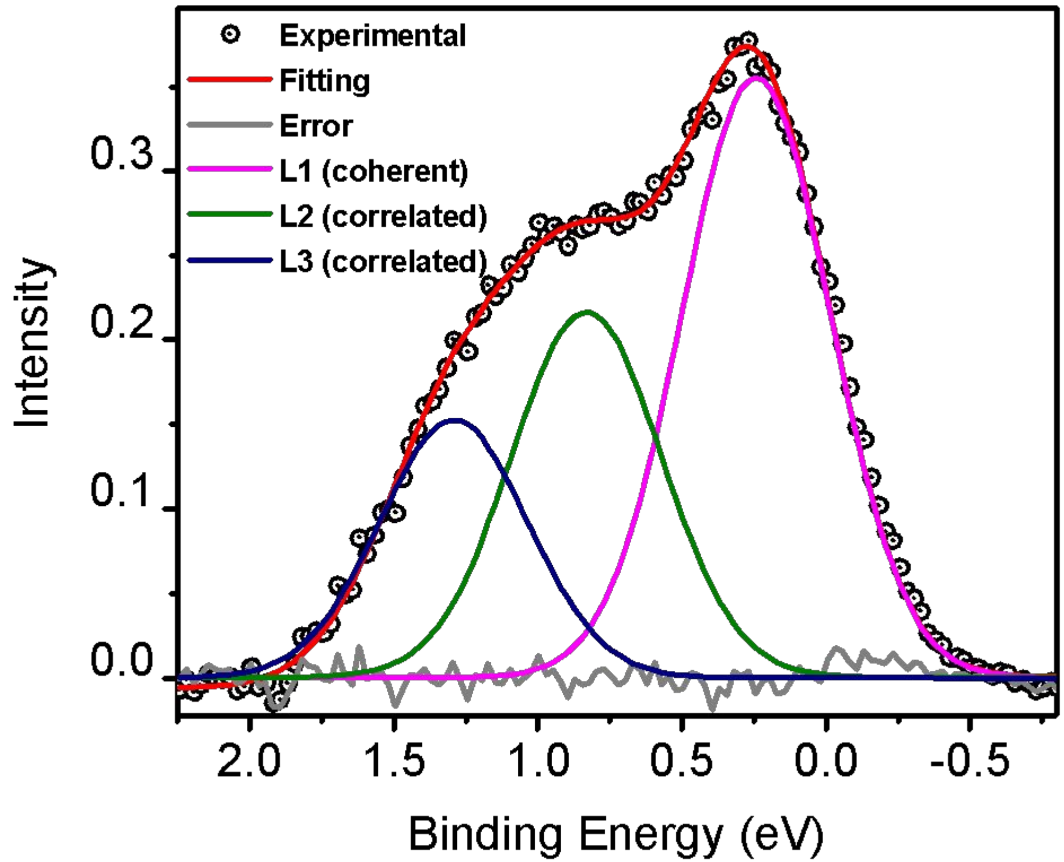
Area Normalised Intensity
Binding Energy (eV)
hv=3.6 keV
hv=4.0 keV
hv=4.4 keV
hv=5.2 keV
hv=5.9 keV
Valence band
SrTiO3 (Ti4+)
LaTiO3 (Ti3+)
TbScO3 (Substrate)
d1
Intensity
Binding energy (eV)
bkg
Ti 3d/O 2p
Increasing hv → Increasing depth
Intensity ratio
Photon Energy (eV)



