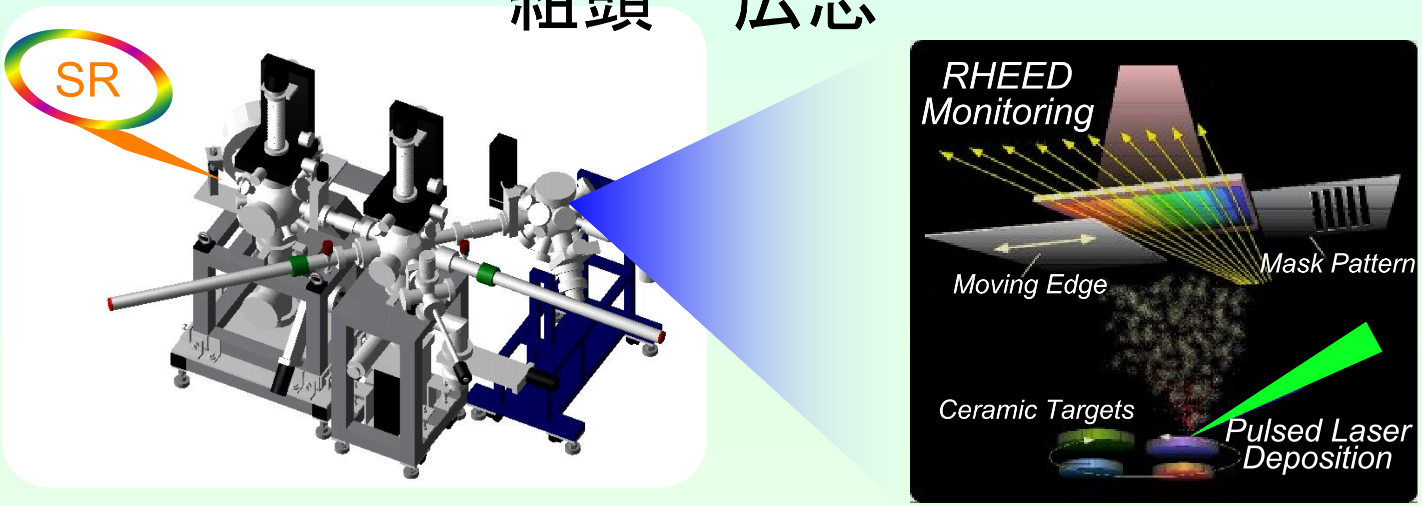
物構研シンポジウム'09
放射光・中性子・ミュオンを用いた表面・界面科学の最前線
2009年11月17-18日（17日（金））@つくば国際会議場エポカル

その場放射光電子分光による強相関ヘテロ界面の電子状態の研究

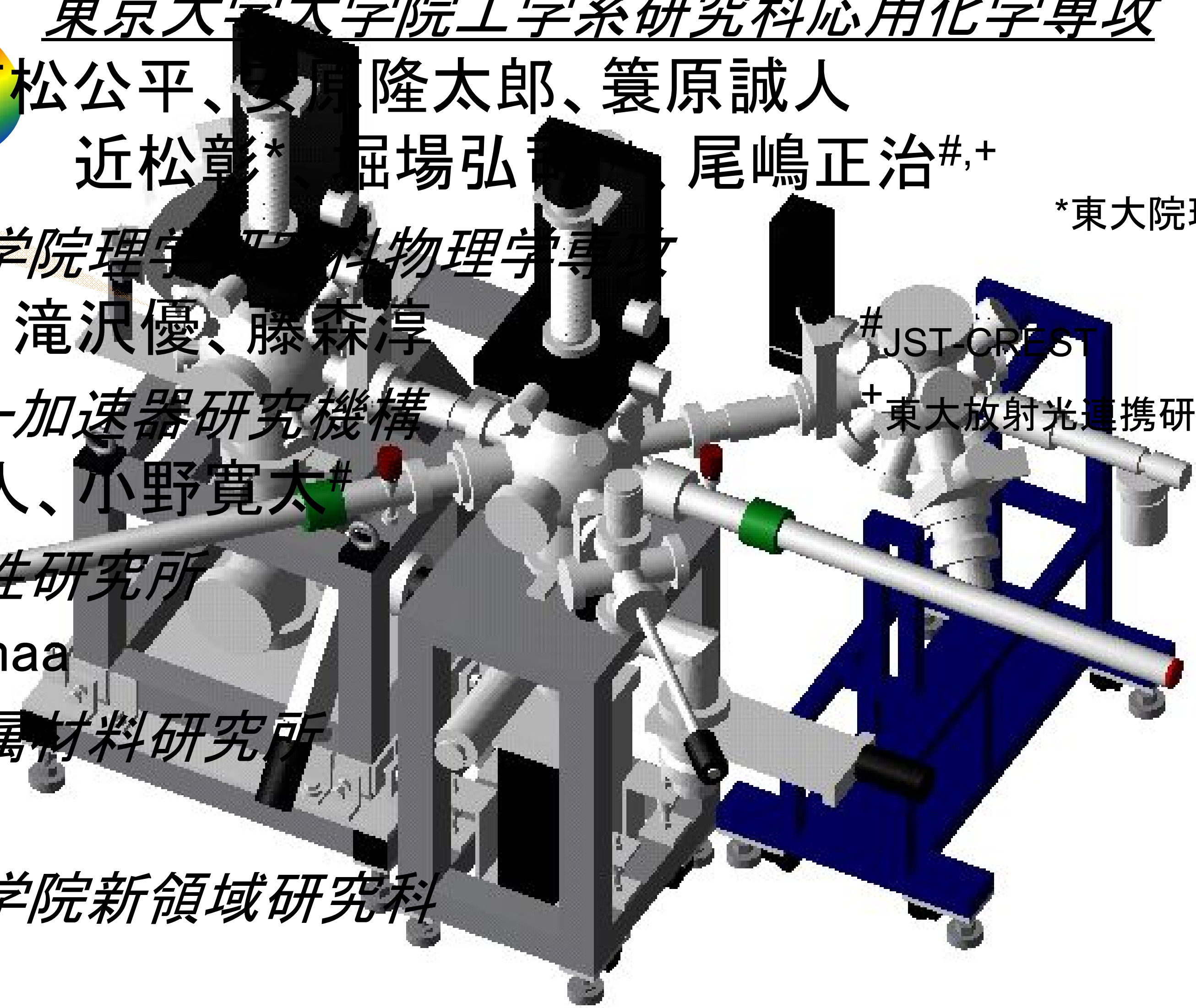
東京大学大学院工学系研究科
JST-さきがけ
東大放射光連携研究機構

組頭　広志



COLLABORATORS

SR



<u>東京大学大学院工学系研究科応用化学専攻</u>
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+東大放射光連携研究機構

はじめに

1. 成膜技術（レーザーMBE法など）の発展により、原子レベルで構造を制御した酸化物薄膜・超格子の作製が可能となった。

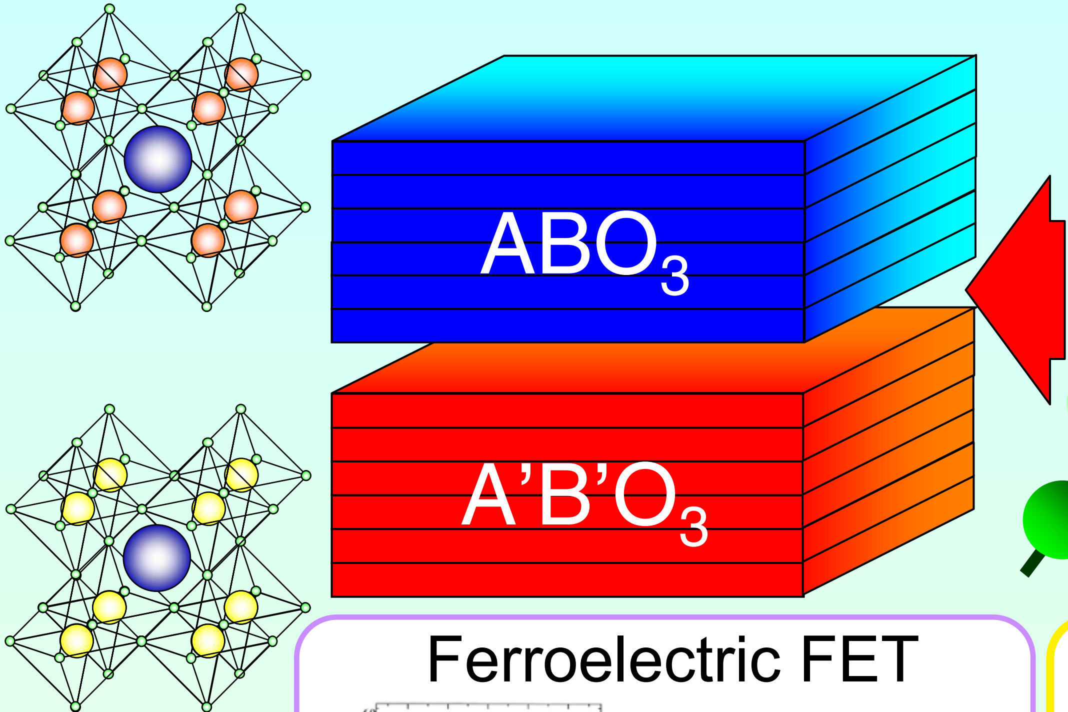
2. 強相関酸化物においても、今後、物質設計の自由度が高く、物性を自由自在に制御可能な「超構造」を用いた研究が主流になる。

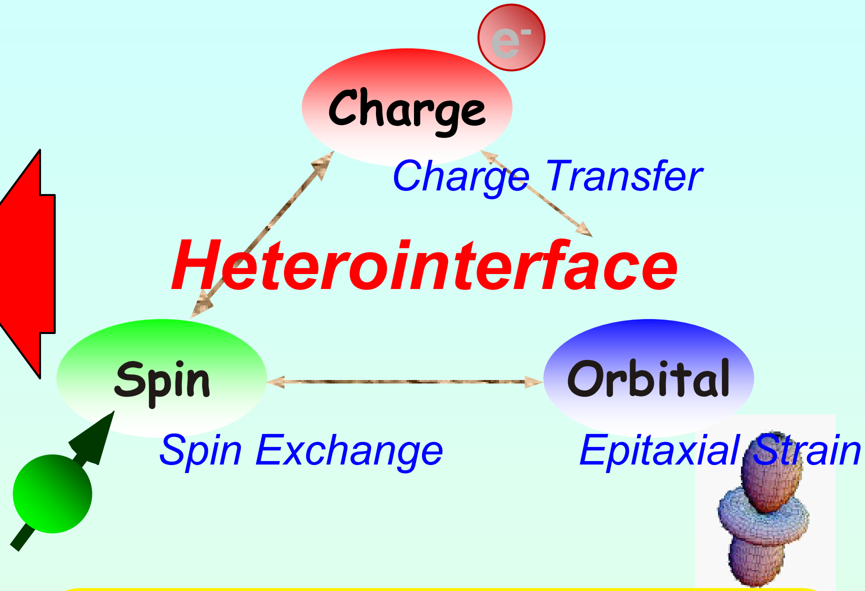
3. 放射光を用いた分光法は、酸化物薄膜・超格子研究の強力な牽引力になる。

INTRODUCTION

Heterojunctions based on Perovskite Oxides

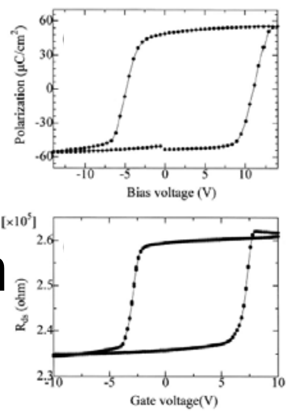
Controlling physical properties using interface effects

