Buffer Layer Strategic Research and Development

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FY 2002 EE/RE Funding: $750 k: 2.5 FTE Staff, 2 FTE Post-Doctoral Fellows

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National Laboratory Collaborators

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- National Institute of Standards & Technology:

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- Sandia National Laboratory: M. Siegal, P. Clem
- Los Alamos National Laboratory: P. Arendt, S. Foltyn, T. Holesinger

Industrial Licensees/Partners

- American Superconductor, 3M, Microcoating Technologies, Neocera, Oxford Superconducting Technology

PURPOSE: To develop a basic understanding of and practical synthesis paths for epitaxial buffer layers on textured metal tapes for coated conductors.

FY2002 OBJECTIVES:

- Optimize sulfur treatment to demonstrate consistent epitaxial seed layer deposition
- Optimize buffer layers on metal alloy substrates
- Investigate single buffer-layers for YBCO/RABiTS

NEW ! Develop cap-buffer layers for MgO-buffered tapes (collaborative with LANL and ANL)

Explore feasibility of buffers on copper substrates for YBCO coatings

OUTLINE

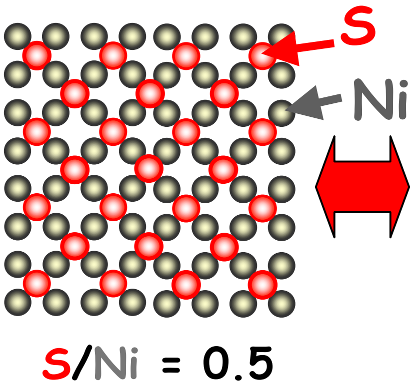
- **FY 2002 Results:**
  - **Studies of sulfur superstructure and influence on epitaxial growth of oxide buffer layers of different structural classes**
  - **Buffer layers on emerging metal tapes**

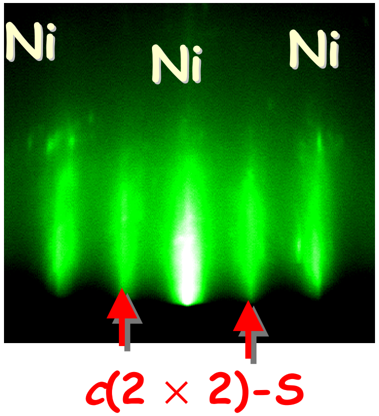
    Non-magnetic copper and NiCr alloys
  - **Single buffer layers for YBCO/RABiTS**
  - **Cap-buffer-layer development for MgO-based tapes (*LANL* IBAD MgO and *ANL* ISD MgO)**

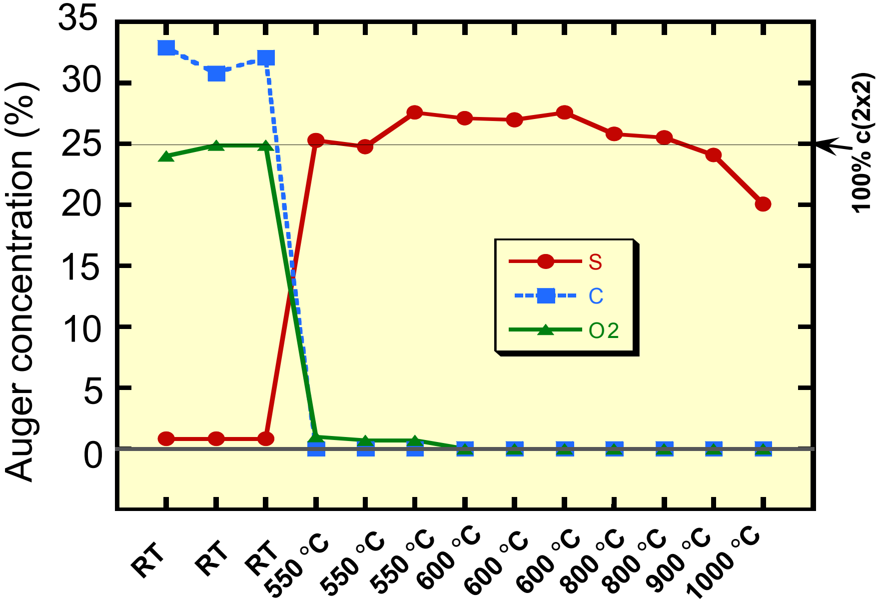
- **FY 2002 Performance and Plans for FY 2003**
- **Research Integration**