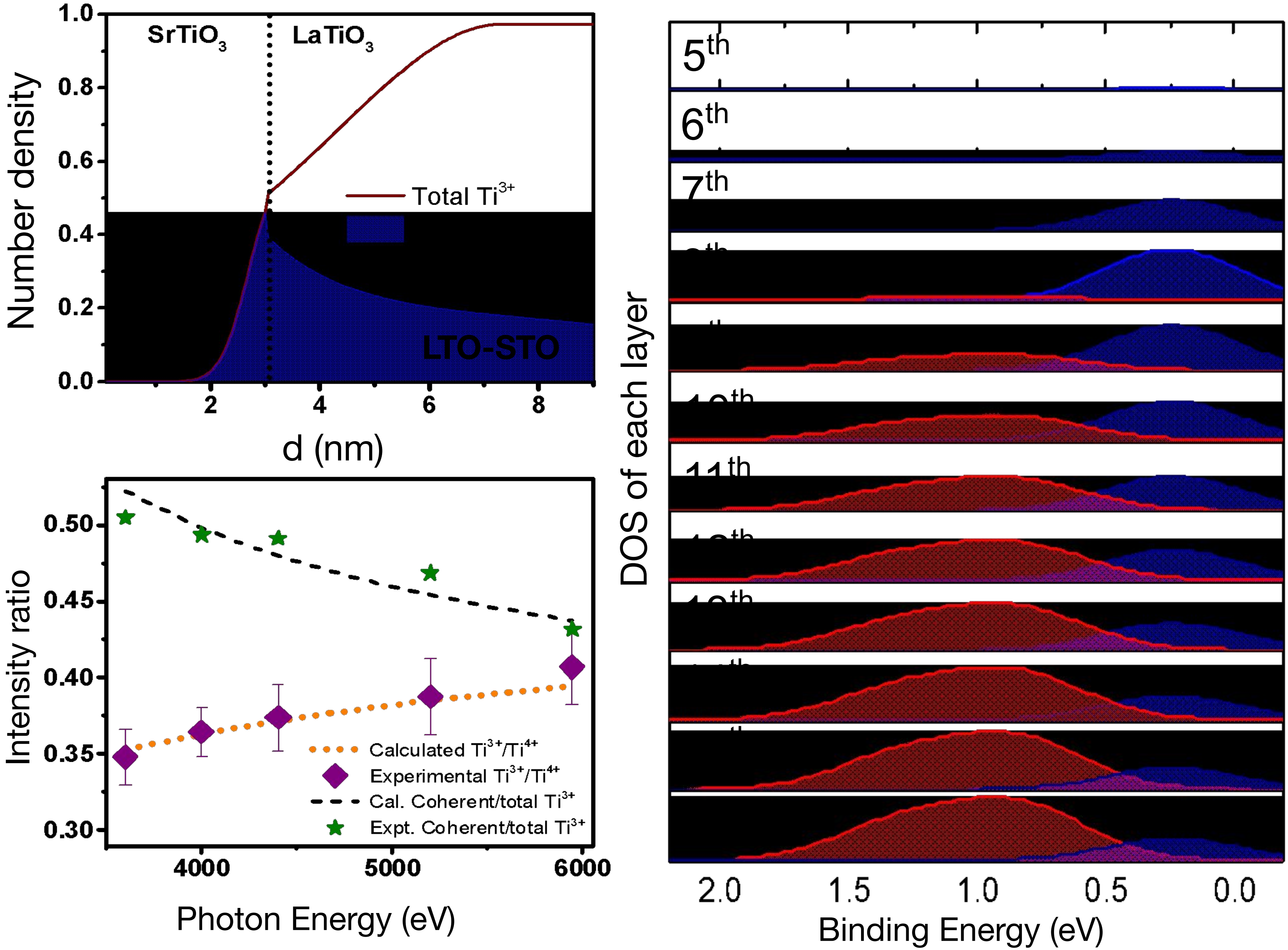
Increasing hv ⇒ Increasing depth



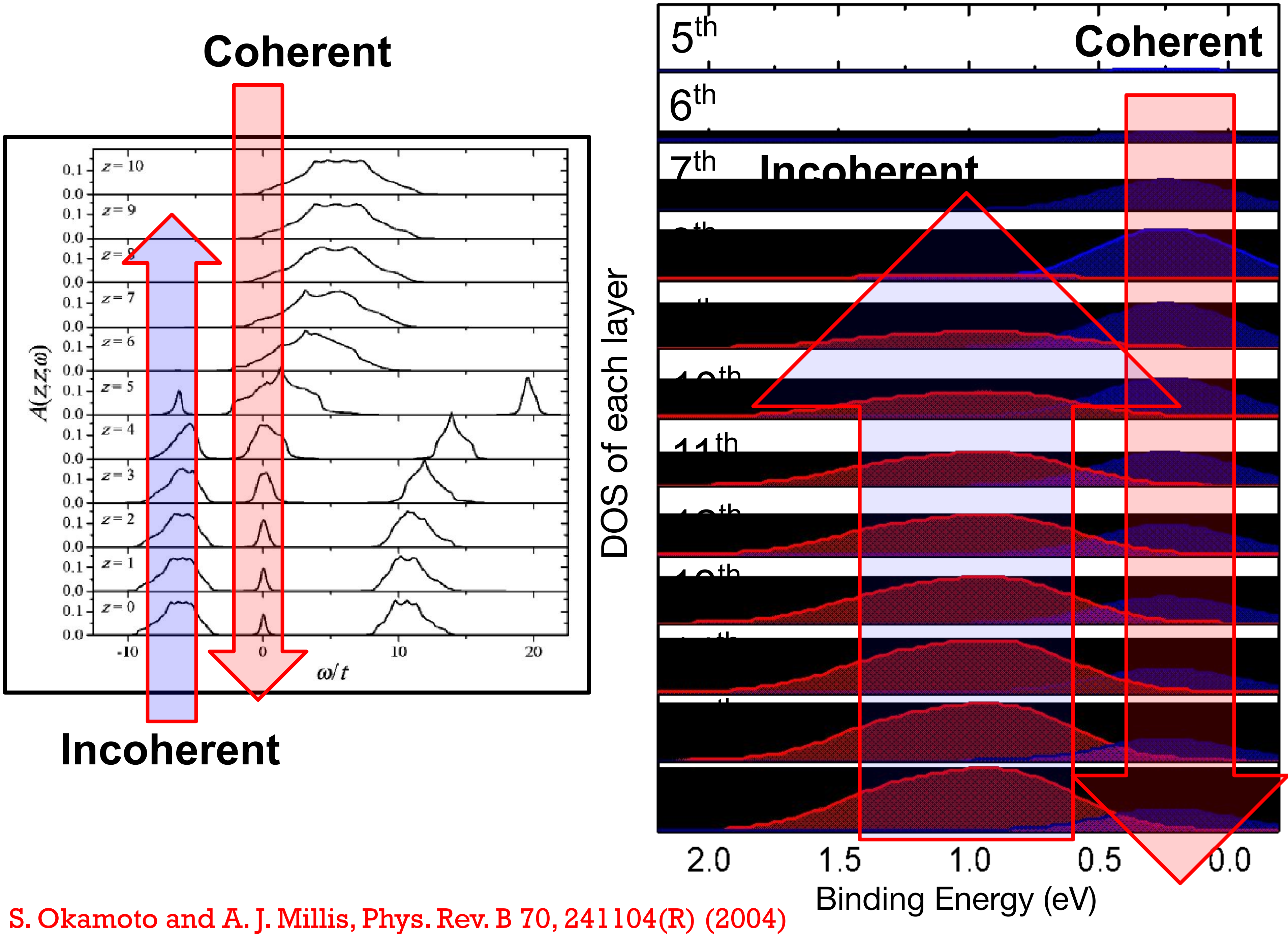
Increasing incoherent peak ⇒ Increasingly correlated



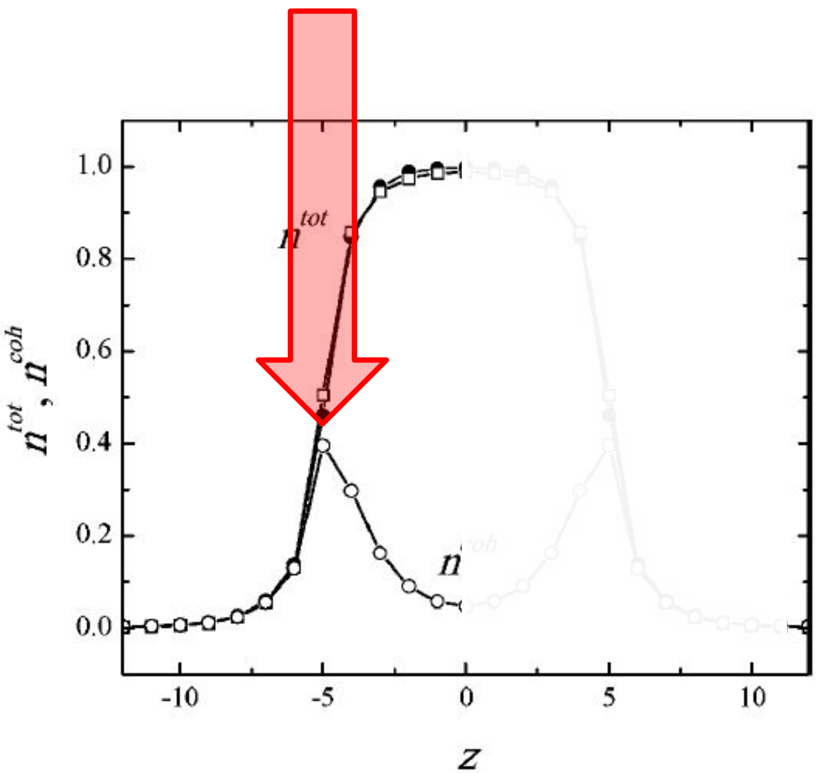
Experimental
Fitting
Error
L1 (coherent)
L2 (correlated)
L3 (correlated)
Intensity
0.0
0.1
0.2
0.3
2.0
1.5
1.0
0.5
0.0
-0.5
Binding Energy (eV)



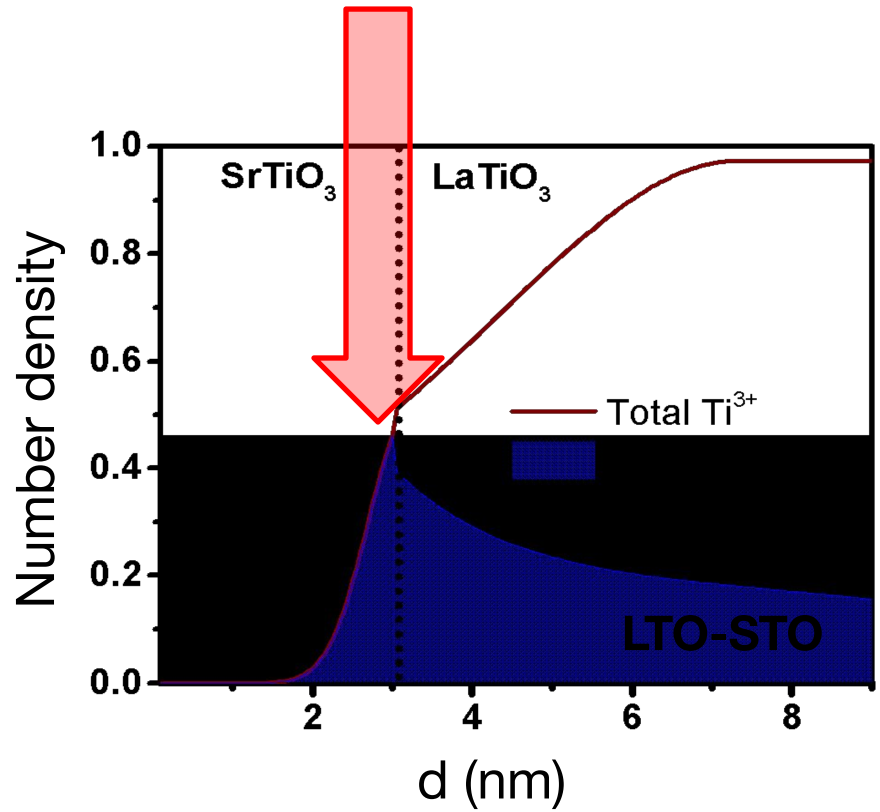
SrTiO3
LaTiO3
Total Ti3+
LTO-STO
Number density
1.0
0.8
0.6
0.4
0.2
0.0
2
4
6
8
d (nm)
Calculated Ti3+/Ti4+
Experimental Ti3+/Ti4+
Cal. Coherent/total Ti3+
Expt. Coherent/total Ti3+
Intensity ratio
0.50
0.45
0.40
0.35
0.30
4000
5000
6000
Photon Energy (eV)
5th
6th
7th
DOS of each layer
2.0
1.5
1.0
0.5
0.0
Binding Energy (eV)