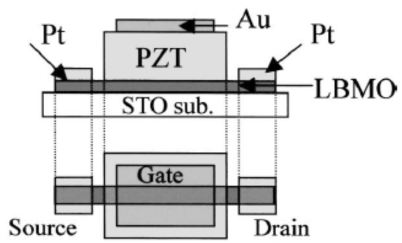




High Tc
CMR
MI transition

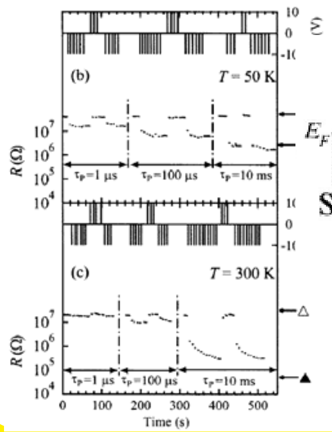
Ferroelectric FET

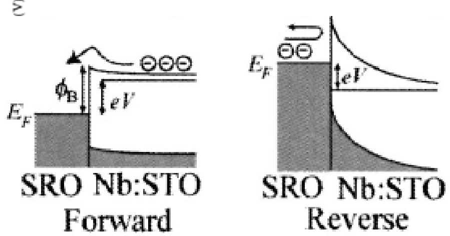




T. Kanki *et al.*, *Appl. Phys. Lett.* **83**, 4860 (2003).

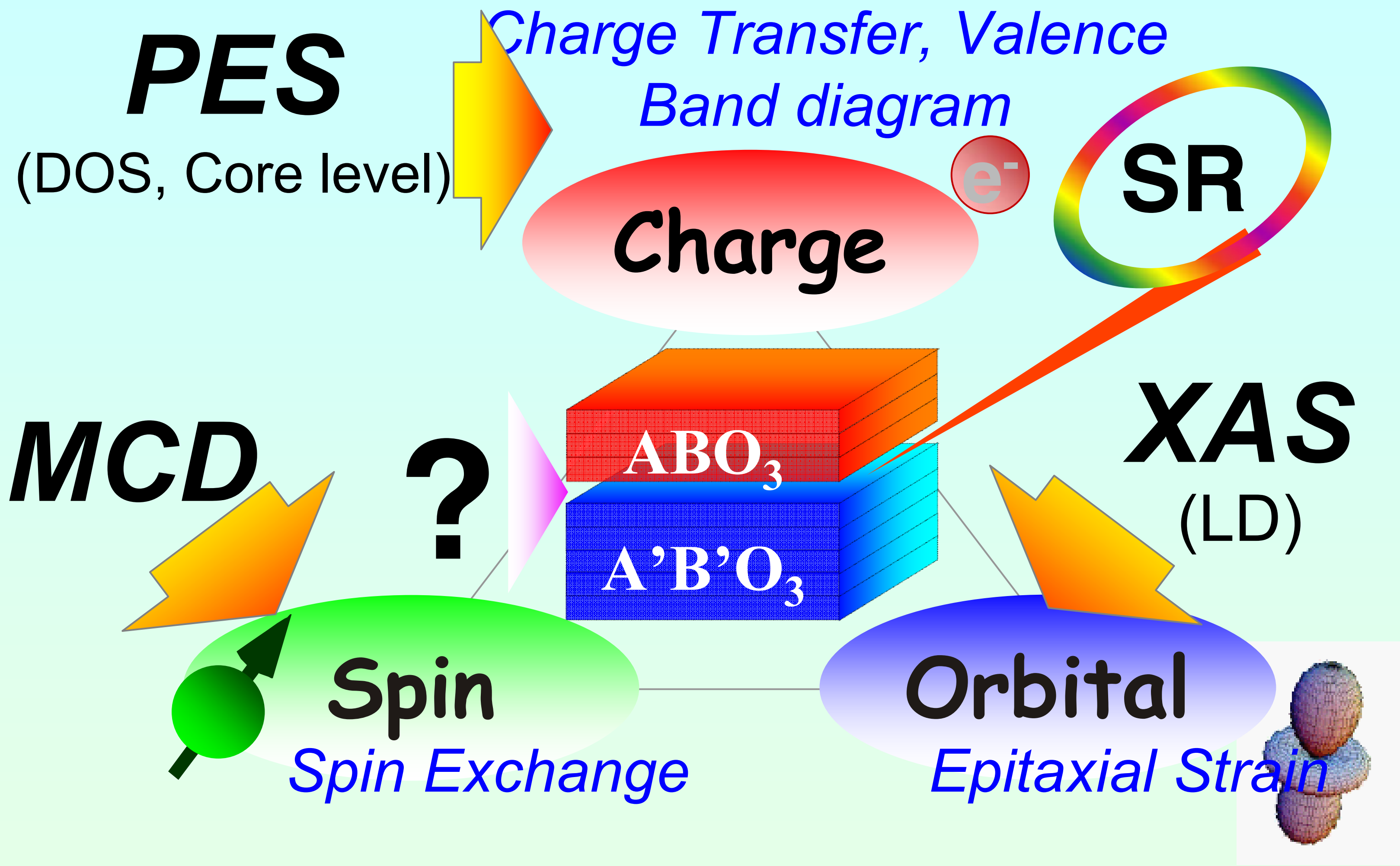
Resistance RAM





T. Fujii *et al.*, *Appl. Phys. Lett.* **86**, 012107 (2005).

SR analysis for oxide heterointerface



界面数nmの領域（少ないボリューム）における
電子・スピン・軌道状態を元素選択的に測定可能

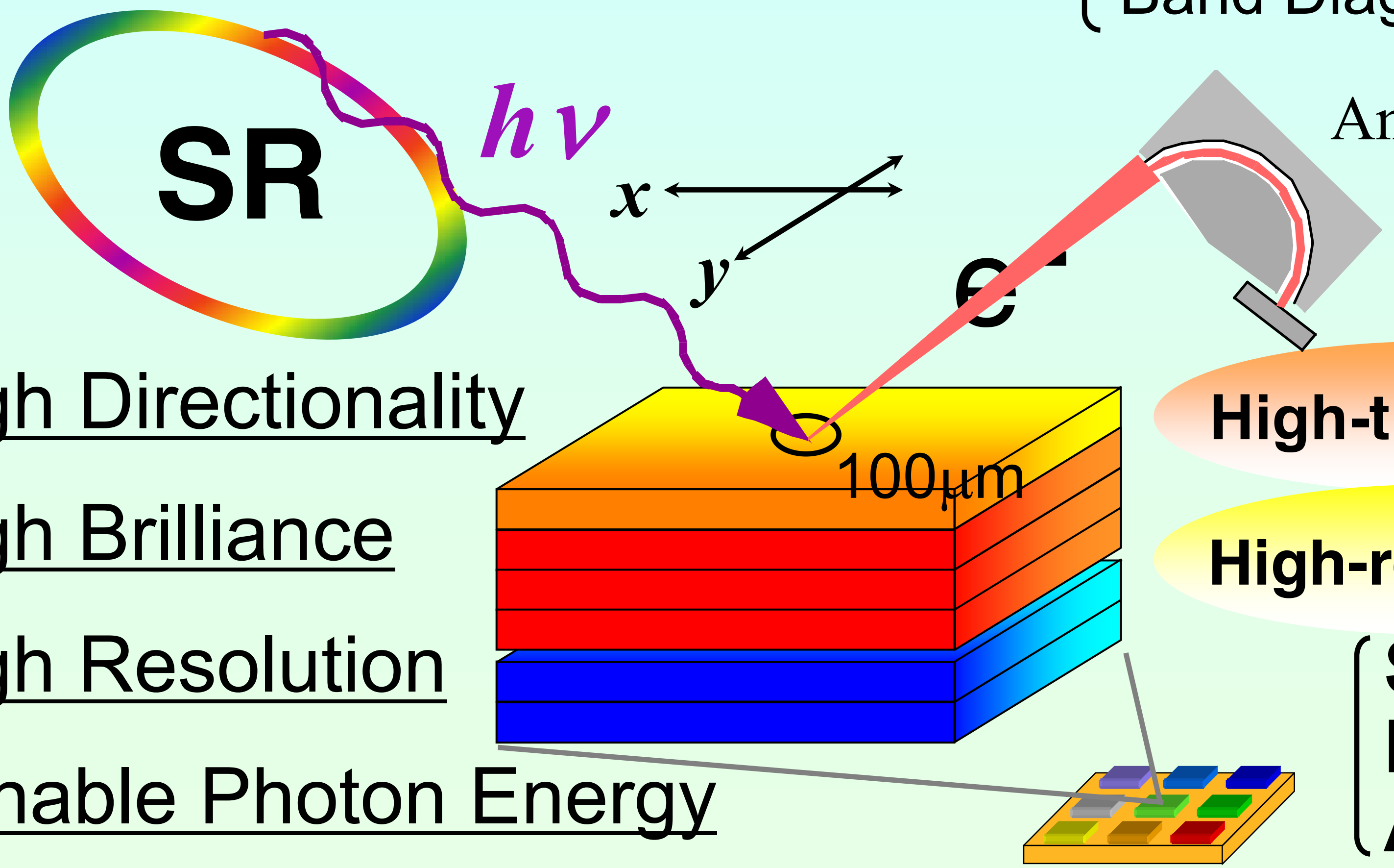
Advantage of SR-PES

☆Non-destructive

Hard-XrayPES@SPring-8 (〜1000 A)