Characteristics of the *c*(2×2) Superstructure on Ni

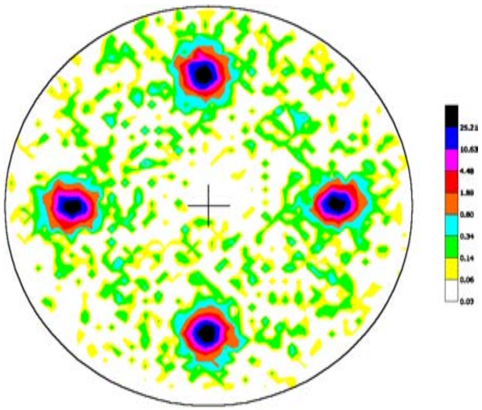
- *Stable at high temperature*
- *c(2×2) does not transform to other structures*
- *Forms by segregation and/or adsorption with identical results on seed layer growth*



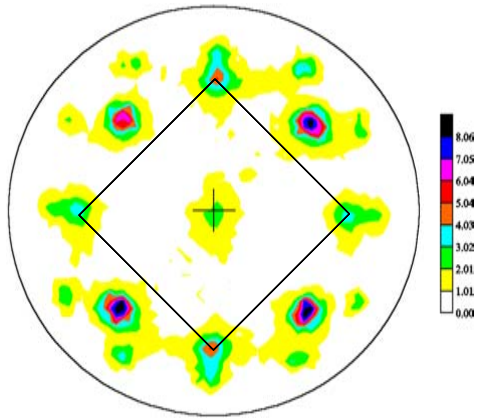




The *c*(2×2)-S Superstructure Promotes Epitaxy



YSZ (111)



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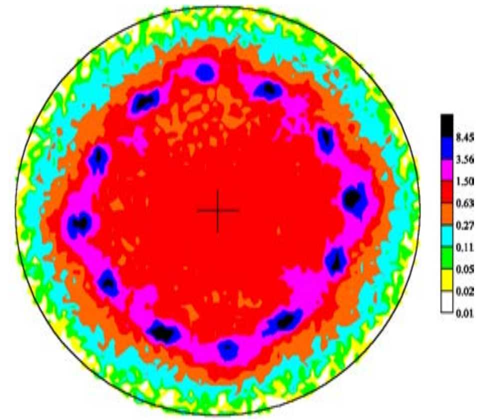

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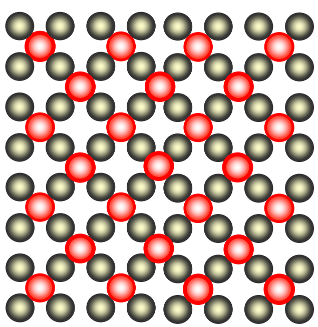
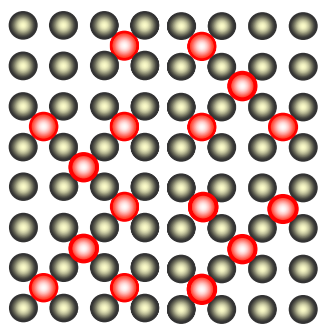
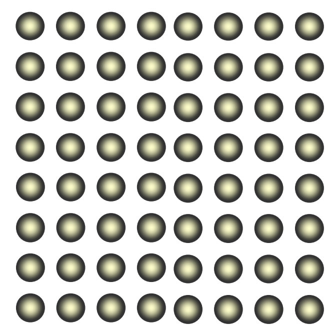


100% c(2×2)