S. Okamoto and A. J. Millis, Phys. Rev. B 70, 241104(R) (2004)



Theoretical



Experimental

S. Okamoto and A. J. Millis, Phys. Rev. B 70, 241104(R) (2004)

Thank you

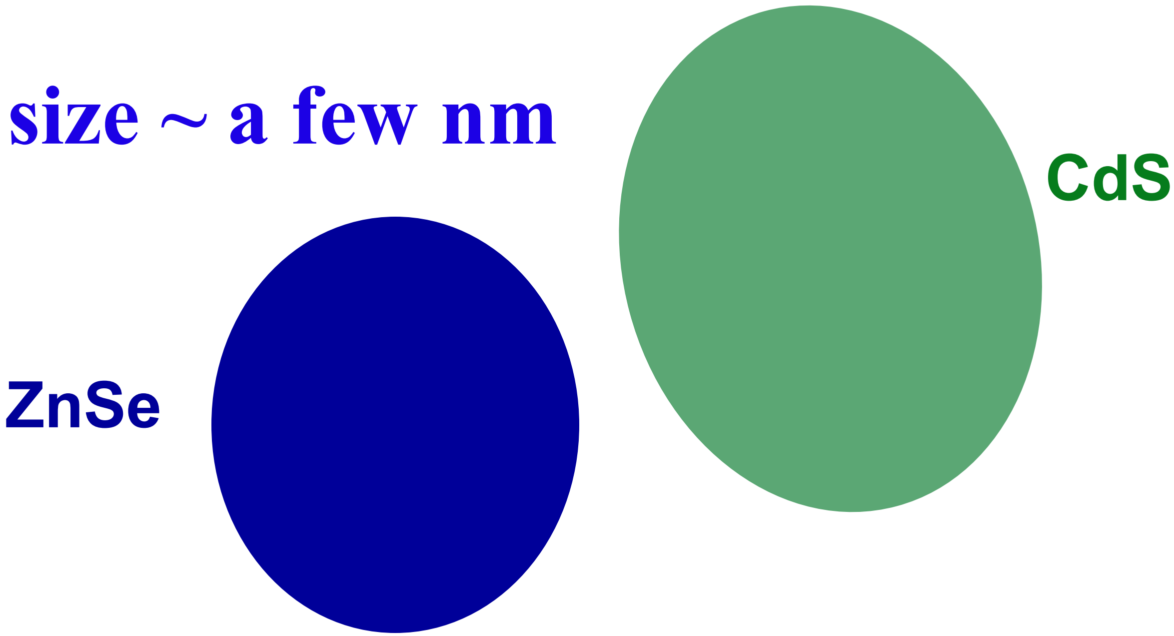

If you win an argument
You loose a friend

Why are we interested in the interface?

One illustration

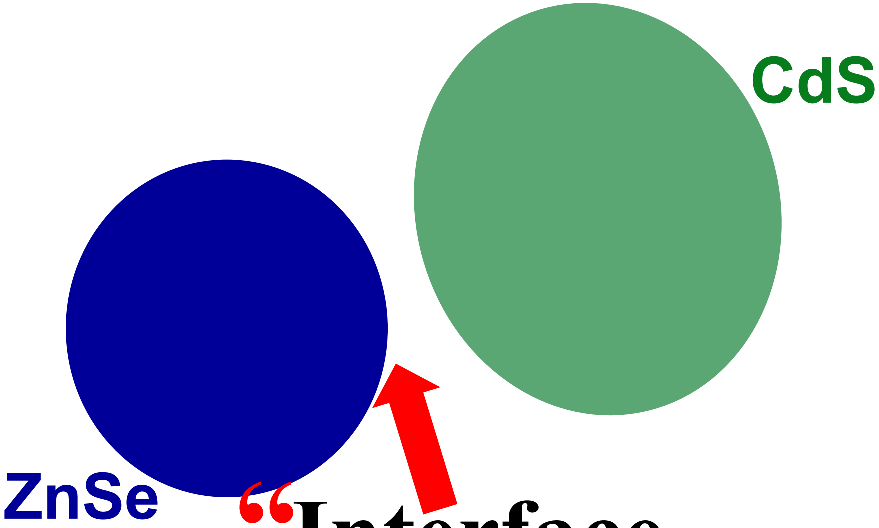
Quantum dots

Typical size ~ a few nm



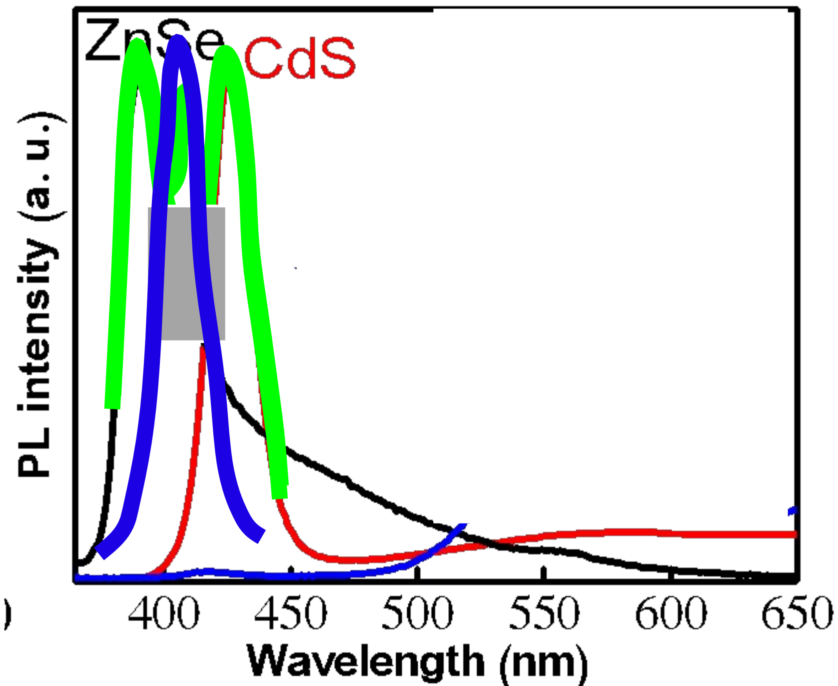
Sucheta Sengupta *et al*.,
Adv. Mater. **23**, 1998 (2011).