☆Surface (Interface) Sensitive （5〜30Å）

☆Direct Determination of Electronic States
- Chemical Shift
- DOS
- Band Diagram



High Directionality

High Brilliance

High Resolution

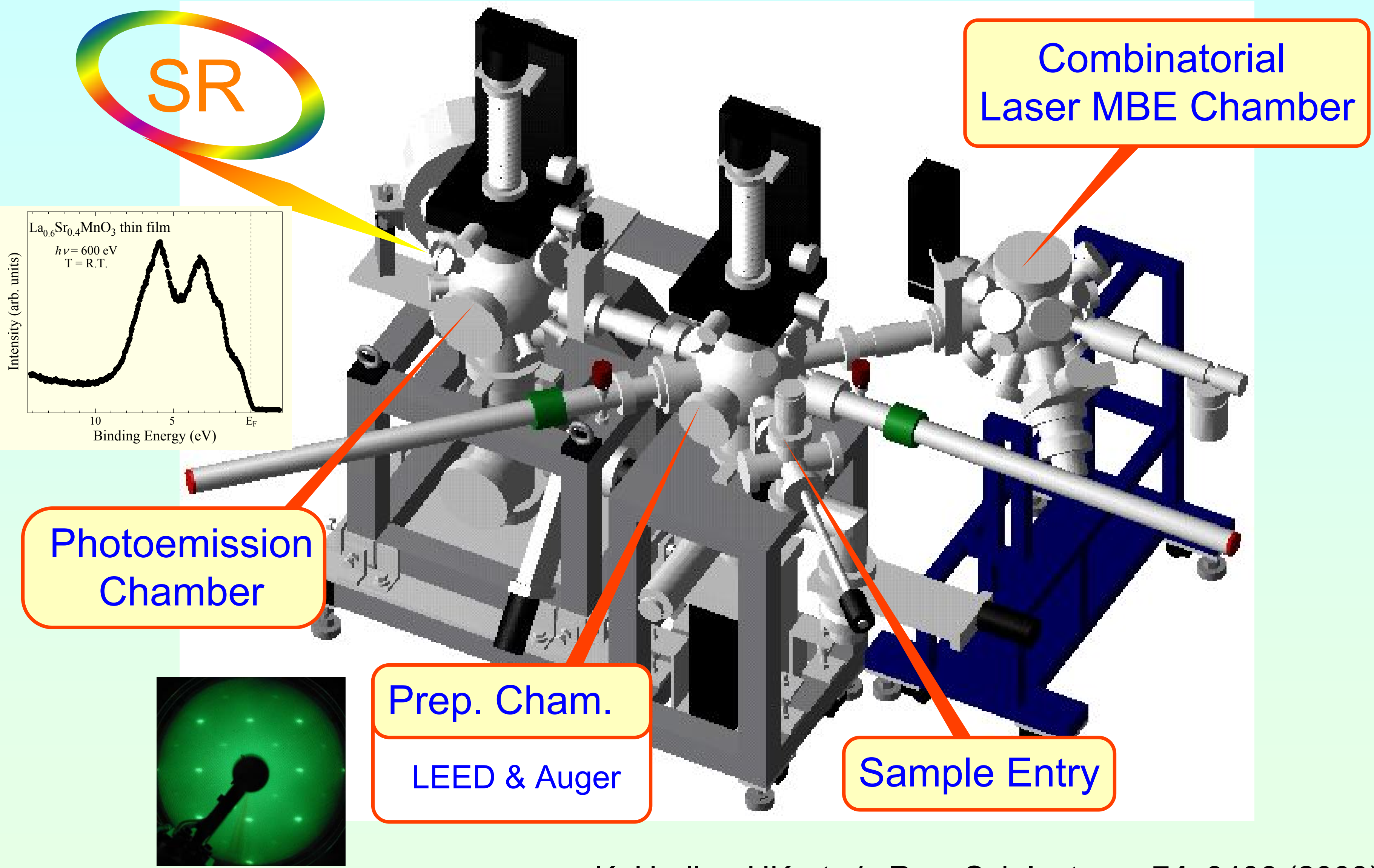
Tunable Photon Energy

High-throughput

High-resolution

Space
Energy
Angle

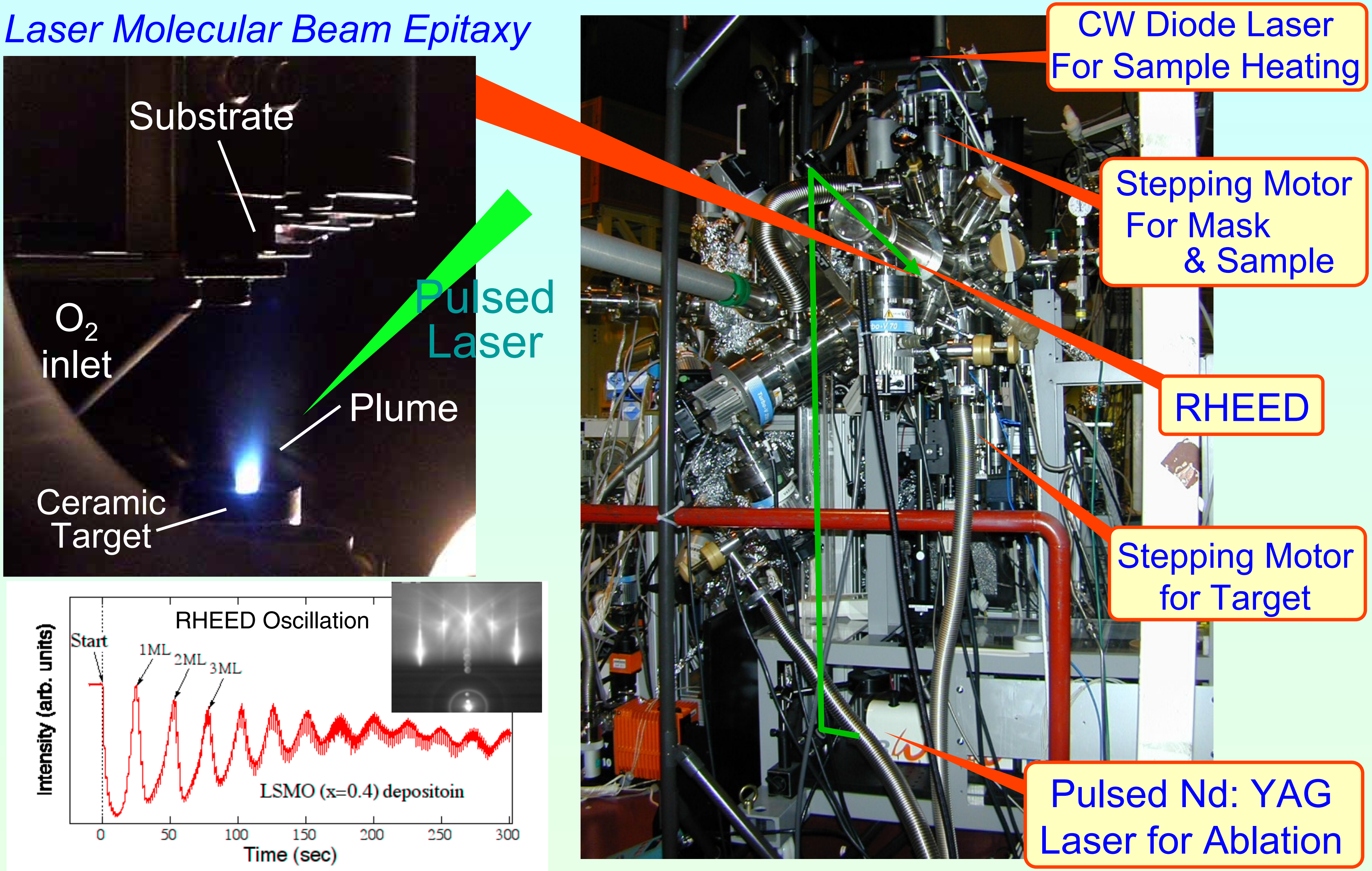
In-situ PES + Laser MBE system

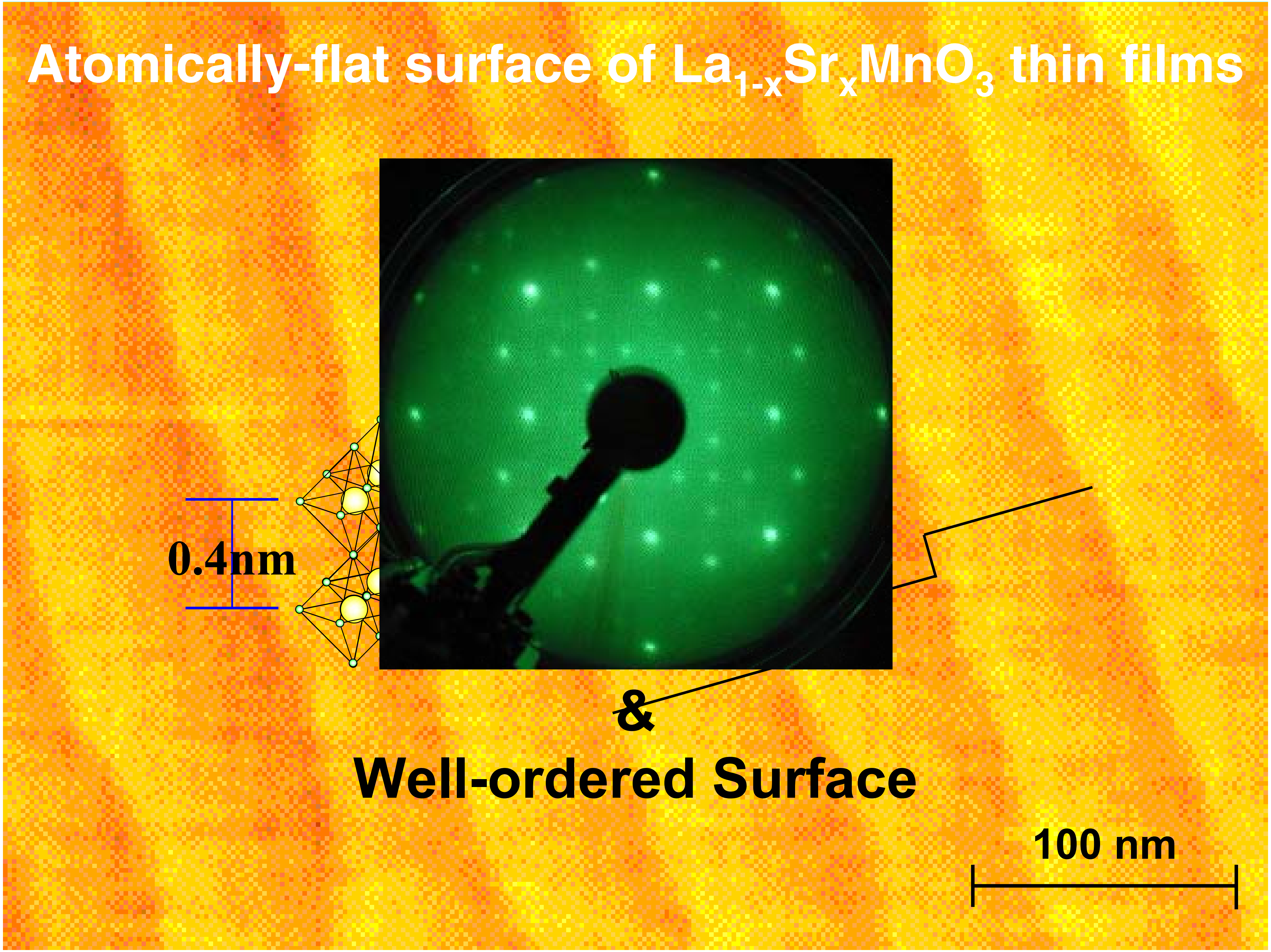


K. Horiba, HK *et al.*, Rev. Sci. Instrum. **74**, 3406 (2003).

Combinatorial Laser MBE Apparatus

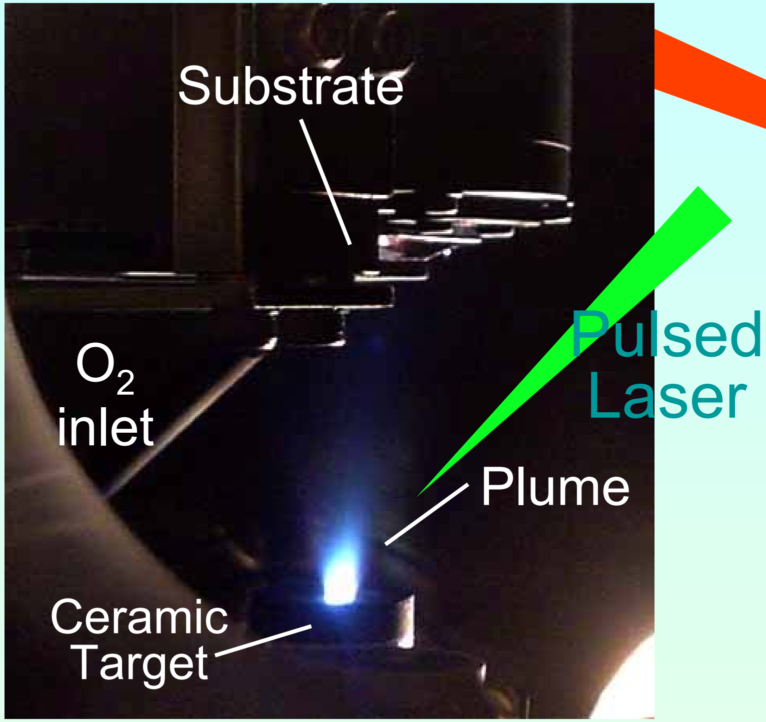
Laser Molecular Beam Epitaxy

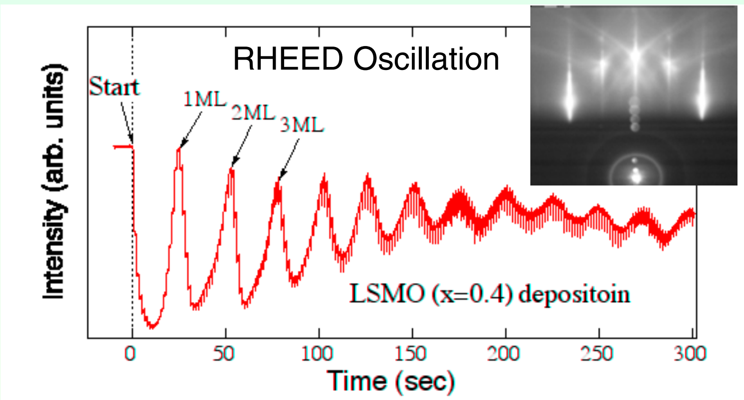


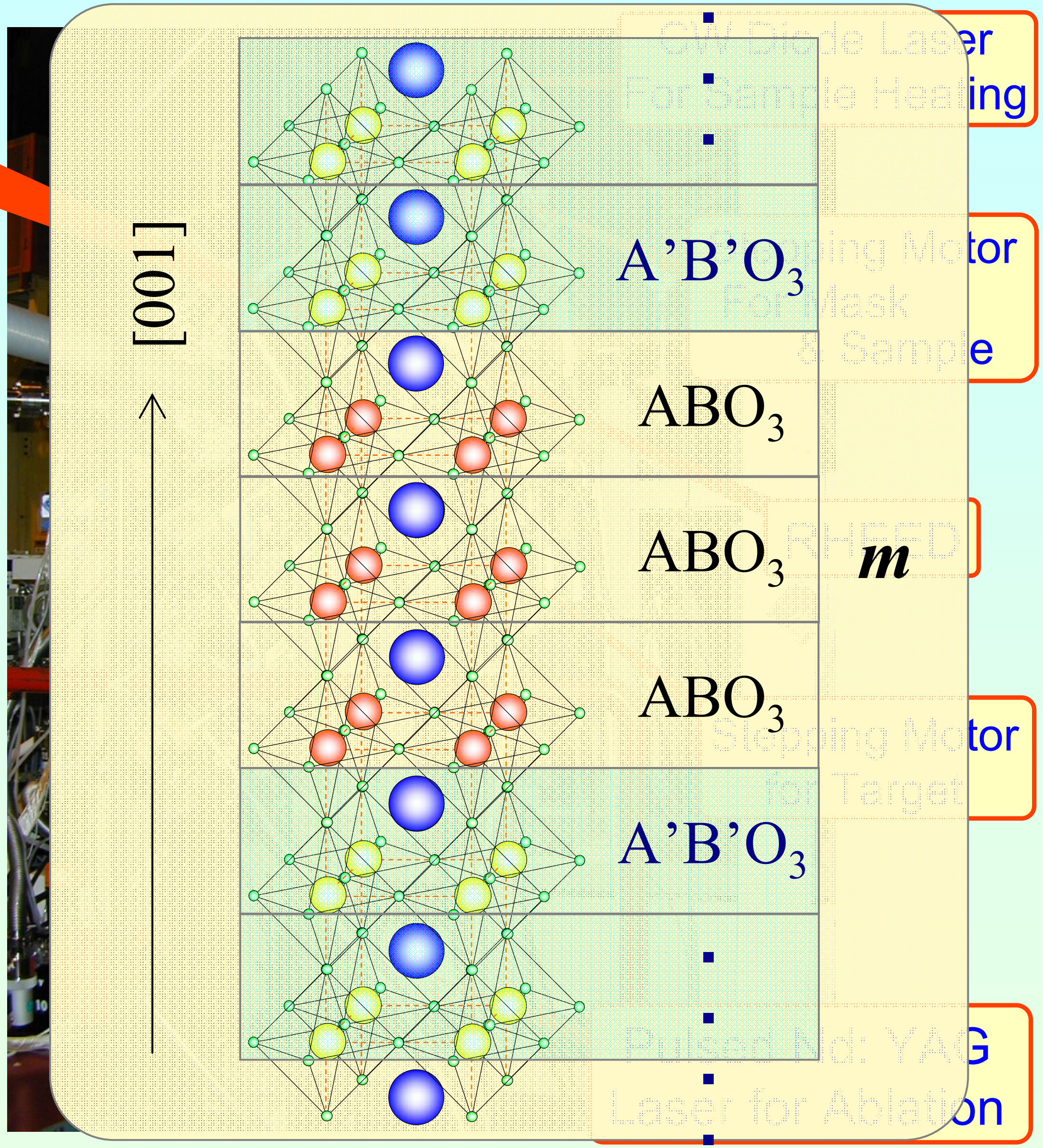

Atomically-flat surface of $La_{1-x}Sr_xMnO_3$ thin films
0.4nm
&
Well-ordered Surface
100 nm

Combinatorial Laser MBE Apparatus

Laser Molecular Beam Epitaxy



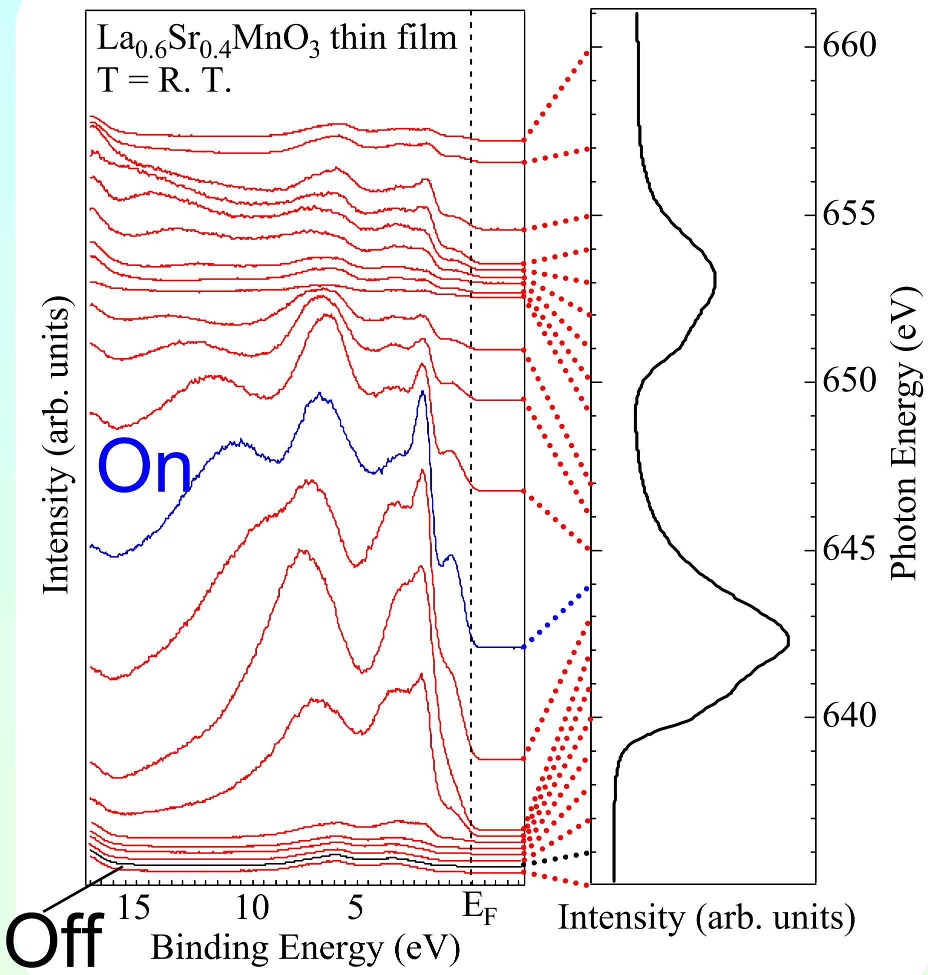


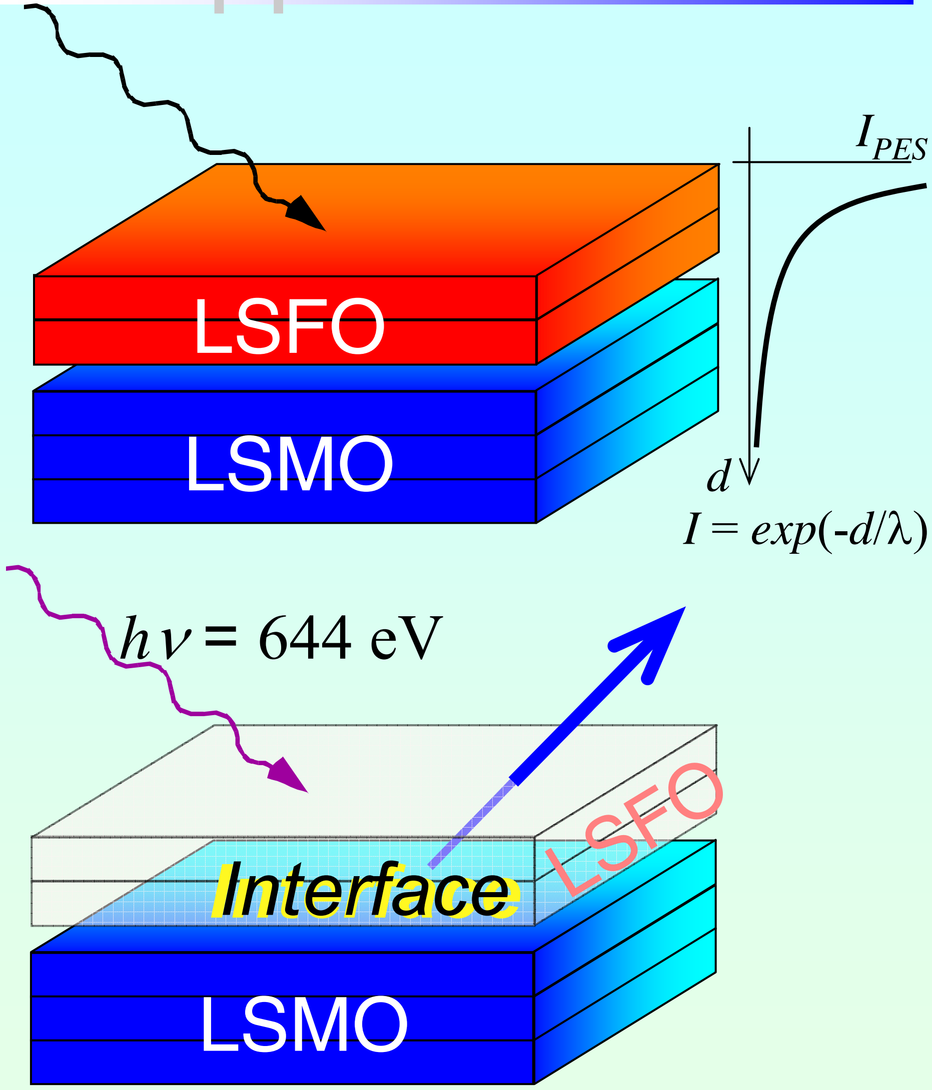


Resonant PES Approach

Resonant PES Approach

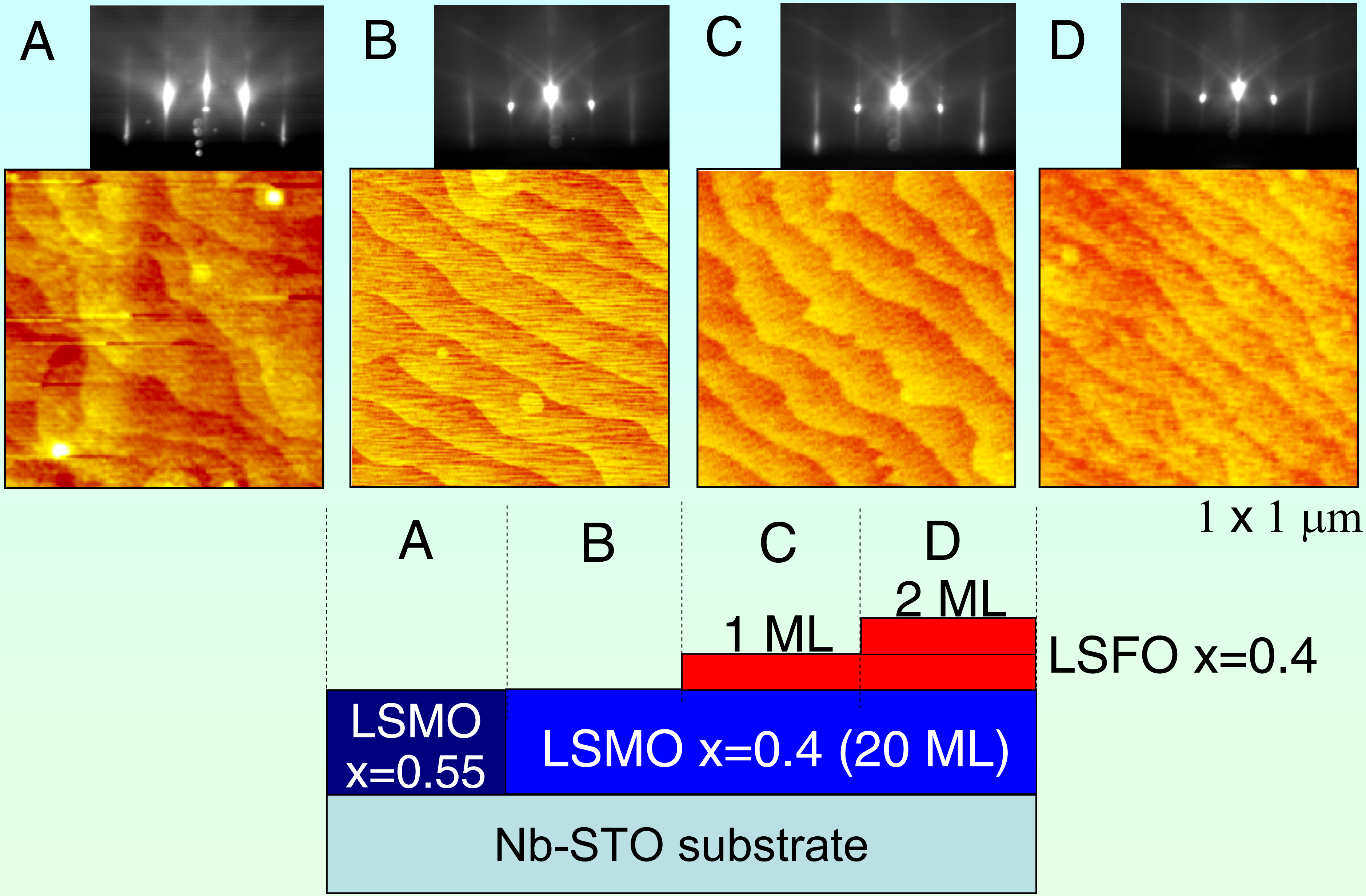
Resonant PES of LSMO (x=0.4)