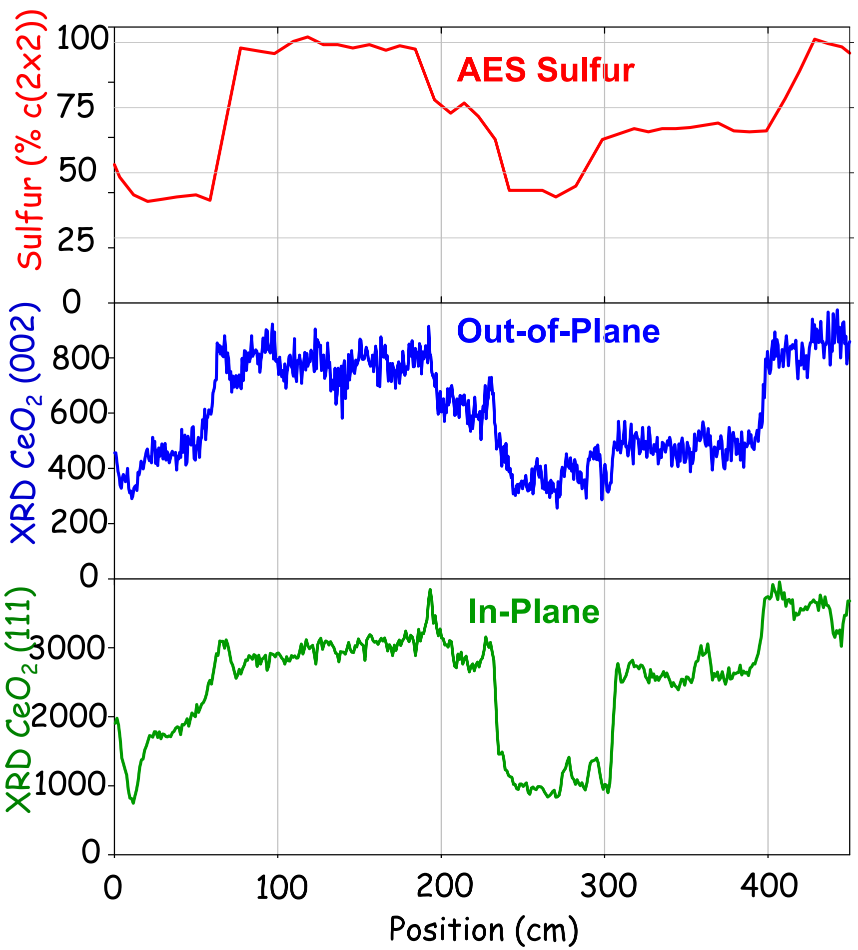
40% c(2×2)

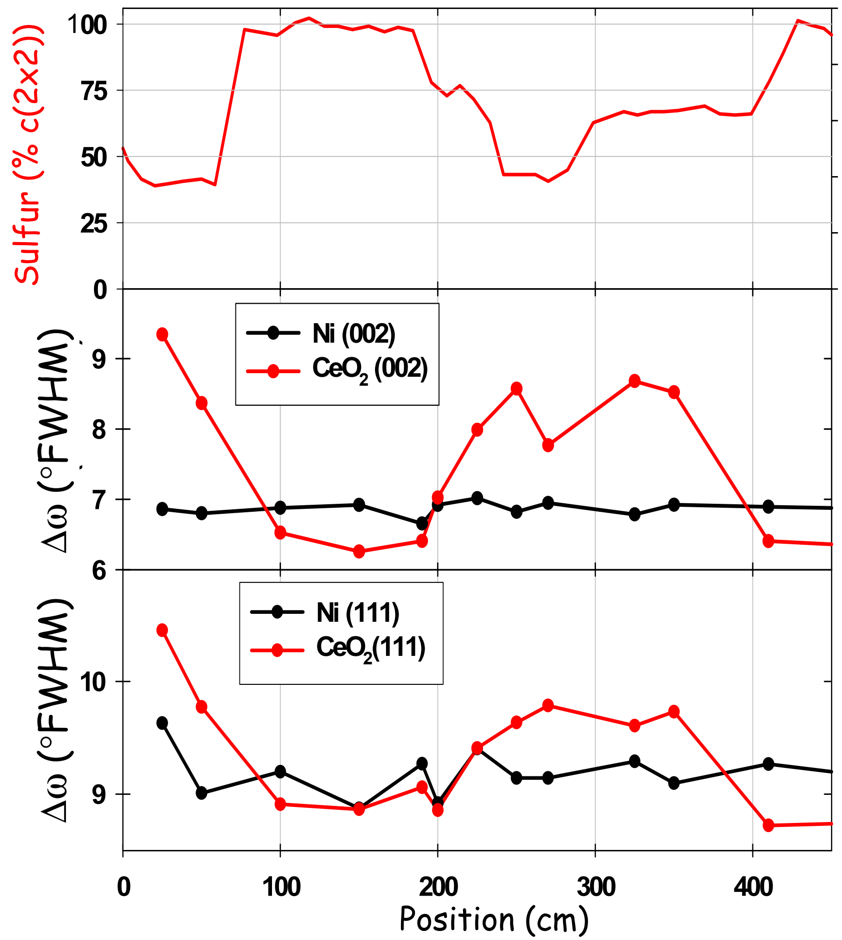


0% c(2×2)