Band-edge engineering for optical tuning



"Interface
is the device!"

– H. Kroemer,
Nobel Lecture, 2000



Important applications in

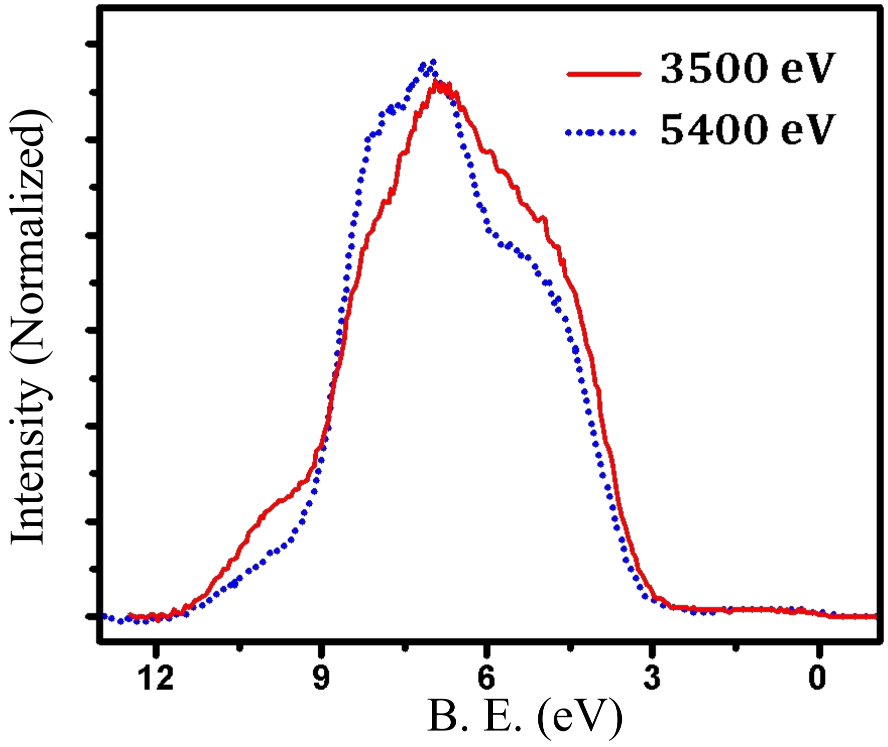
- PL without self-absorption
- Photovoltaic

Sucheta Sengupta *et al*., Adv. Mater. 23, 1998 (2011).

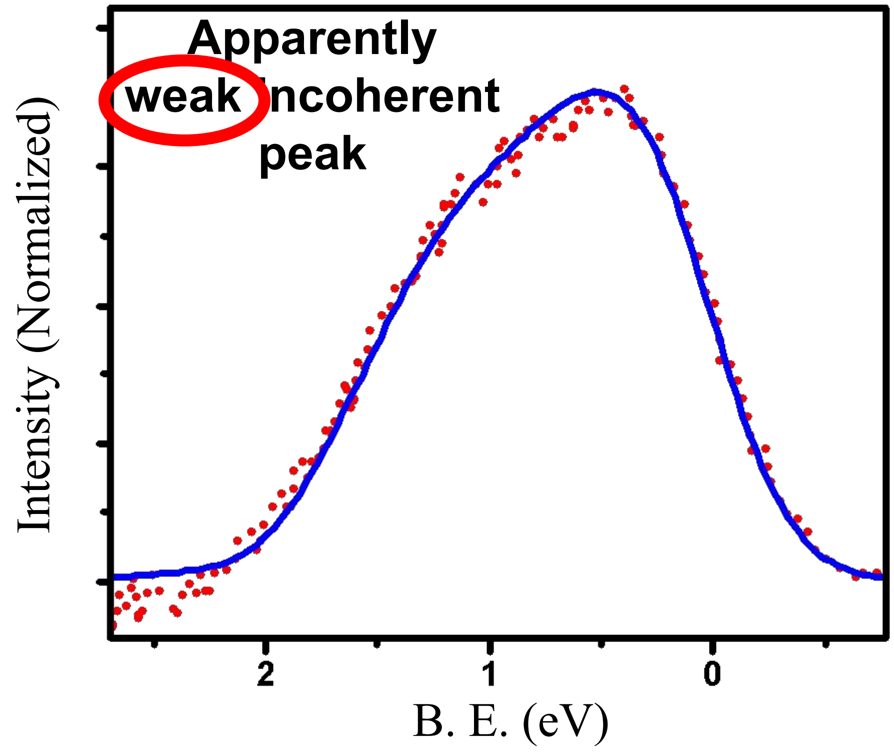
N. Pradhan et al., JACS (2010)

How correlated each of these electron distributions are?

Valence Band Study

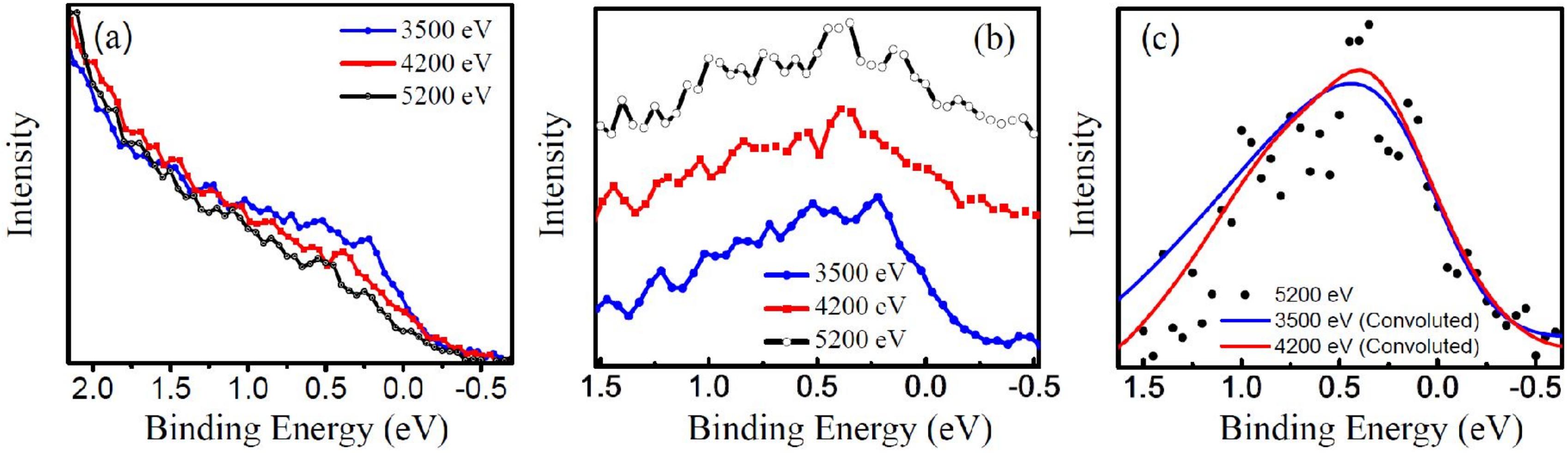


How weak is this “weak” peak?