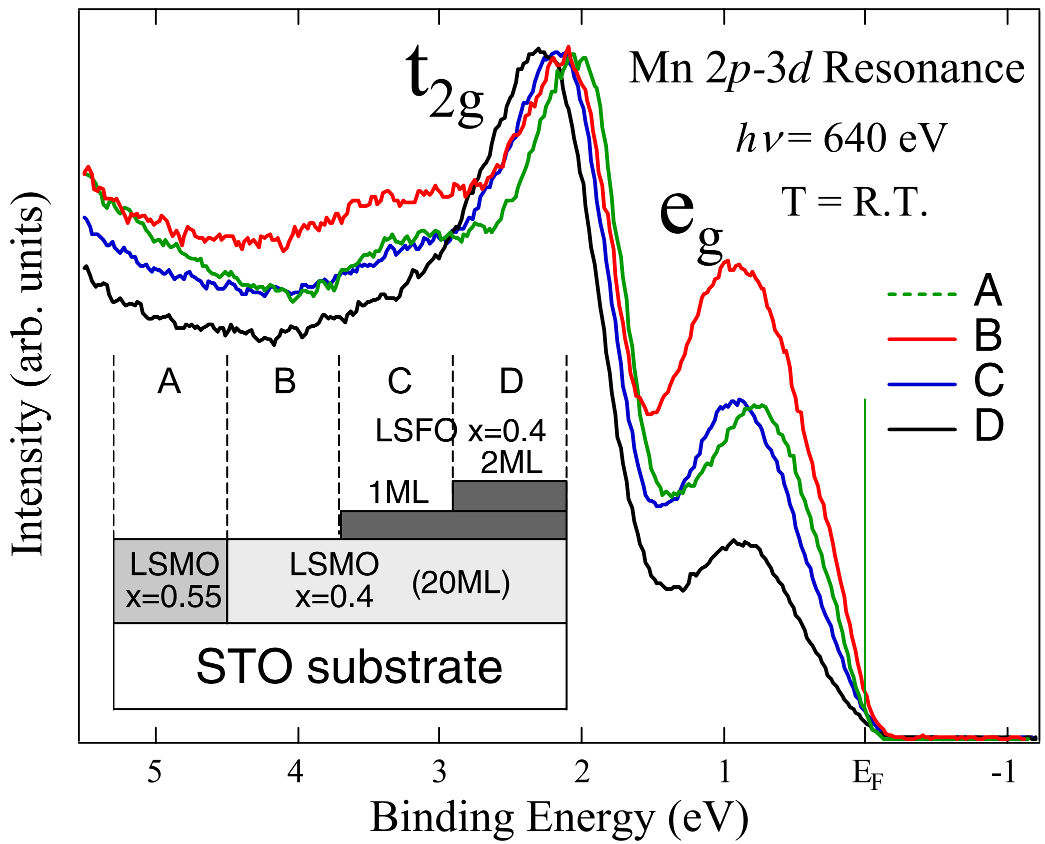
Probing Electronic Structure at the Interface (Mn 3*d* PDOS)

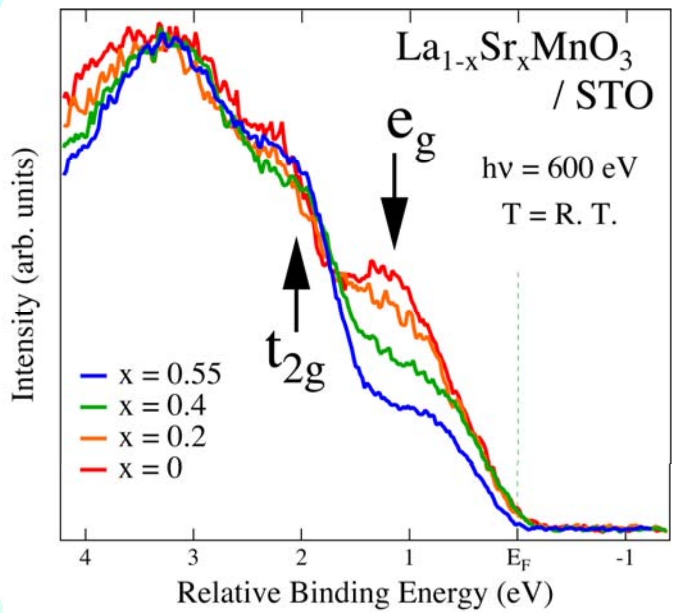
RHEED Pattern & AFM Images



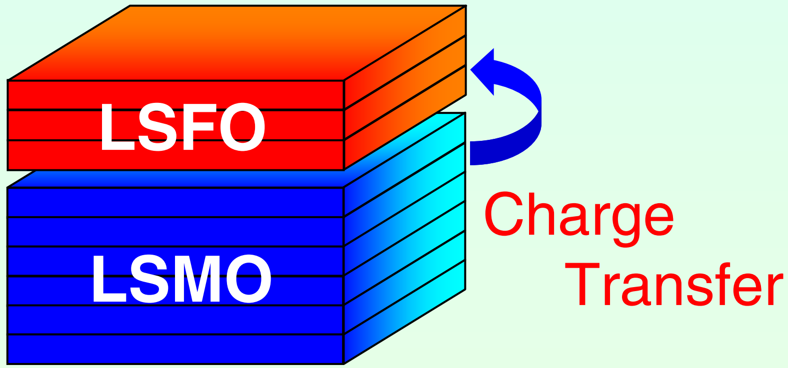
Resonant PES of LSMO at Interface

Mn 2*p*-3*d* Resonant PES





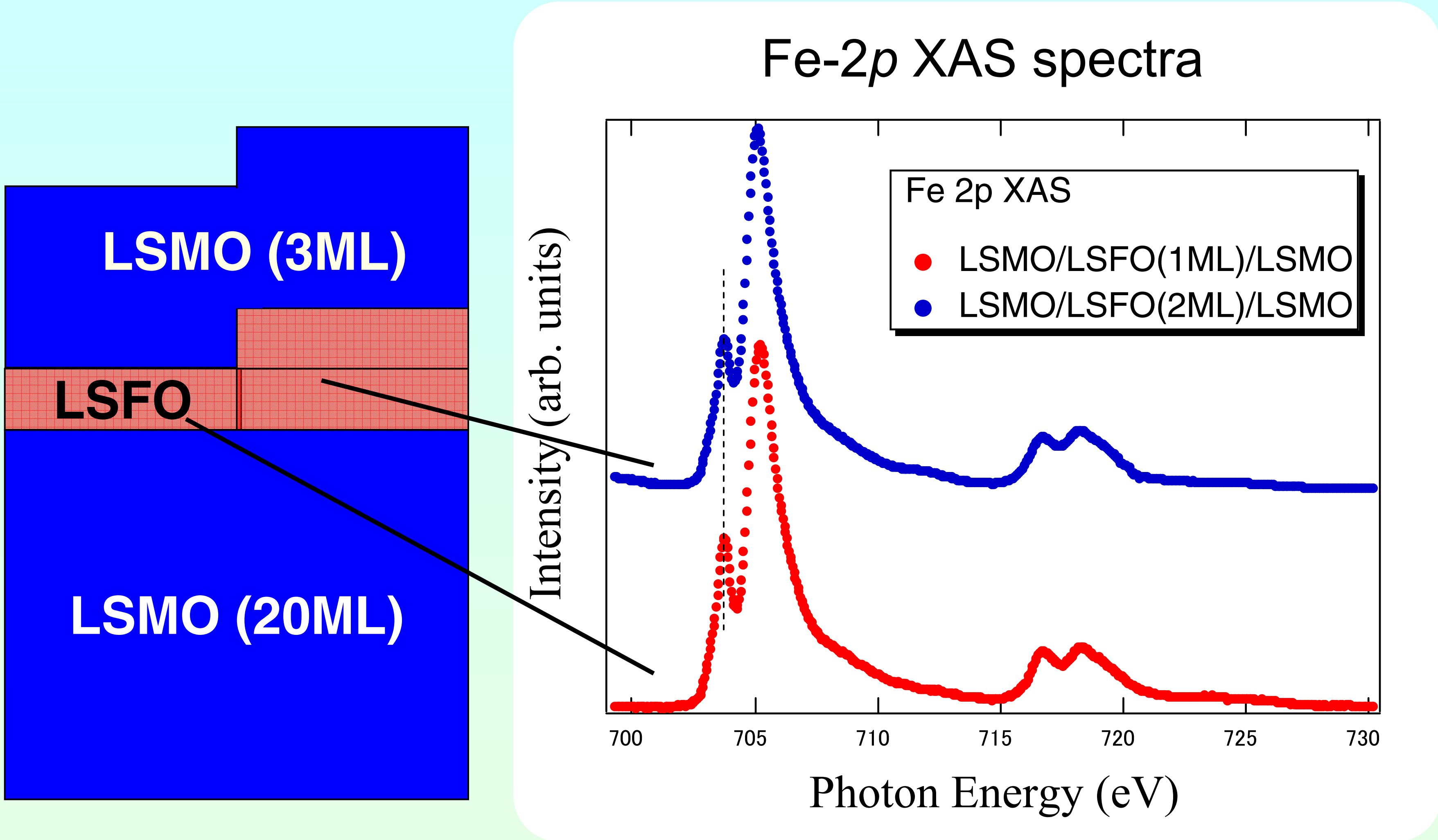
K. Horiba, H.K. *et al*., Phys. Rev. B **71**, 155420 ('05)



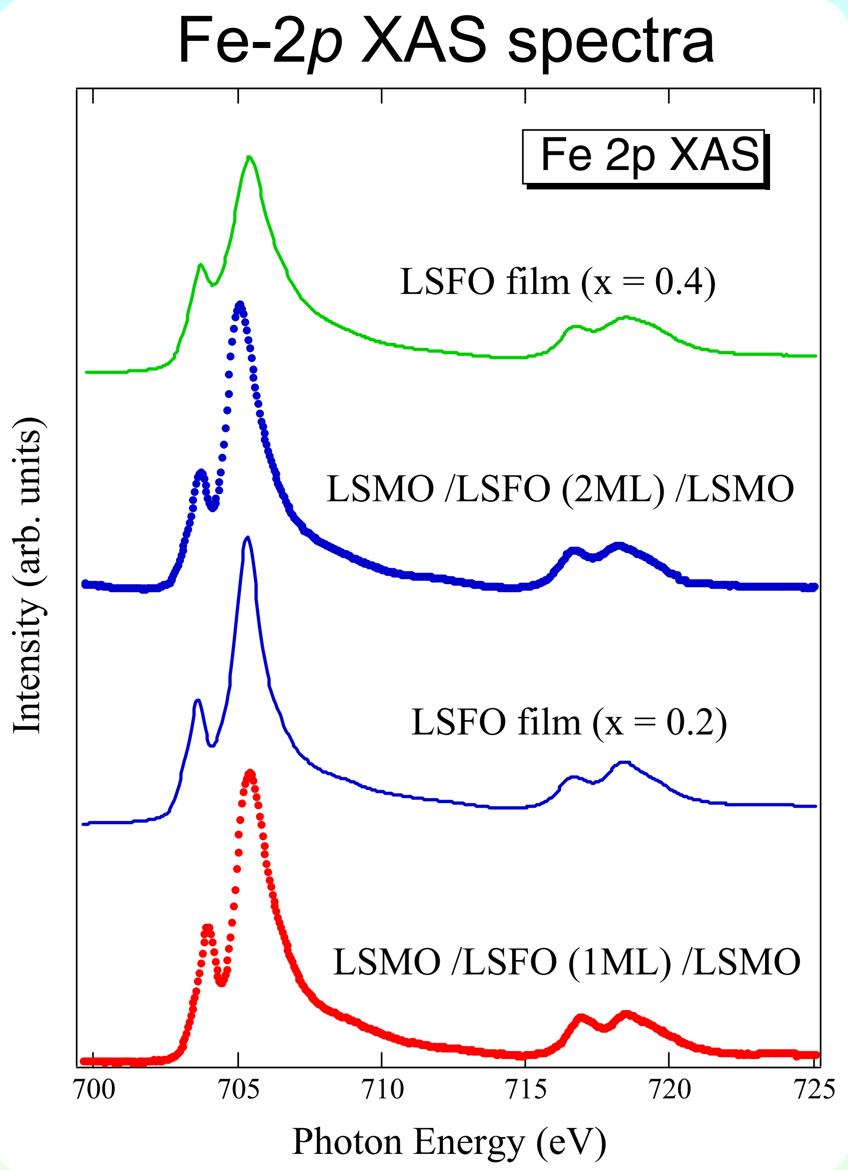
<u>Spectral Evidence of Charge Transfer at LSMO/LSFO Interface</u>

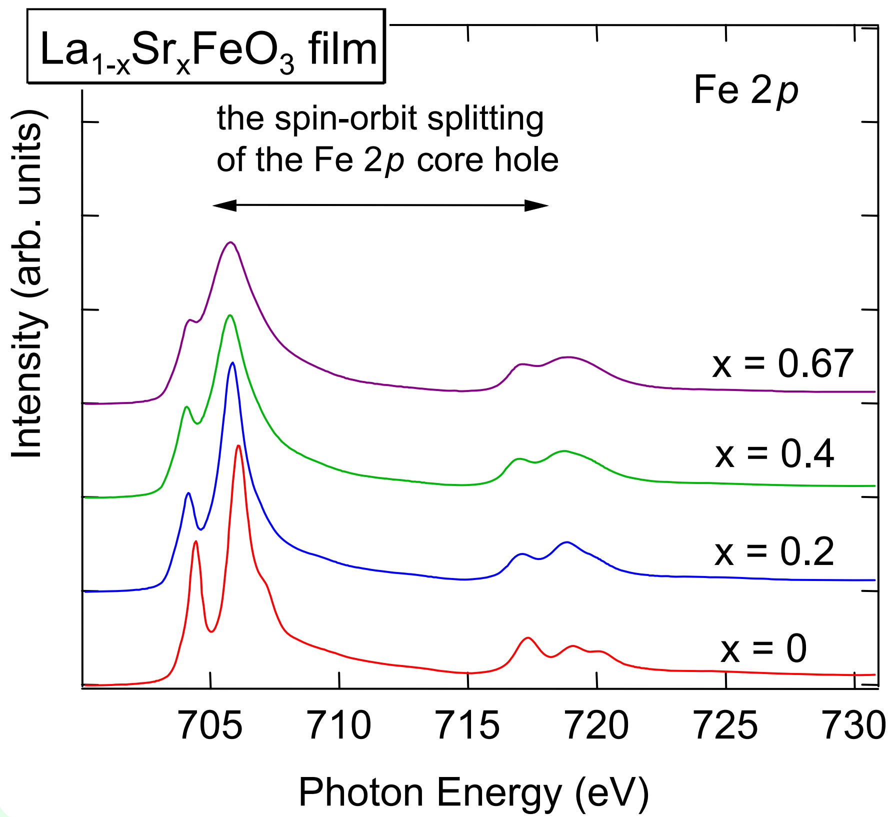
H. Kumigashira *et al*., *Appl. Phys. Lett*. **84**, 5353 (2004).