H_2S Treatment Controls the c(2×2)-S Needed for Buffer Layer Epitaxy

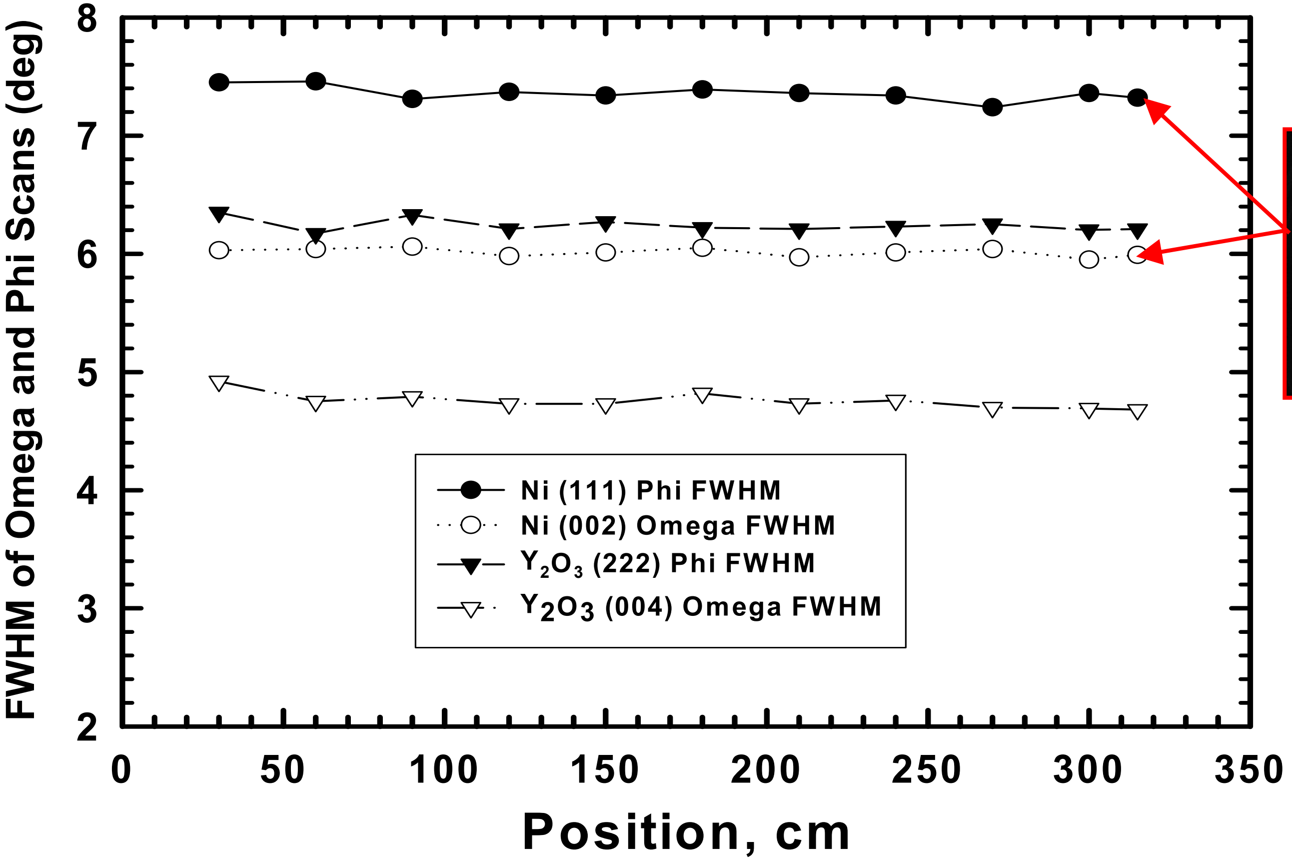
- Exposure times of few s are sufficient to produce a complete c(2×2) layer

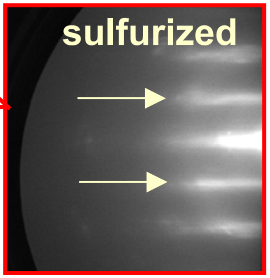




S Treatment Transferred to AMSC Yields Consistent Epitaxial Seed Layer Deposition