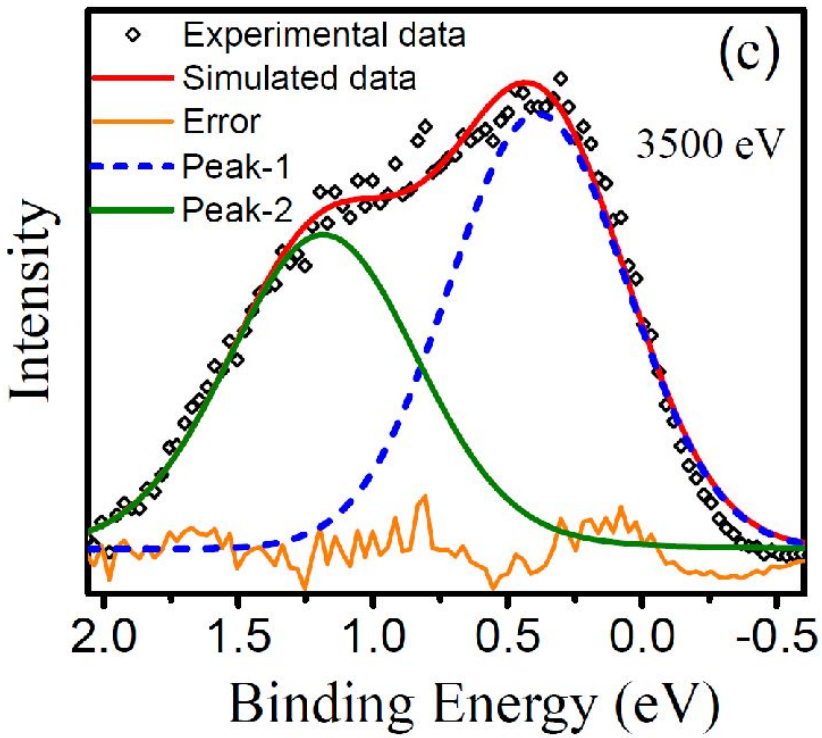


Electron states do not significantly change with the depth!

6 uc case


(a)
3500 eV
4200 eV
5200 eV
Intensity
2.0
1.5
1.0
0.5
0.0
-0.5
Binding Energy (eV)
(b)
3500 eV
4200 cV
5200 eV
Intensity
1.5
1.0
0.5
0.0
-0.5
Binding Energy (eV)
(c)
5200 eV
3500 eV (Convoluted)
4200 eV (Convoluted)
Intensity
1.5
1.0
0.5
0.0
-0.5
Binding Energy (eV)

Large spectral weight in the second ("incoherent") peak!



DMFT results from Ambroise van Roekeghem and Silke Biermann on doped STO:

Expected weights of the QP peak and LHB:

Electron number	Weight of QP peak (Z0)	LHB (1-Z0)
n = 0.05	1	0
n = 0.1	0.99	0.01
n = 0.2	0.96	0.04
n = 0.3	0.92	0.08

Simulation of the Sr 3d core level spectra to find possible plasmonic effects

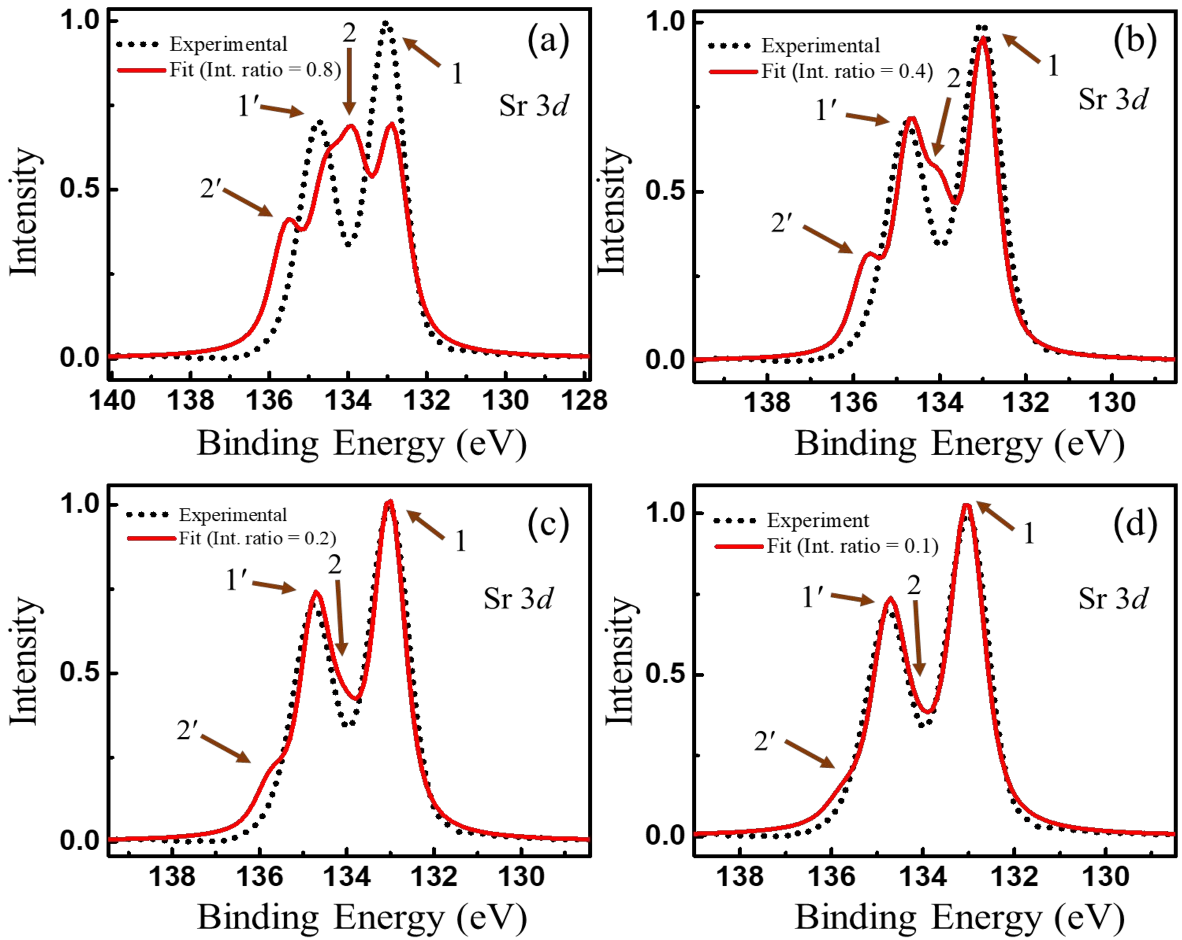
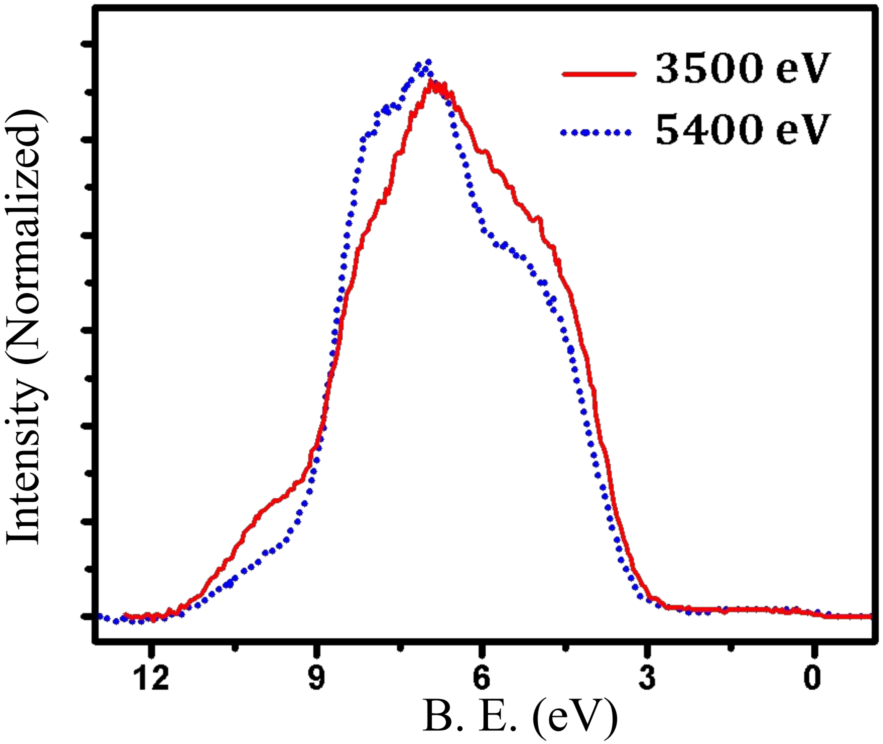
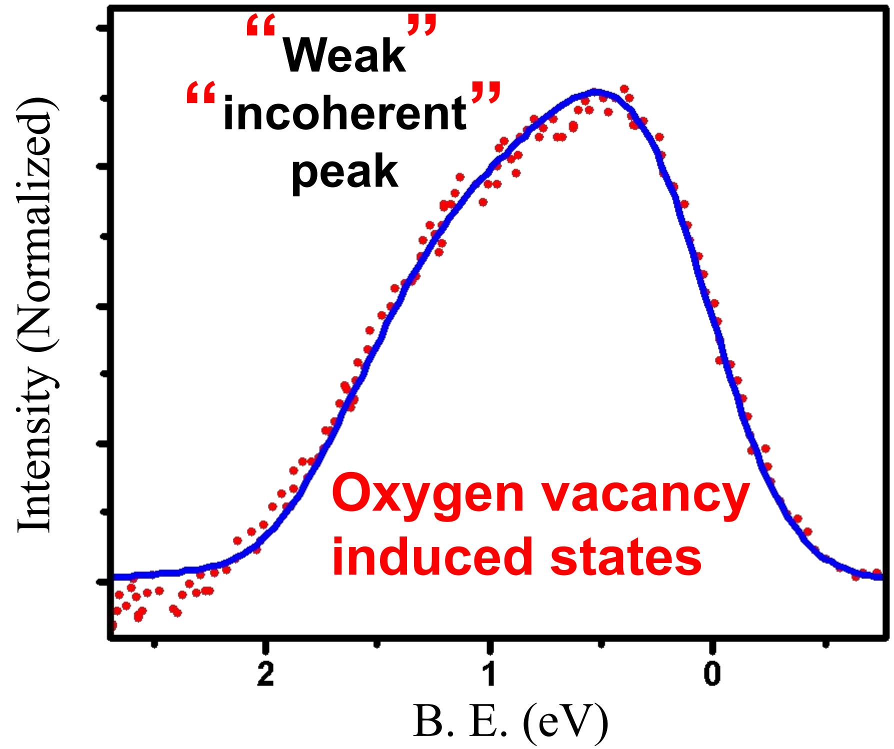