XAS Spectra of Interfacial LSFO Layer



Comparison of Fe-2*p* XAS spectra between Interfacial LSFO layer and LSFO films

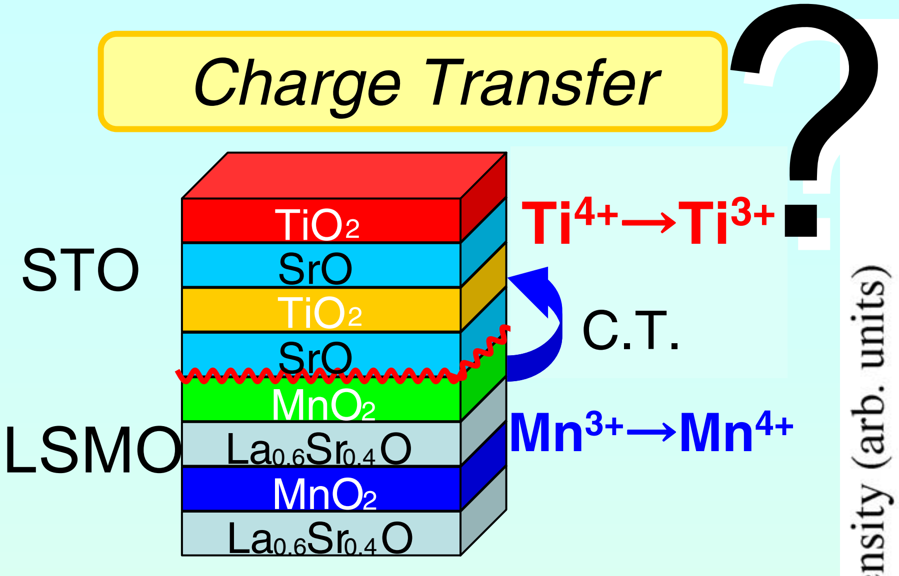


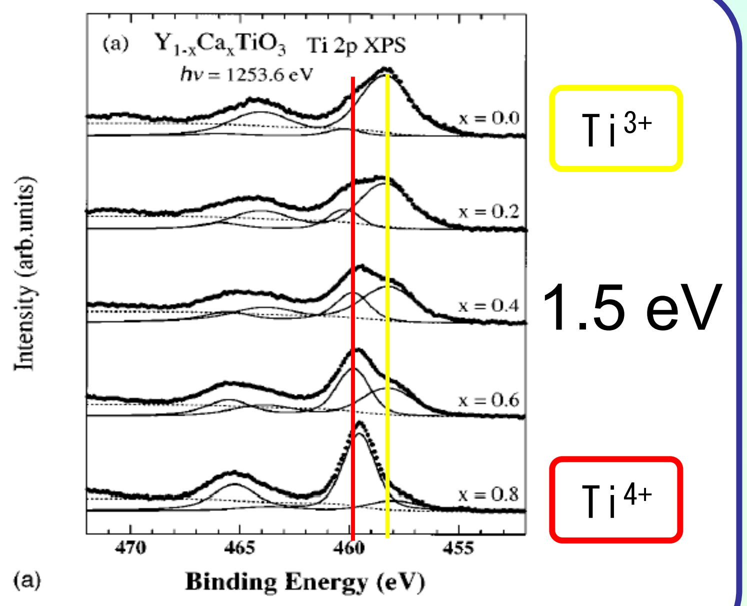


H. Wadati, H.K. et al., *Phys. Rev. B* **71**, 035108 (05).

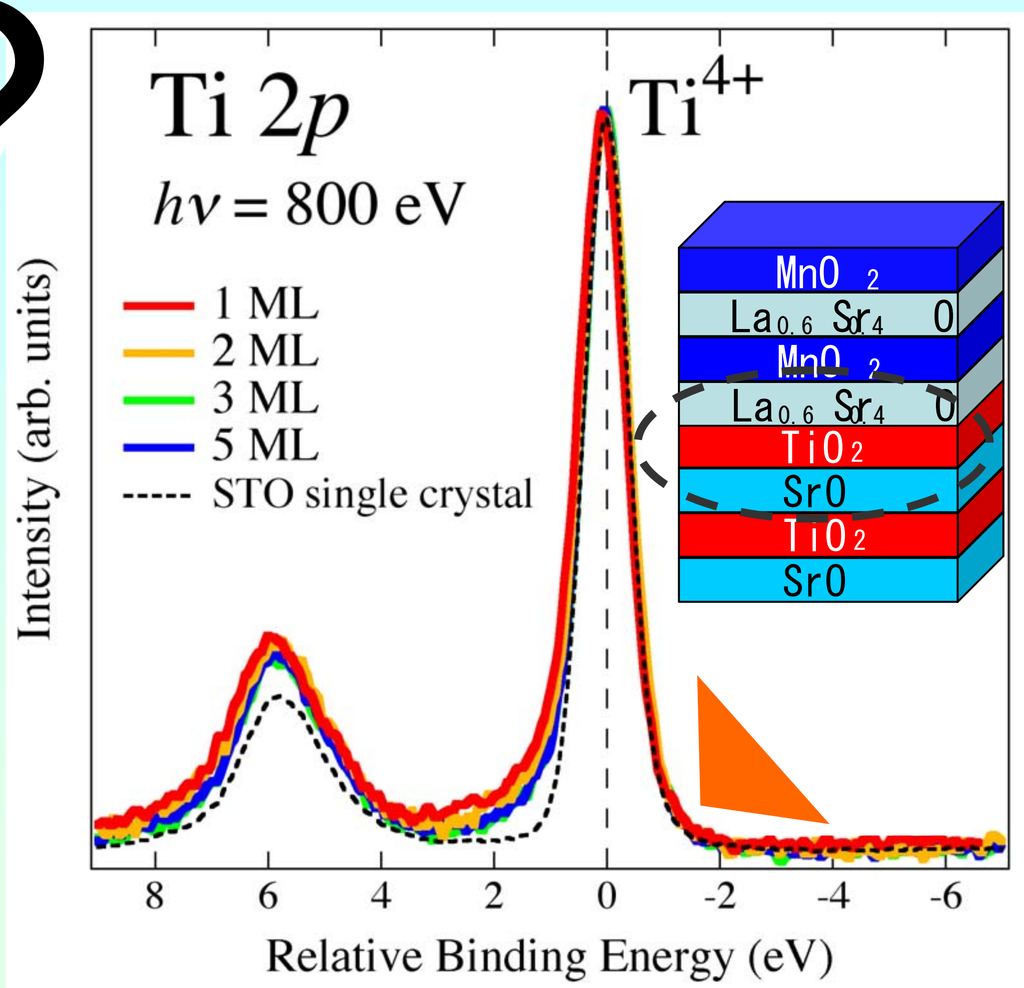
Evidence of Charge Transfer from LSMO to LSFO

Ti 2*p* Core Level Spectra at Interfaces





K. Morikawa *et al.*, Phys. Rev. B **54**, 5446 (1996).

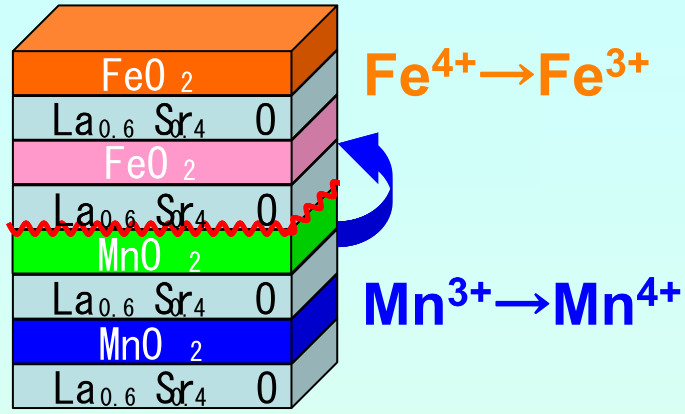


H. Kumigashira *et al.*, Appl. Phys. Lett. **88**, 192504 ('06).

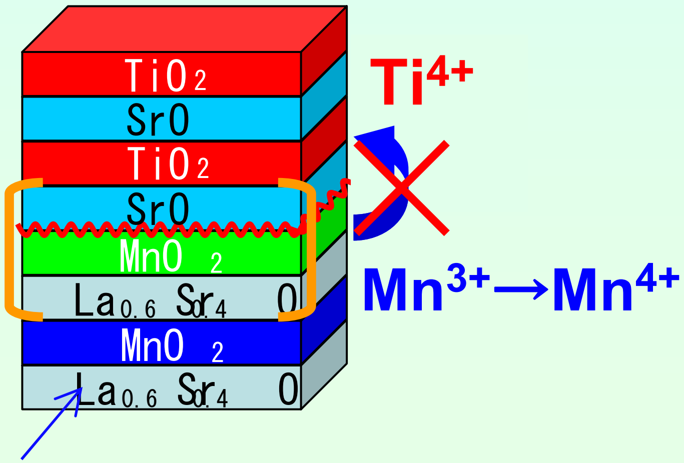
Robust Ti^{4+} states

Origin of Charge Transfer

LSFO/LSMO

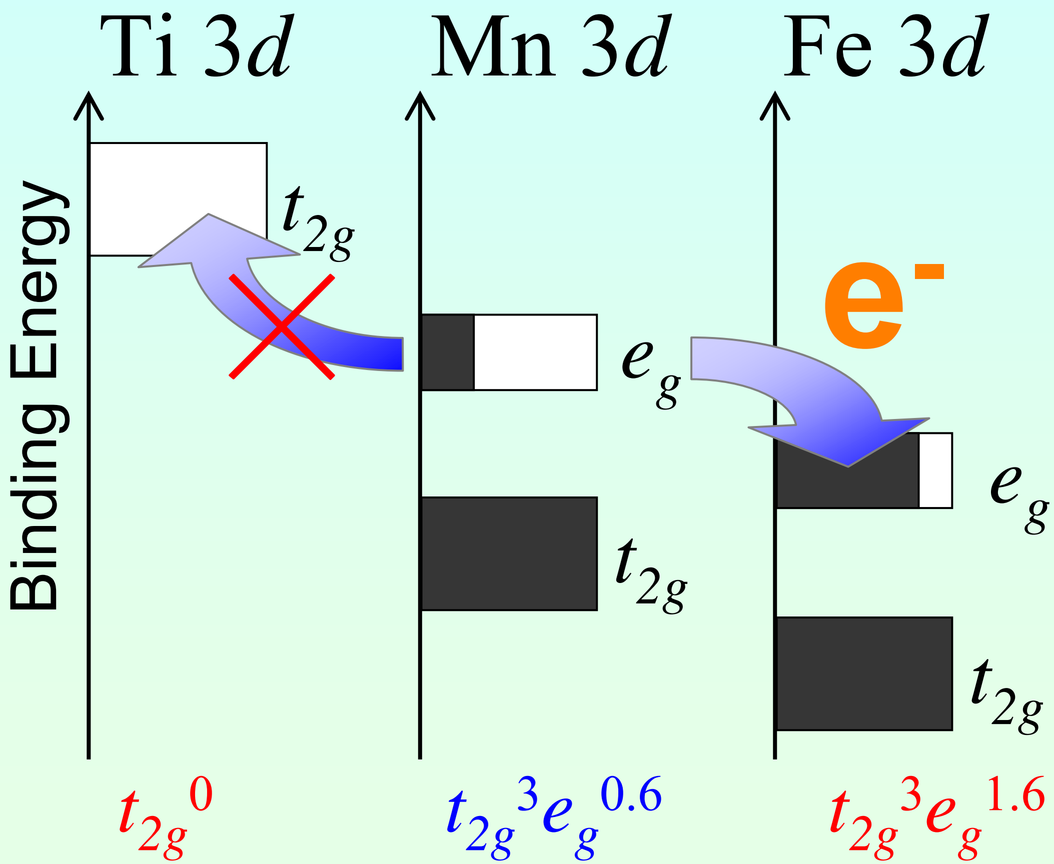


STO/LSMO



Electron-donor layer

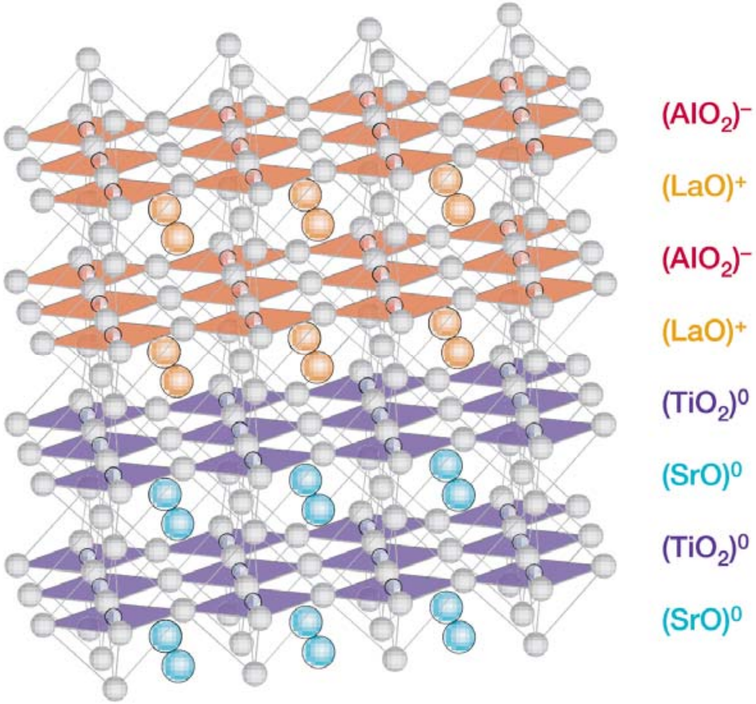
Difference of 3*d* levels among transition metals



Charge redistribution at interface

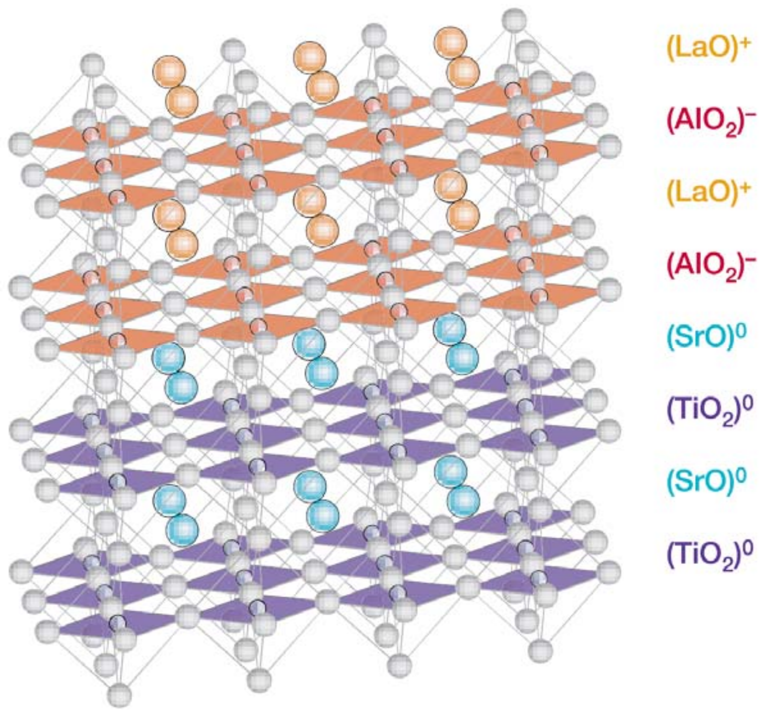
Interfacial Electronic Structure of $LaAlO_3$/ $SrTiO_3$ Heterojunctions

$LaAlO_3$ /TiO_2-$SrTiO_3$



n-type (Metallic)

$LaAlO_3$ /SrO-$SrTiO_3$



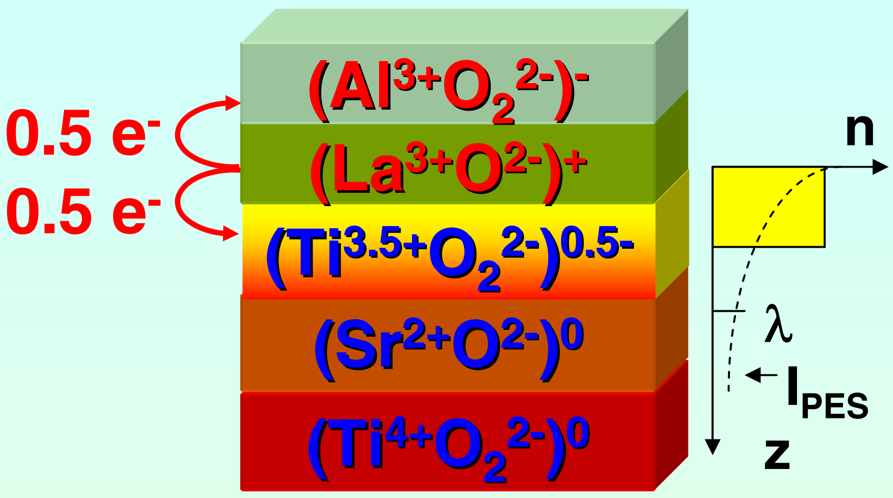
p-type (Insulating)

A. Ohtomo and H. Y. Hwang, Nature **427**, 423 ('04).

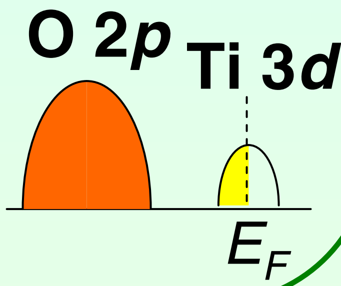
Origin of the Metallic Interface

1. Charge Transfer

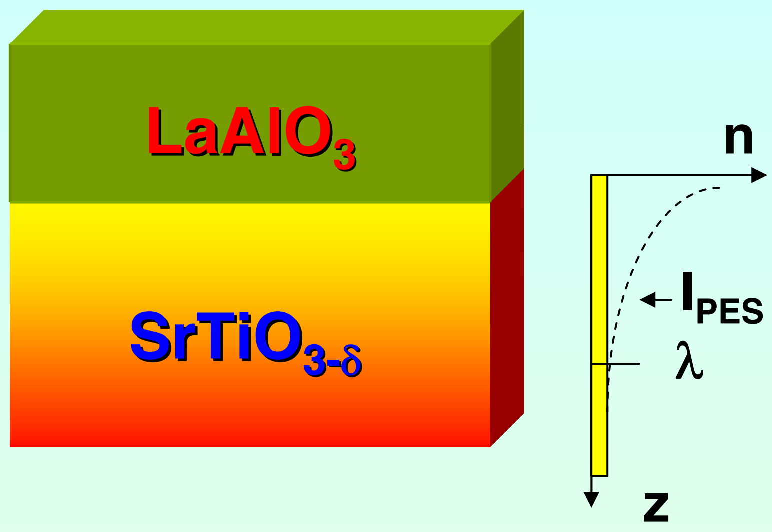
$2Ti^{4+}(d^0) + e^- \rightarrow Ti^{3+}(d^1) + Ti^{4+}$



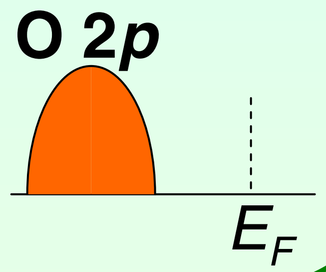
N. Nakagawa *et al.*, Nature Mater. **5,** 204 (2006).