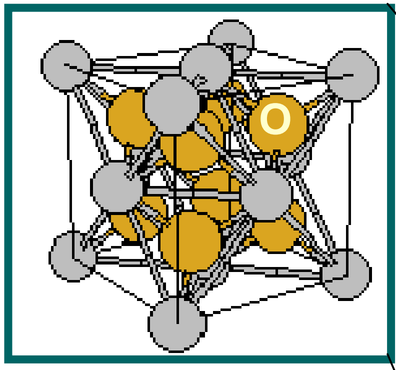
Reel-to-reel X-ray on 3-meter long Y_2O_3 seed on sulfurized Ni-W tape

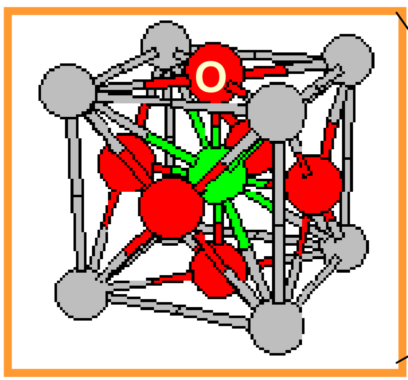




Seed Layers that Require *c* (2×2)-S

fluorite

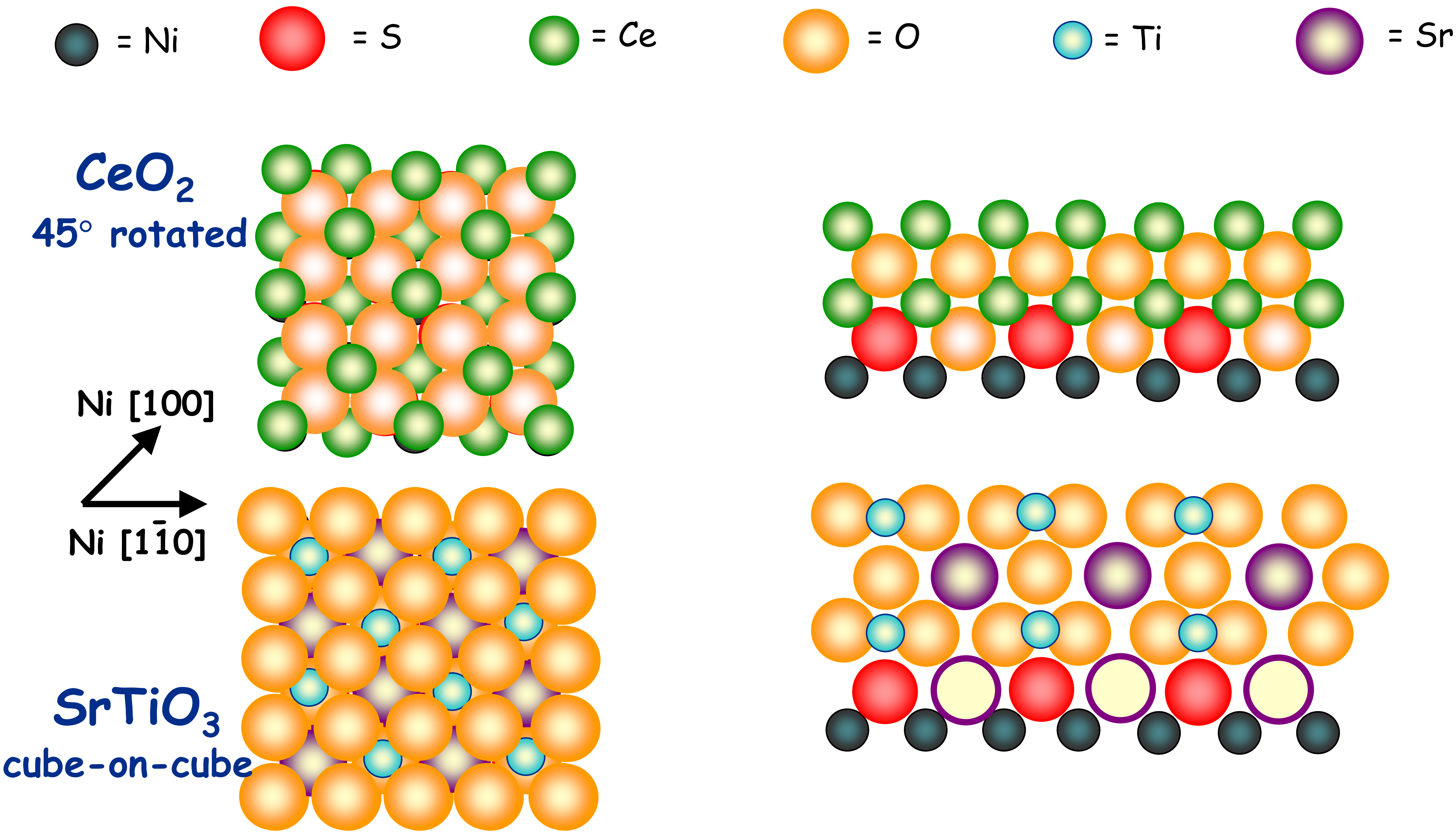




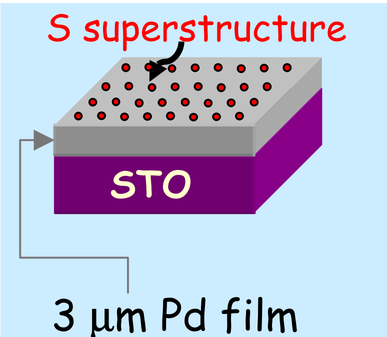
perovskite

Seed Layer	H_2O pressure (Torr)	O_2 pressure (Torr)
CeO_2	1×10^{-5}	$\sim 7\times10^{-8}$