FIG. S3. (color online) (a) to (d) shows the simulation of Sr 3*d* spectra of 6uc sample recorded with photon energy of 3500 eV. See text for details. 1 and 1′ in each panel mark the position of the main Sr $3d_{5/2}$, Sr $3d_{3/2}$ spectra, respectively, while 2 and 2′ mark the position of the corresponding plasmonic replicas, shifted by 1 eV from the main peaks.

How correlated each of these electron distributions are?

Valence Band Study





Electron states do not significantly change with the depth!

Ambroise van Roekeghem, a former student of mine, now a permanent researcher at the CEA in Grenoble and first author of the EPL paper I sent you, has revived the machinery of that paper.

The result reads as follows:

Electron number => Weight of QP peak
n = 0.05 -> Z0=1.
n = 0.1 -> Z0=0.99
n = 0.2 -> Z0=0.96
n = 0.3 -> Z0=0.92

The Hubbard band would have weight 1-Z0. The model is really for the SrTiO3 case, calculated within Screened Exchange + DDMFT (see your birthday issue of J. Spec and Rel. Phen. :-)

Conclusions:

1. La/Sr mixing minimal across the layer.

2. Clearly two different distributions of charges in the system:

> **(i) 2DEG at the interface with a thickness (~1-2 nm) compatible with the interface thickness. Appears to be controlled by oxygen vacancies at the LAO surface.**
>
> **(ii) A broader distribution of electron gas is found to reside throughout the bulk of STO. Appears to be controlled by oxygen vacancies in the bulk of STO.**

3. Charge carriers are weakly correlated.

4. The additional VB feature is possibly due to oxygen vacancies.

Plan of the talk:

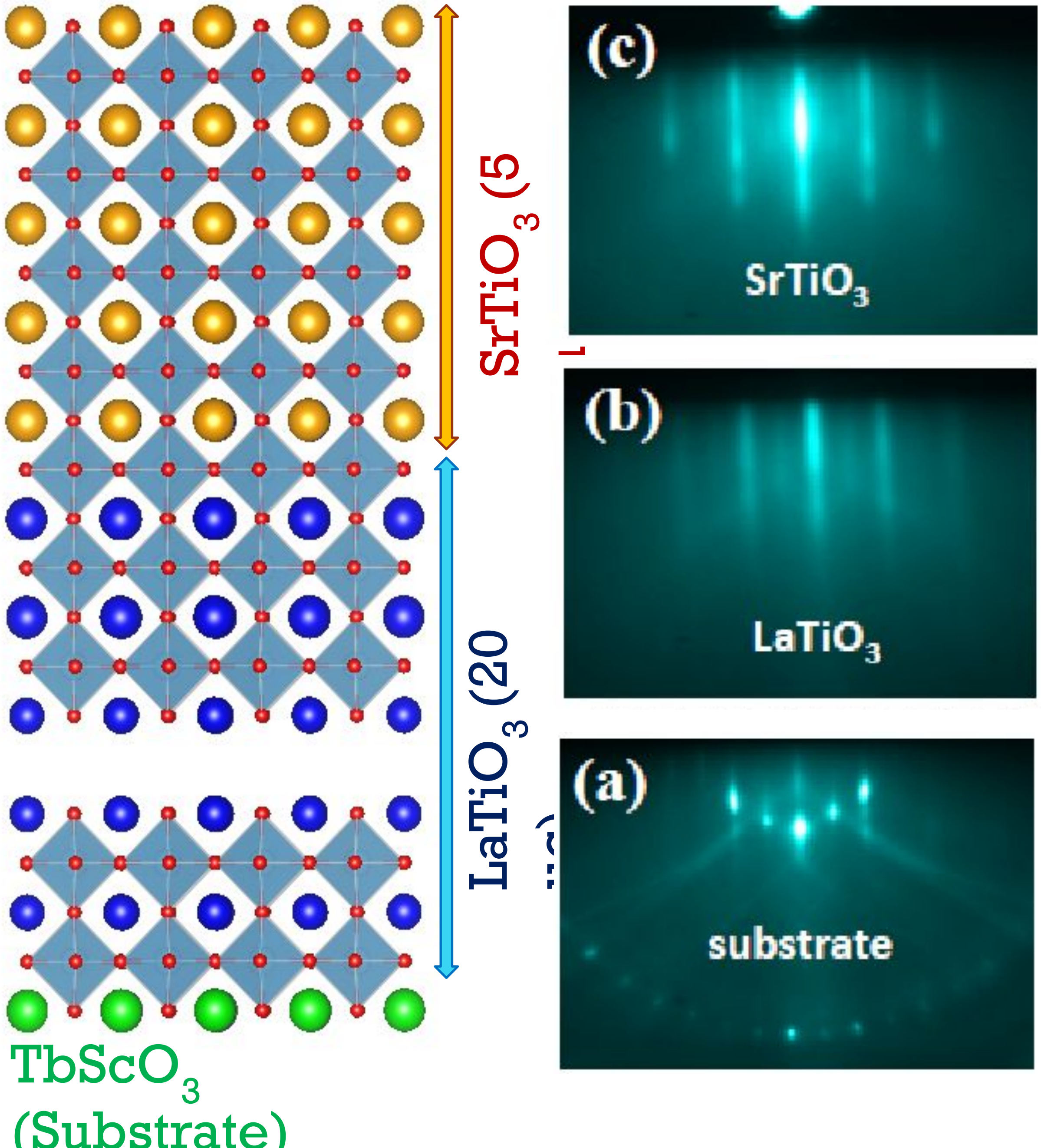
1. Motivation

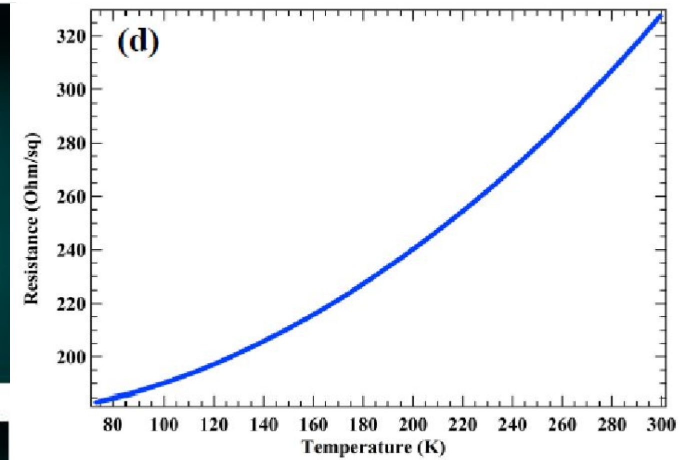
2. The technique employed

3. Our results on LAO-STO

4. **Our results on $SrTiO_3$-$LaTiO_3$ interface**

Banabir Pal et al., Unpublished.





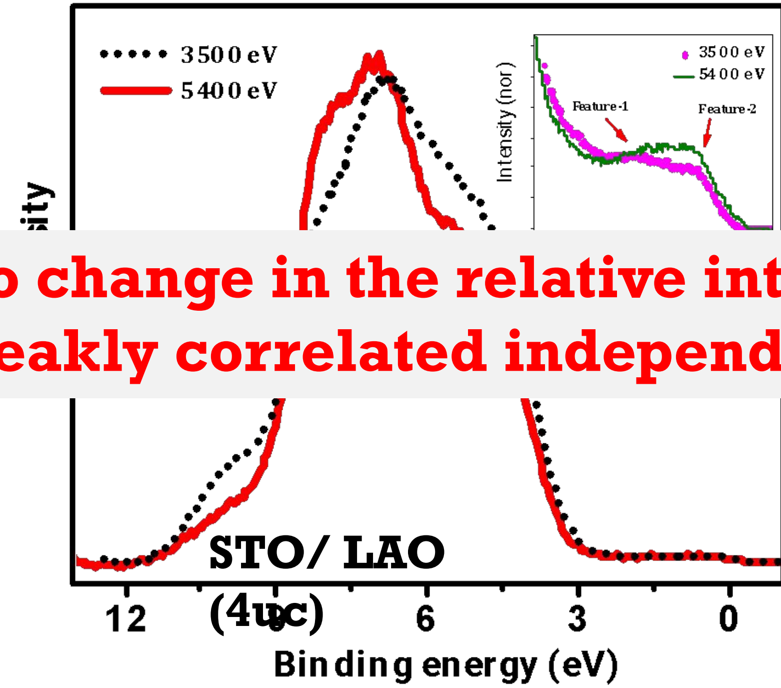
- RHEED pattern confirms high quality epitaxial growth of $LaTiO_3$ (LTO) and $SrTiO_3$ (STO).
- Sheet resistance suggests metallic nature of the heterostructure

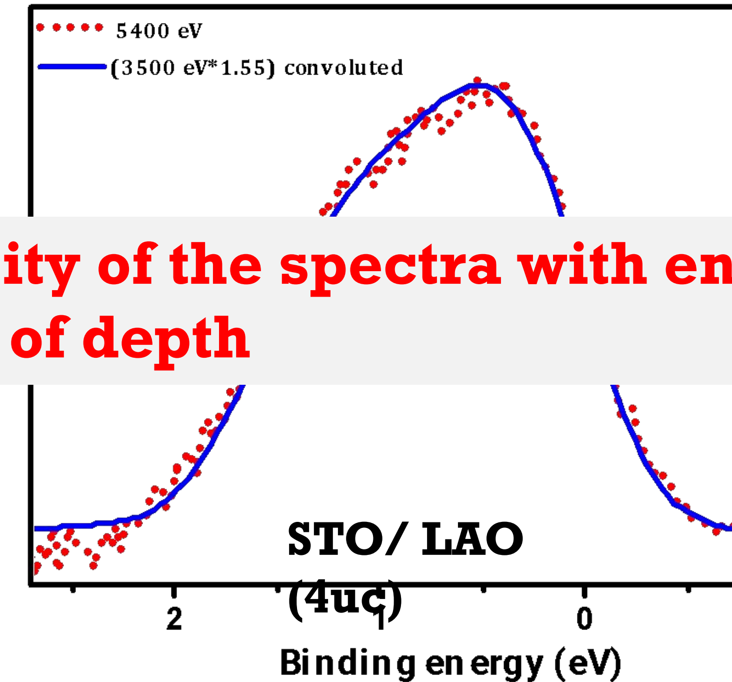
Can we determine

the layer-resolved electronic structure experimentally?