2. Oxygen Vacancies



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

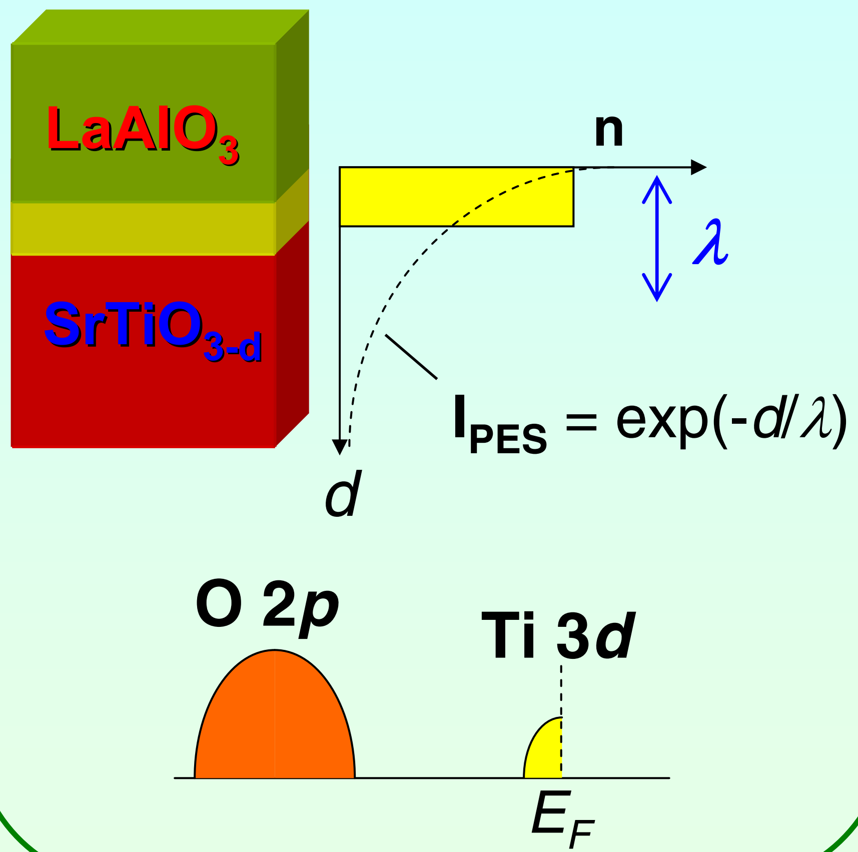


DOS at E_F is different between the two scenarios.

Detection Limit of PES Mearuements

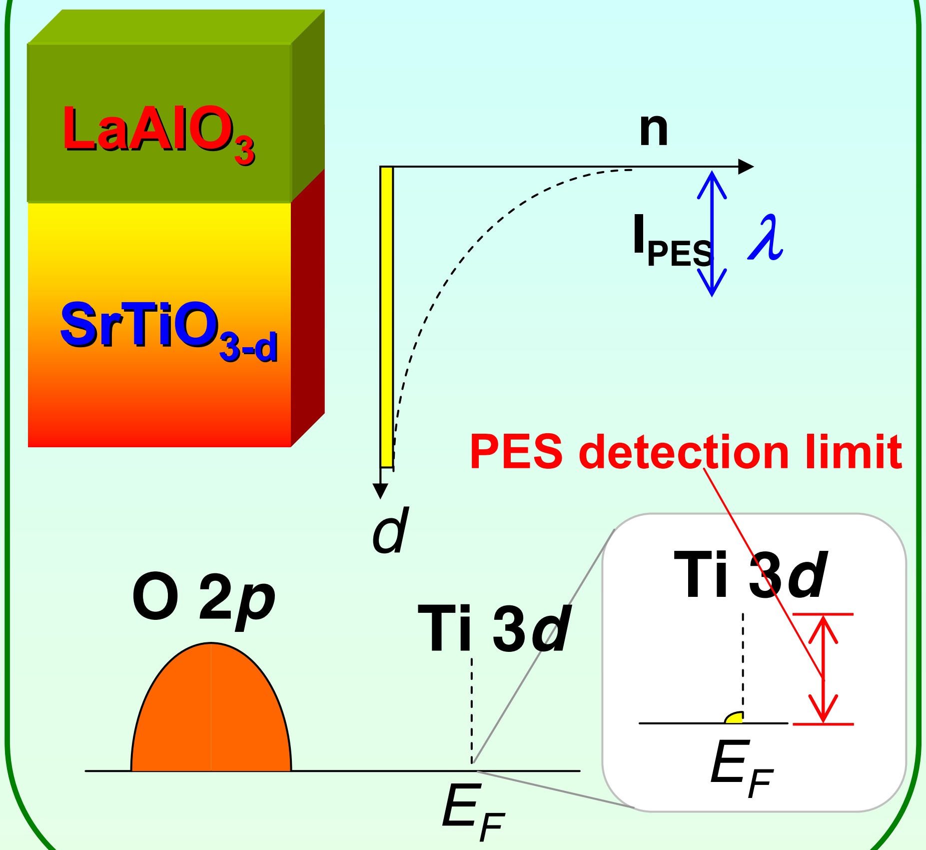
1. Charge Transfer

(Confinement@interface region)



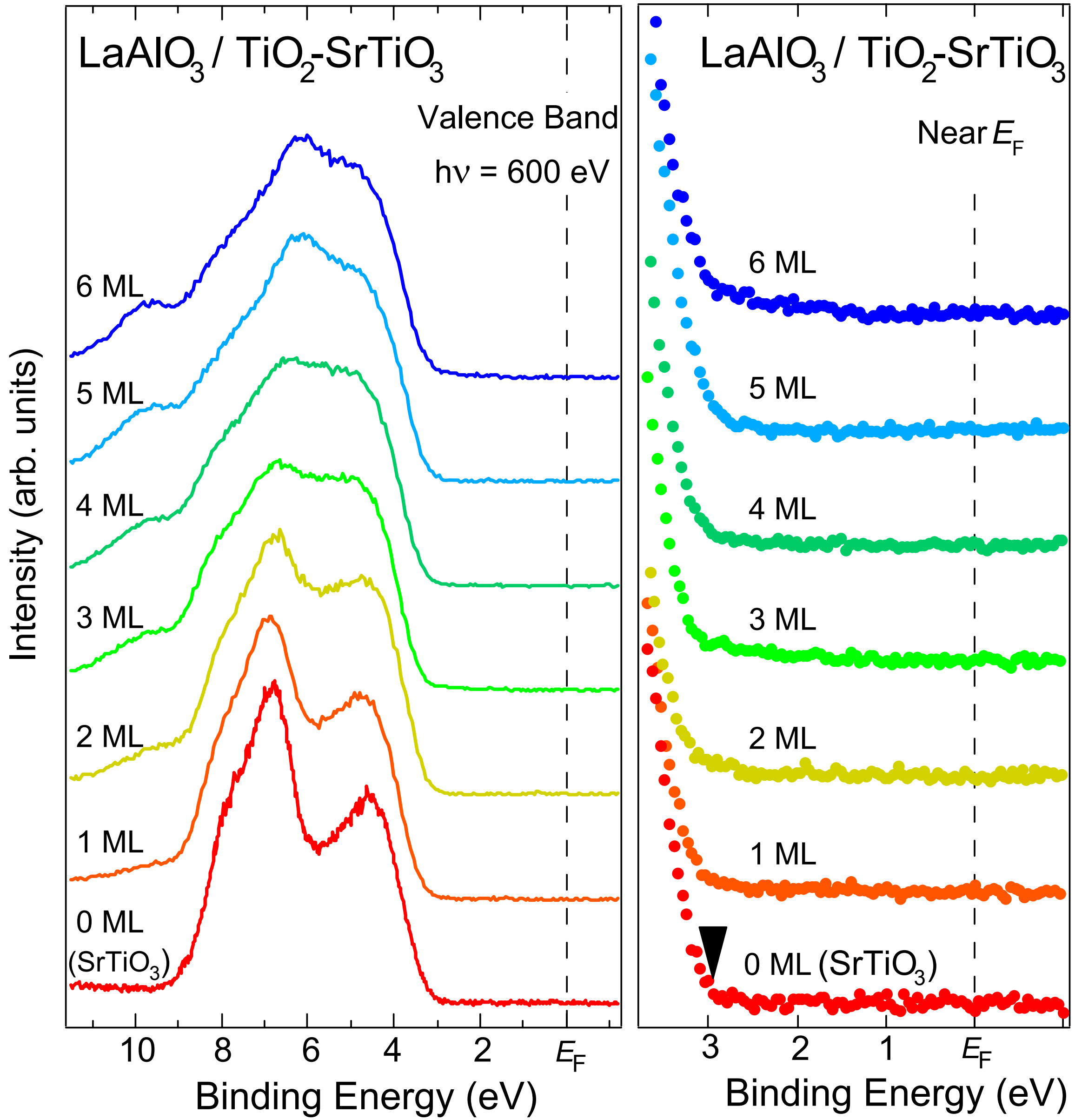
2. Oxygen Vacancies

(wide distribution over STO)



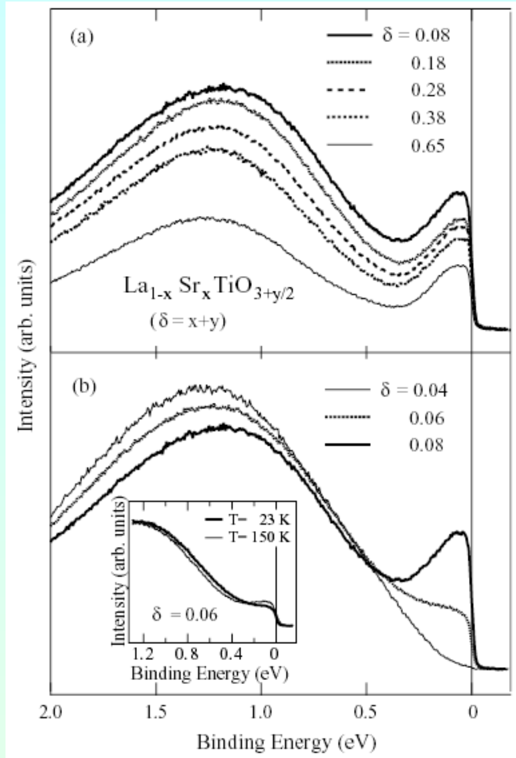
DOS at E_F is different between the two scenarios.