YSZ	1×10^{-8}	$\leq 1\times10^{-9}$
Y_2O_3	1×10^{-5}	$\sim 7\times10^{-8}$
Gd_2O_3	1×10^{-5}	$\sim 7\times10^{-8}$
$SrTiO_3$	6×10^{-8}	$\geq 1\times10^{-9}$
$LaMnO_3$	6×10^{-3}	$\geq 10^{-6}$

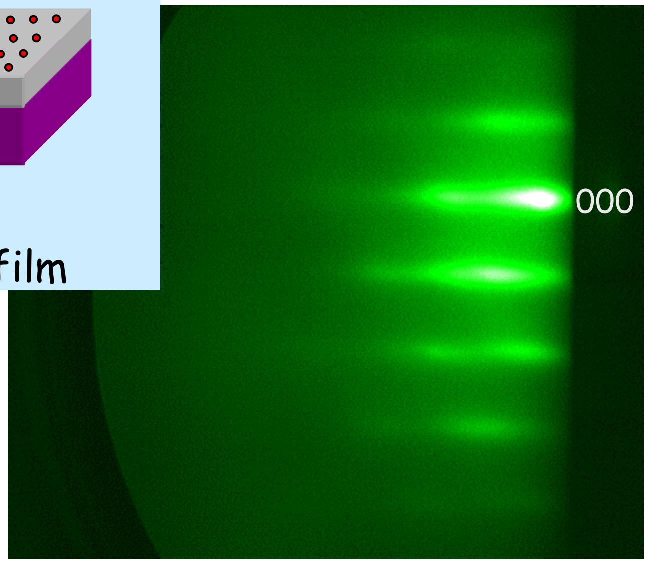
Models for $c(2\times2)$ Mediated Epitaxy



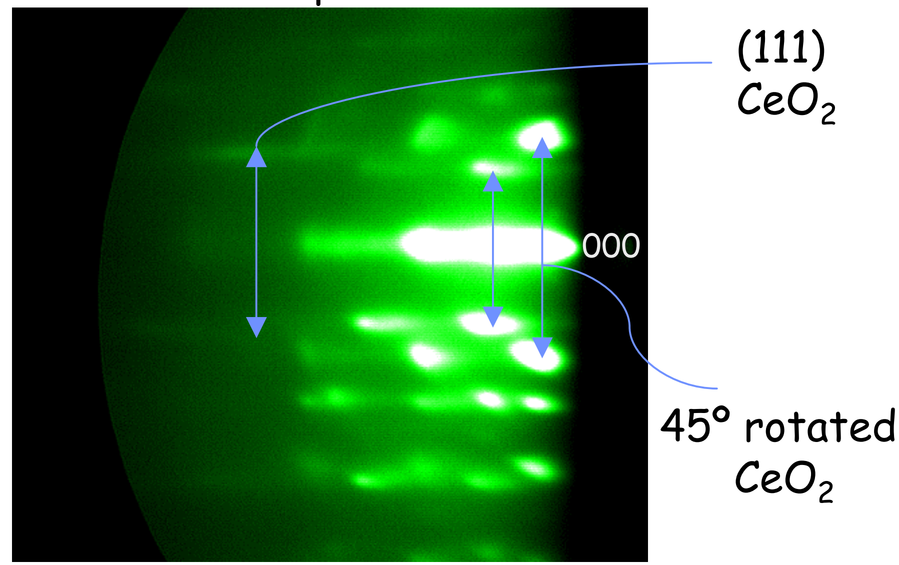
Epitaxial Growth of CeO_2 and STO on Pd Requires *c* (2×2)-S