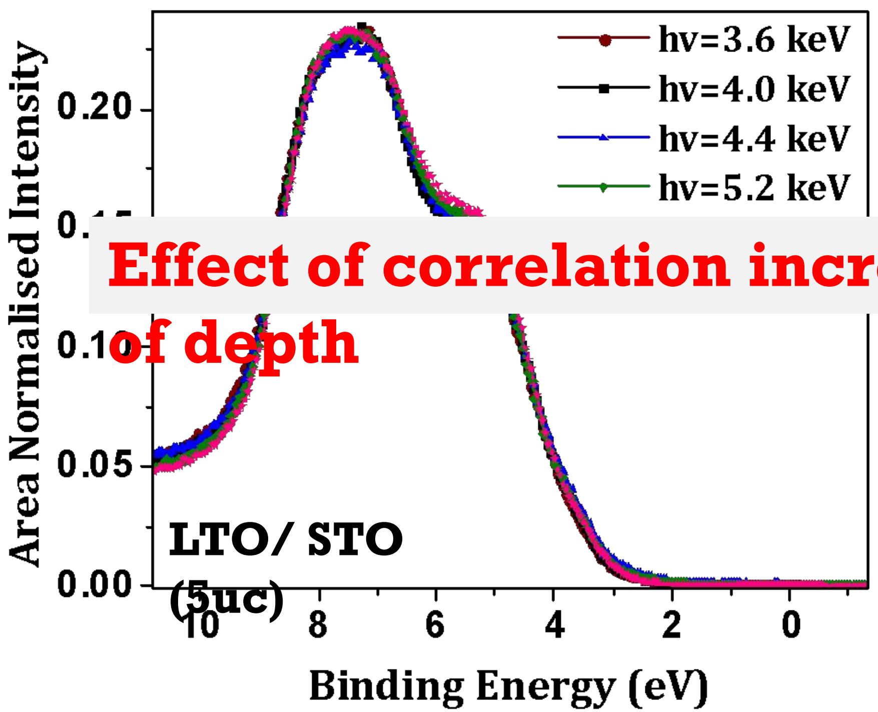
⇩

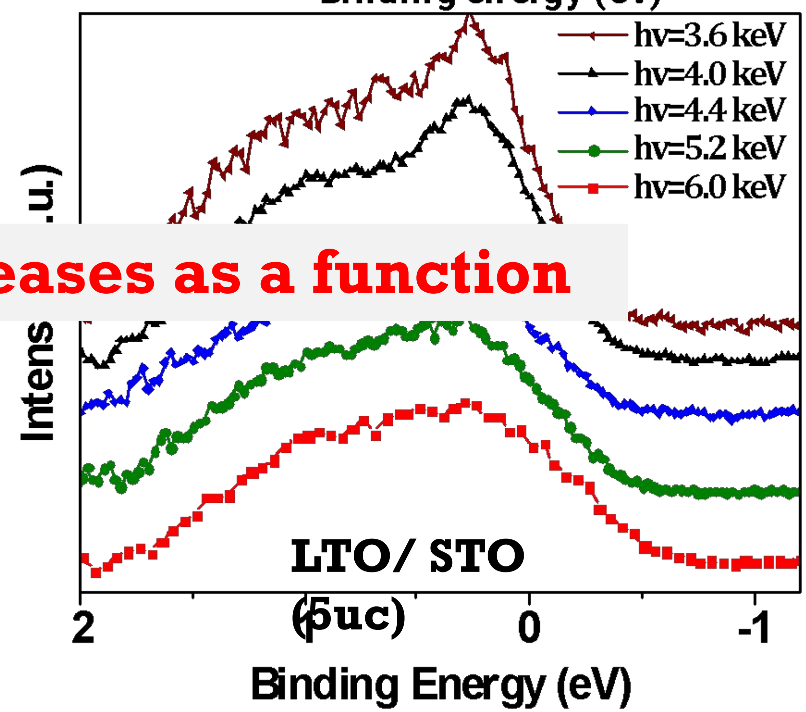
Layer-resolved one-particle spectral function





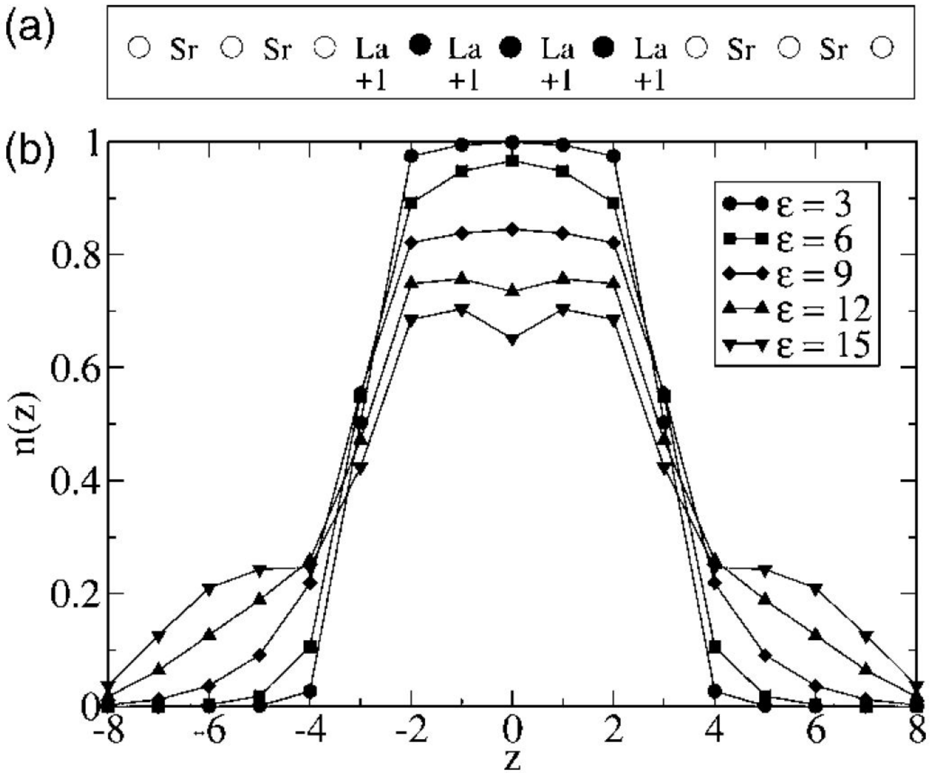
No change in the relative intensity of the spectra with energy. Weakly correlated independent of depth

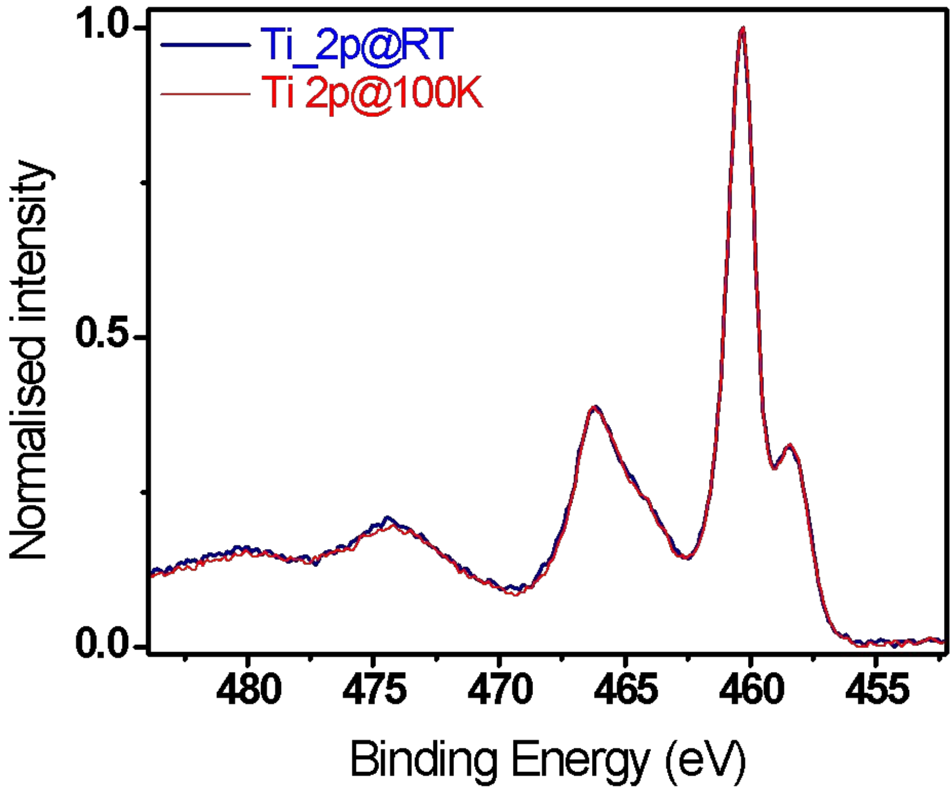




Effect of correlation increases as a function of depth

Dependence of Charge distribution on dielectric constant





Charge distribution pattern is **independent** of the dielectric constant of $SrTiO_3$

S. S. Kancharla and E. Dagotto Phys. Rev. B **74**, 195427 (2006)