Valence Band Spectra of n-type Interfaces



K. Yoshimatsu *et al.*, *Phys. Rev. Lett.* **101**, 026802 (08).

PES spectra of LSTO

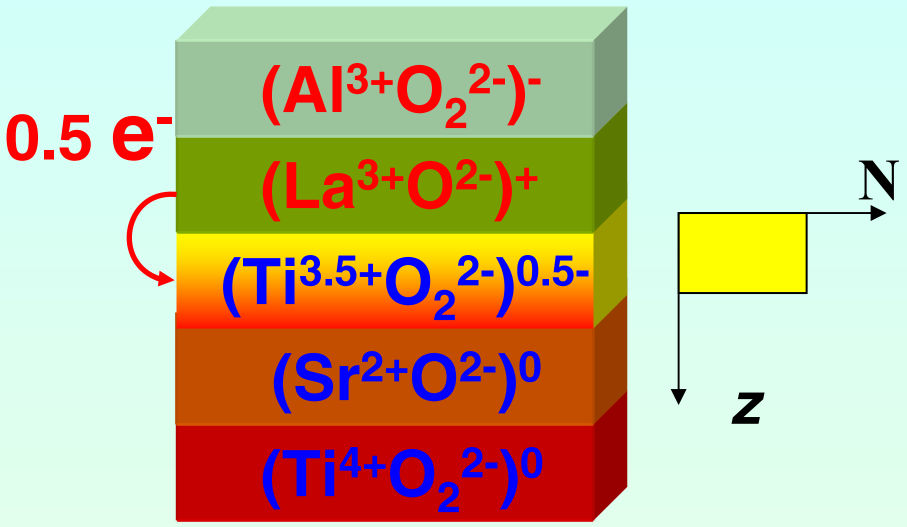


T. Yoshida *et al.*, Europhys. Lett. **59**, 258 ('02)

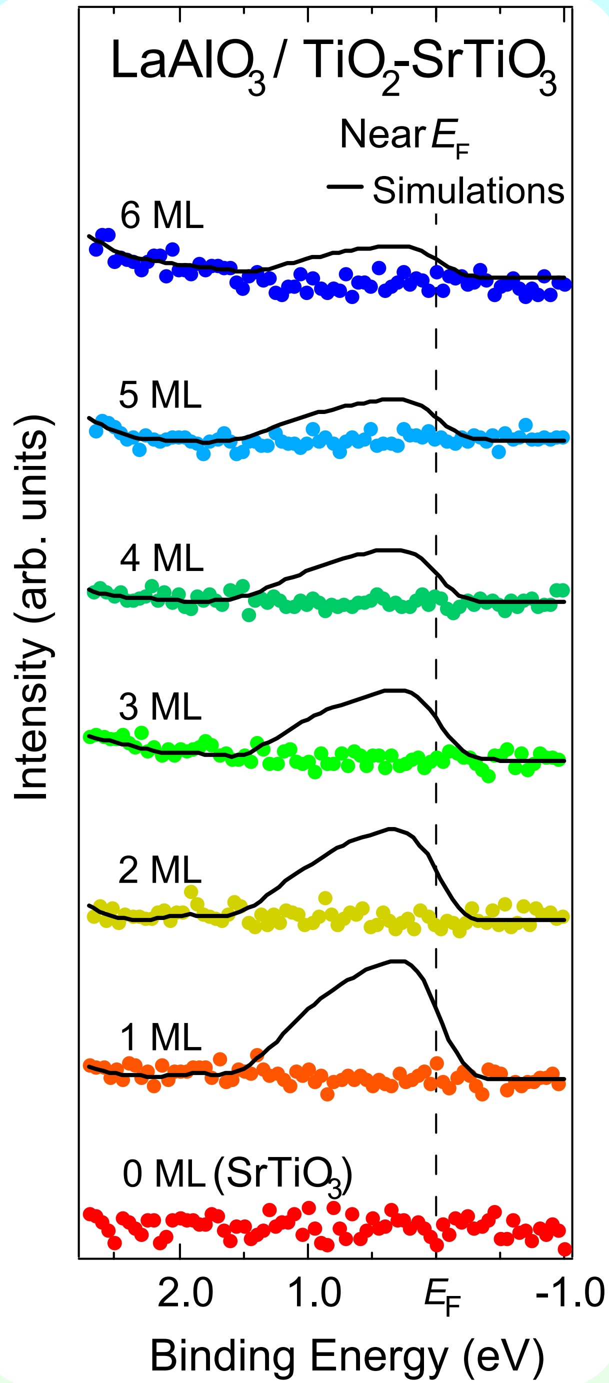
No detectable Ti 3*d* DOS at E_F

Numerical Simulations

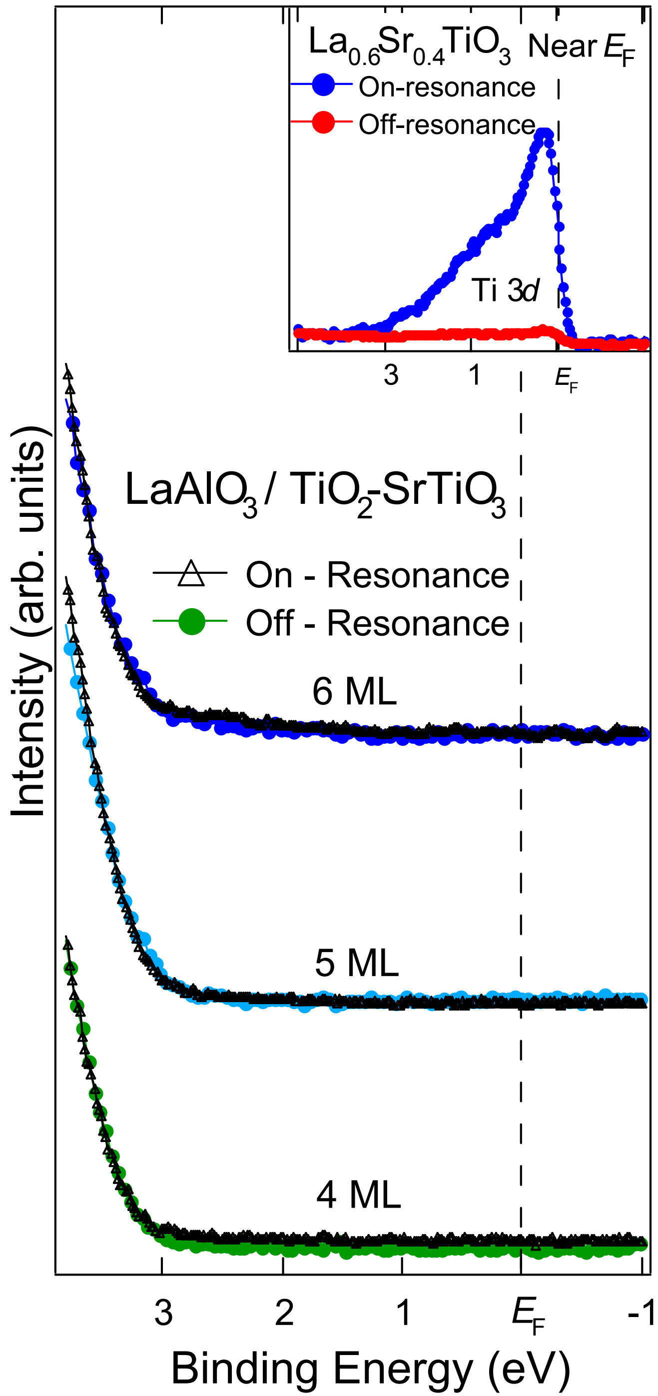
Confinement at the interface
(δ function)



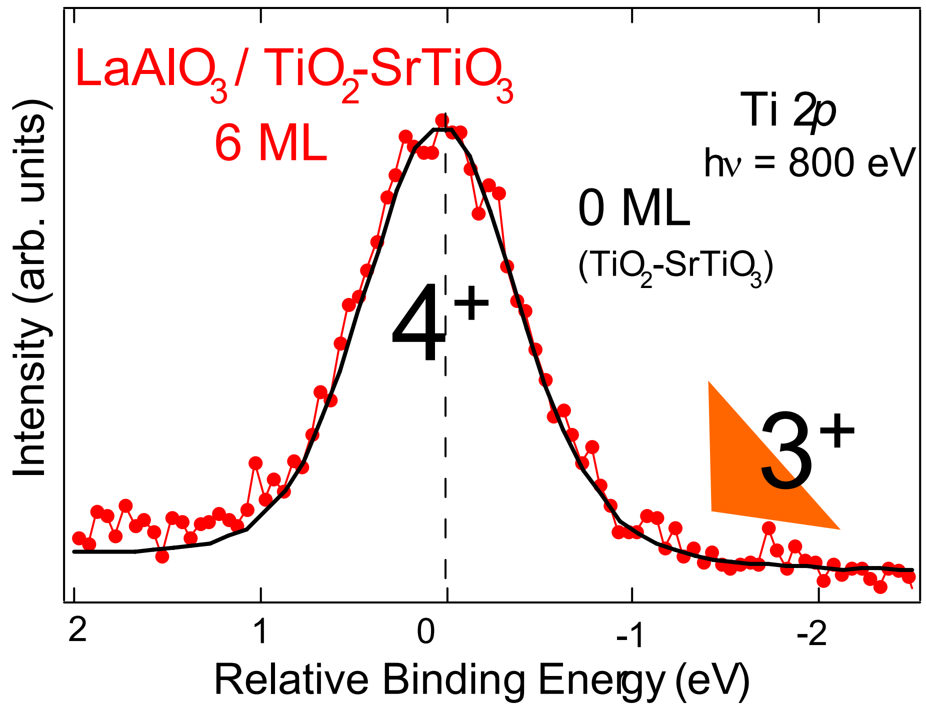
The 3*d* electrons only exist at TiO_2 layer adjacent to (LaO)+ layer.



Ti 2*p* → 3*d* Resonant Spectra



Chemical stabilities of Ti^{4+} states in TiO_2 irrespective of the neighboring donor LaO layer

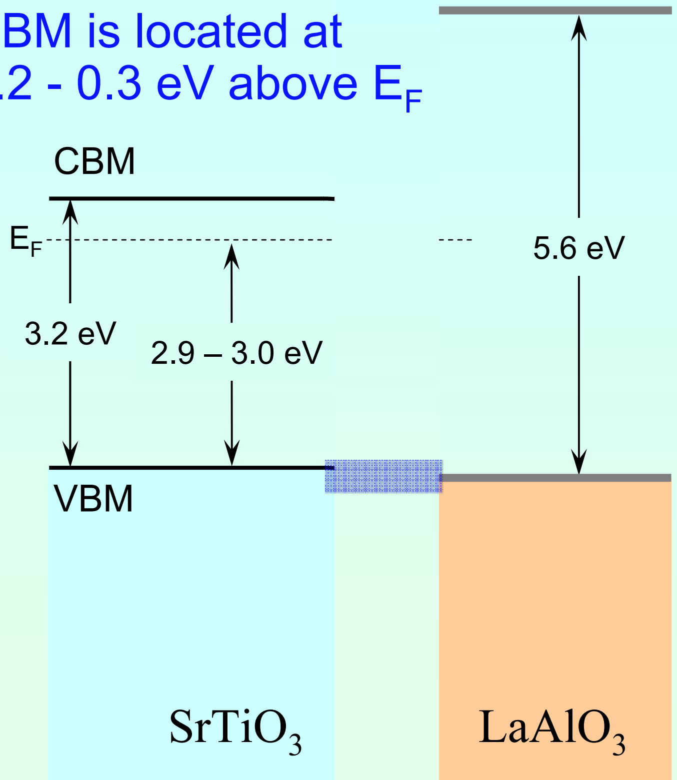


Charge transfer doesn't occur at the LAO/STO interface.

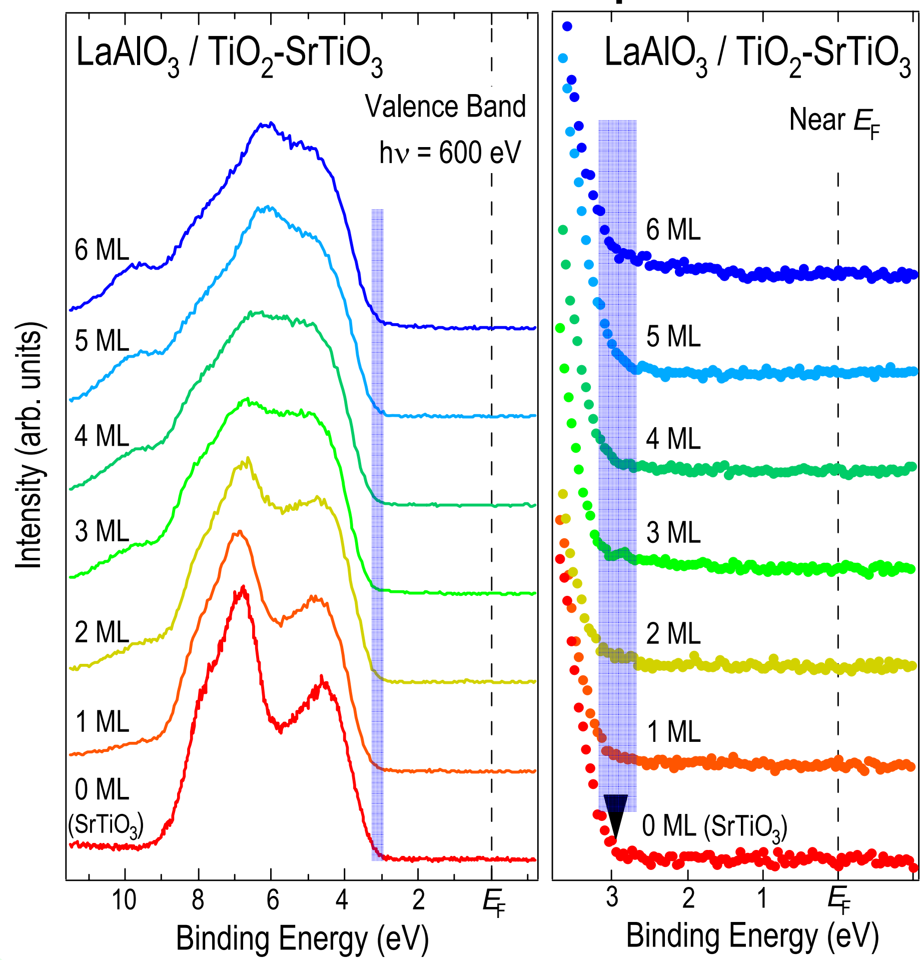
Band Diagram of the n-type Interface

Eg(STO) = 3.2 eV
Eg(LAO) = 5.6 eV

CBM is located at 0.2 - 0.3 eV above E_F



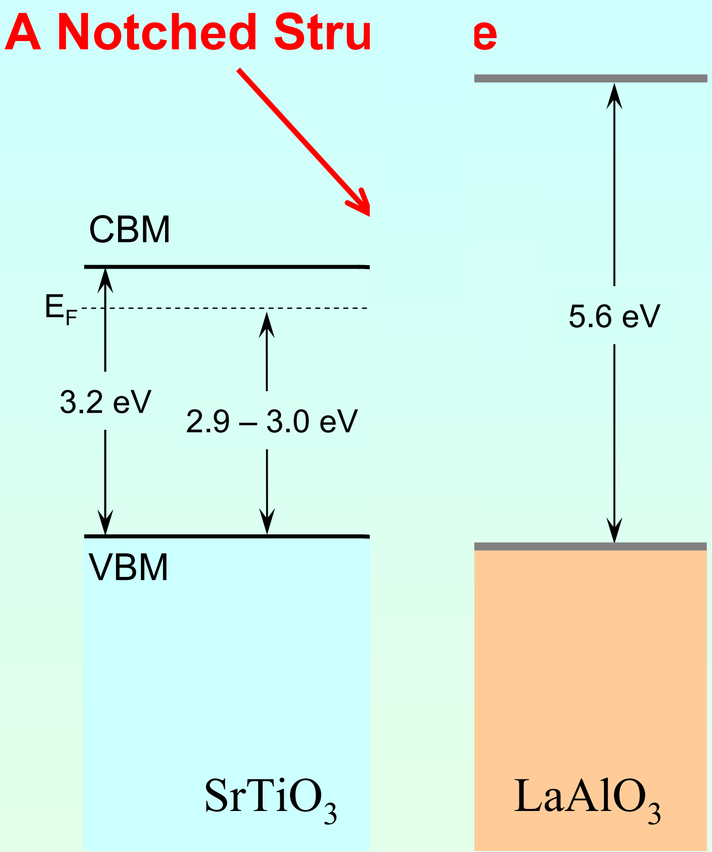
Valence band spectra



1. VBM of STO is located at 2.9-3.0 eV below E_F.
2. VBM is nearly continuous between STO and LAO.

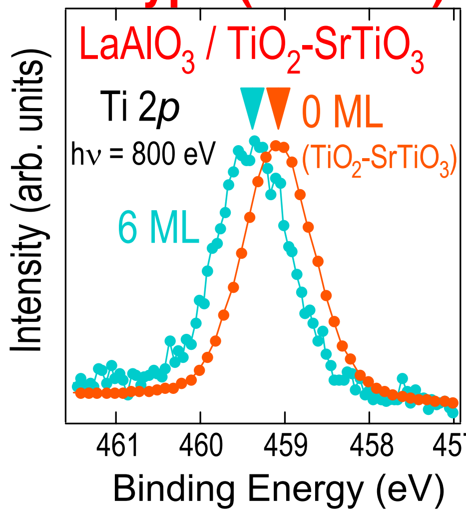
(The leading edge of valence band structures is located at almost constant energy position.)

Band Diagram of the n-type Interface

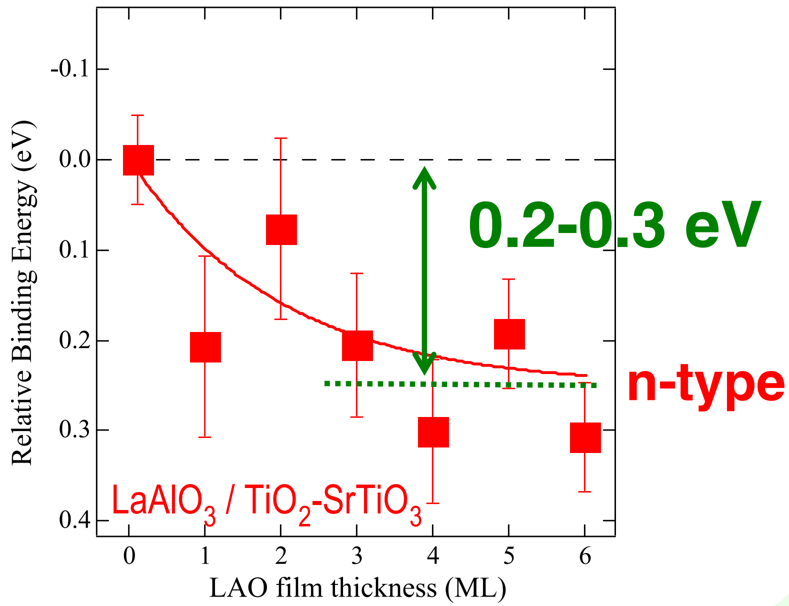


Ti 2*p* core level spectra

n-type (metallic)

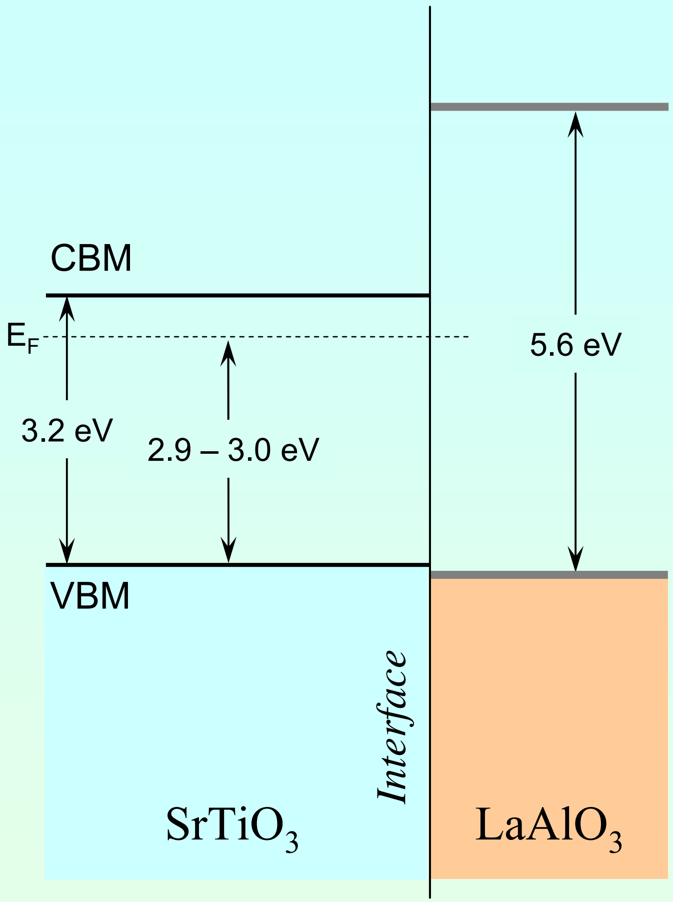


Band bending of 0.2-0.3 eV to higher binding energy from STO to the metallic interface.



CBM in STO is nearly attained at E_F

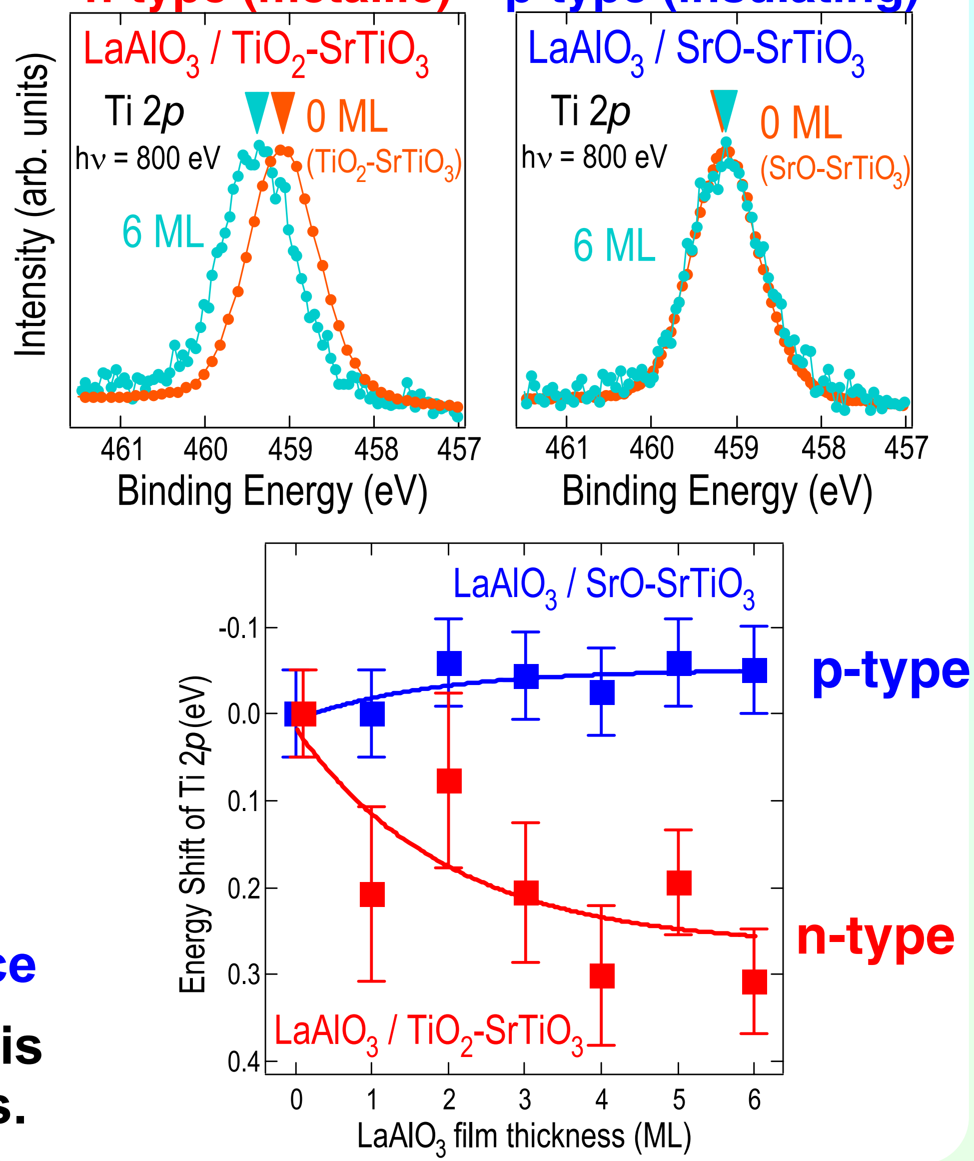
Band Diagram of LAO/STO Interface



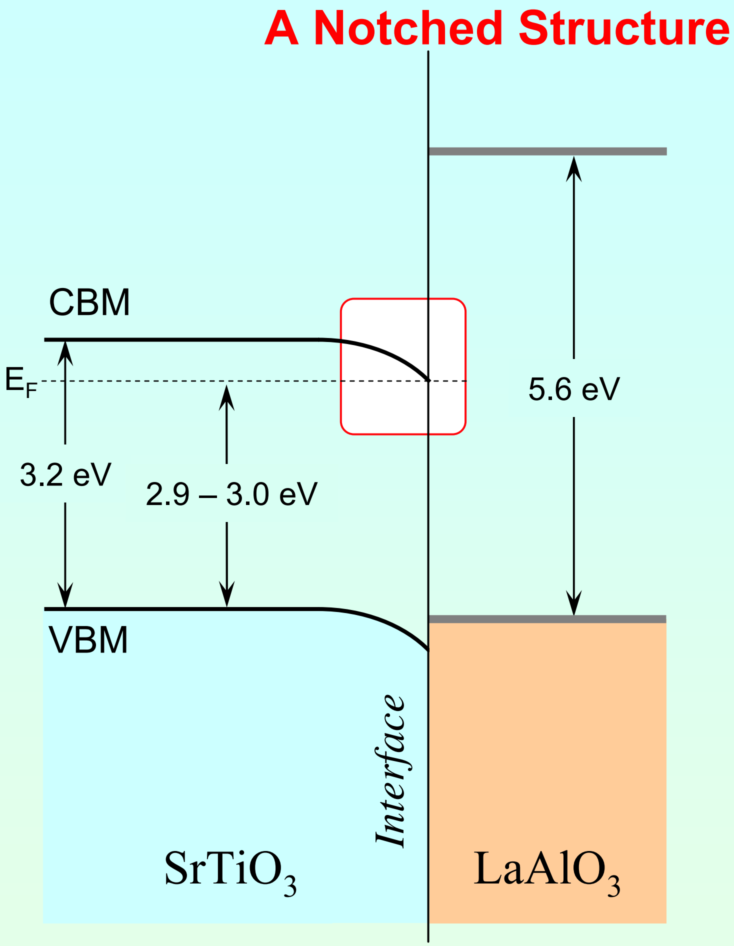
No peak shift at the p-type interface

Band bending on the STO side is responsible for the metallic states.

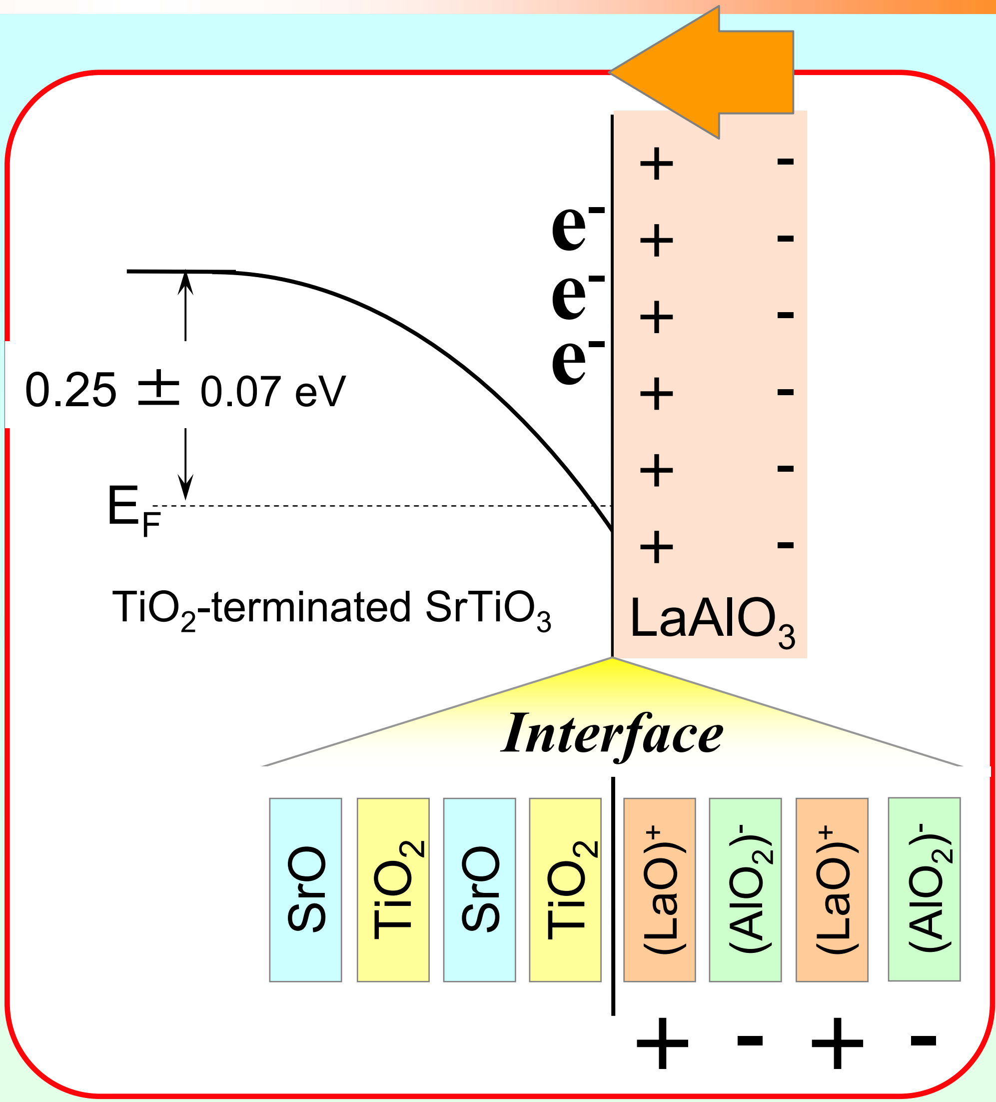
Ti 2*p* core level spectra



Origin of Metallic Conductivity in LAO/STO

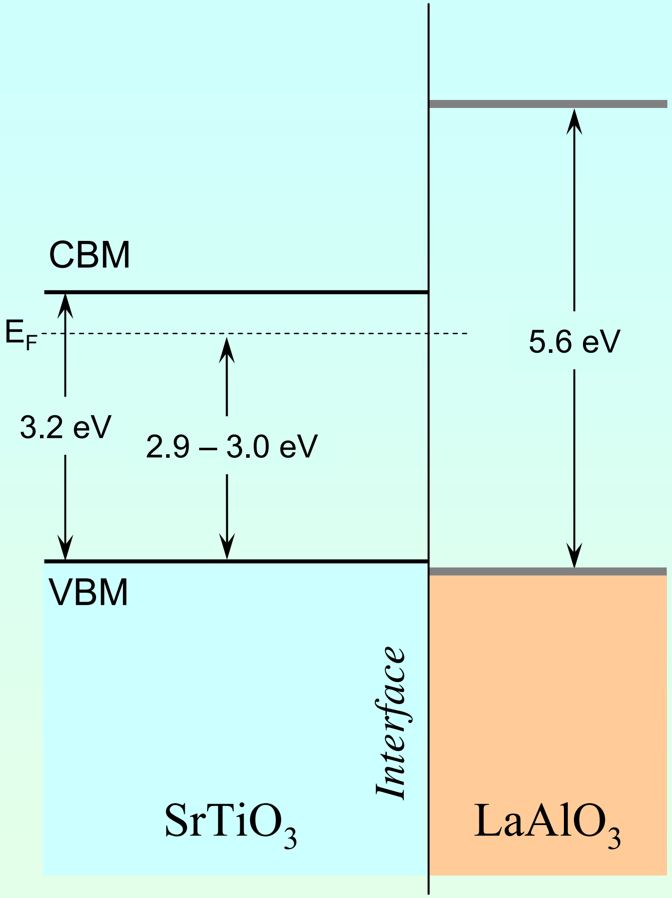


K. Yoshimatsu *et al.*, *Phys. Rev. Lett.* **101**, 026802 (08).

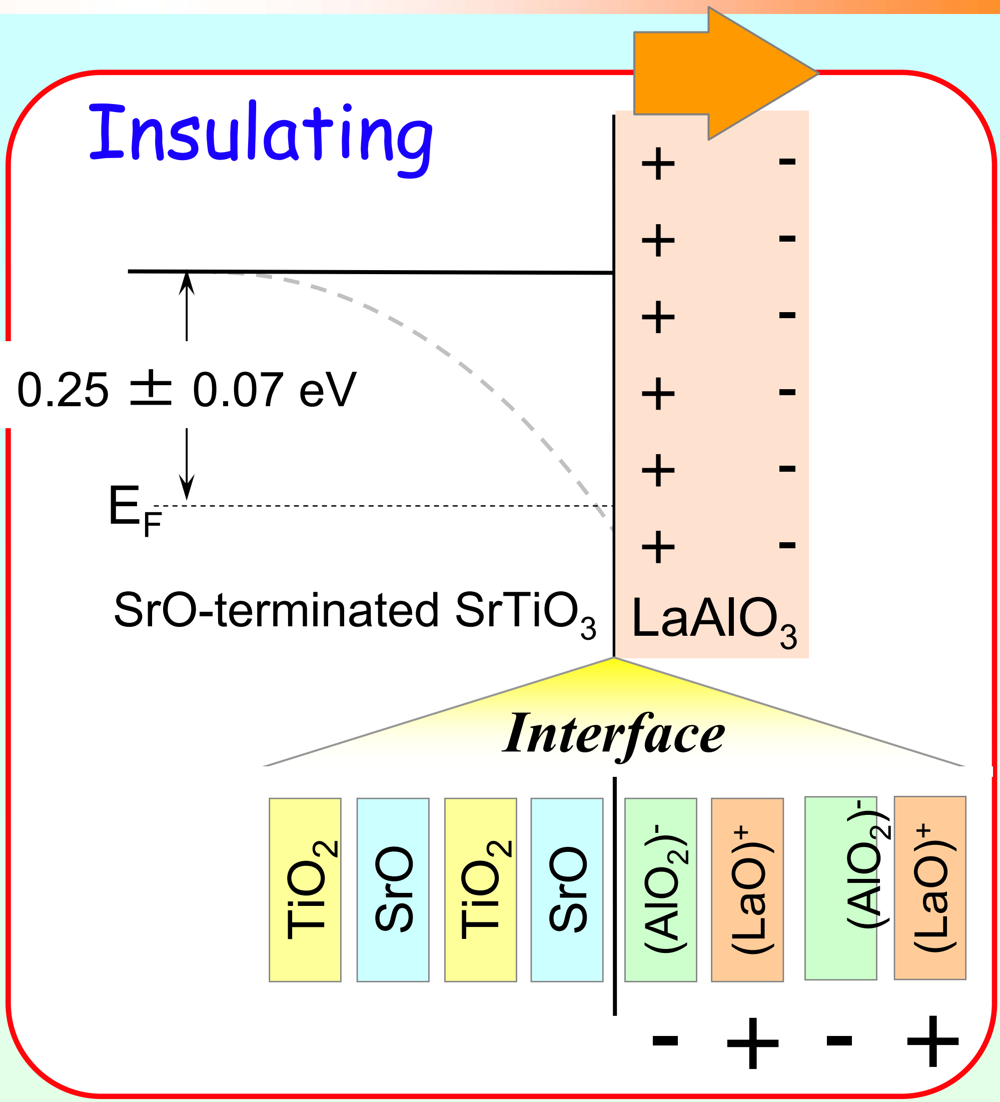


The metallic conductivity originate from the accumulation of carriers on the notched structure formed at the interface.

Origin of M-I Transition by Inserting SrO



K. Yoshimatsu *et al.*, *Phys. Rev. Lett.* **101**, 026802 (08).



The notched structure disappears by inserting SrO atomic layer between LAO and STO.

Summary in LAO/STO Interface

We determined the band diagrams of LAO/STO heterojunctions by using *in situ* photoemission spectroscopy.

We have found

1. There is no detectable Ti 3d DOS at EF expected from charge transfer through the interface.
2. Owing to the band discontinuity of LAO/STO, a notched structure is formed at the metallic interface.
3. The structure, however, is absent at the insulating interface.

⇒ The metallic states at the interface between band insulators LAO/STO originate not from charge transfer through the interface on a short-range scale but from the accumulation of carrier on a long-range scale.

Conclusion

1. レーザーMBE法（PLD法）の発展により、原子レベルで構造を制御した酸化物薄膜・超格子の作製が可能となった。

2. 強相関酸化物においても、今後、物質設計の自由度が高く、物性を自由自在に制御可能な「超構造」を用いた研究が主流になる。

3. 放射光を用いた分光法は、酸化物薄膜・超格子研究の強力な牽引力になる。