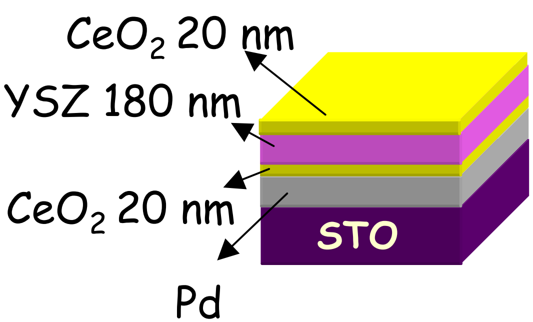


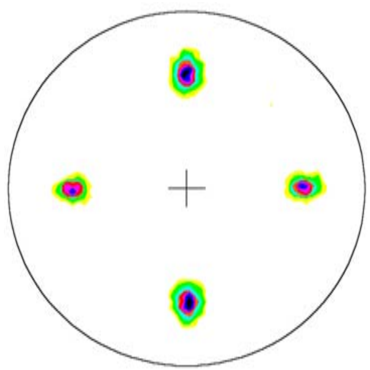
With superstructure



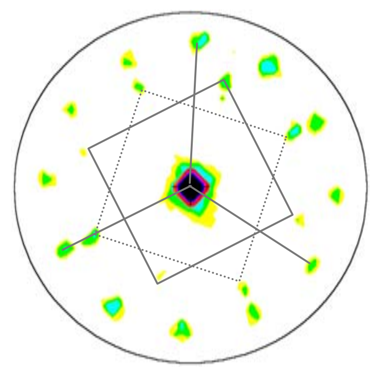
Without superstructure





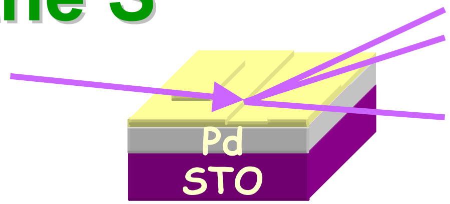


YSZ (111)

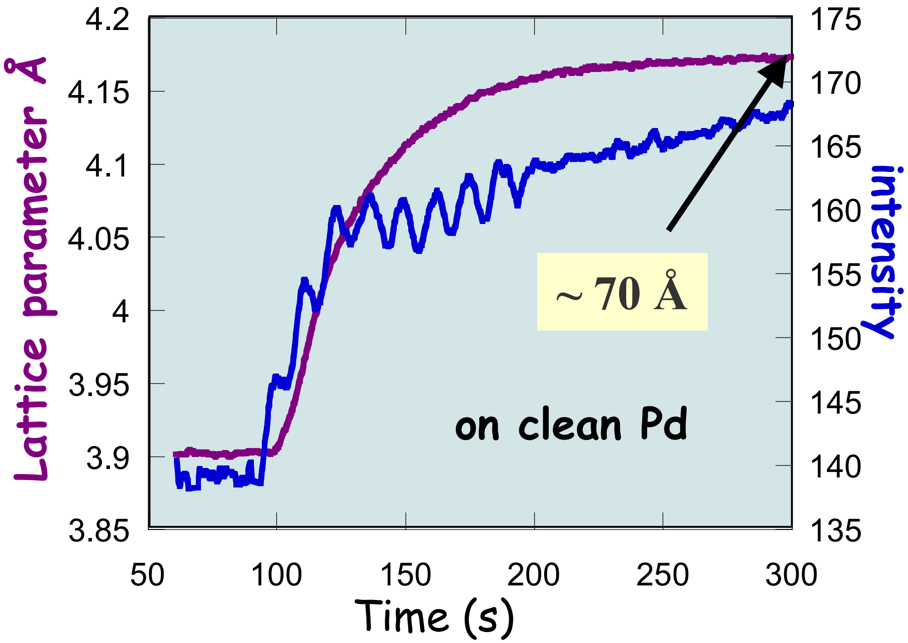


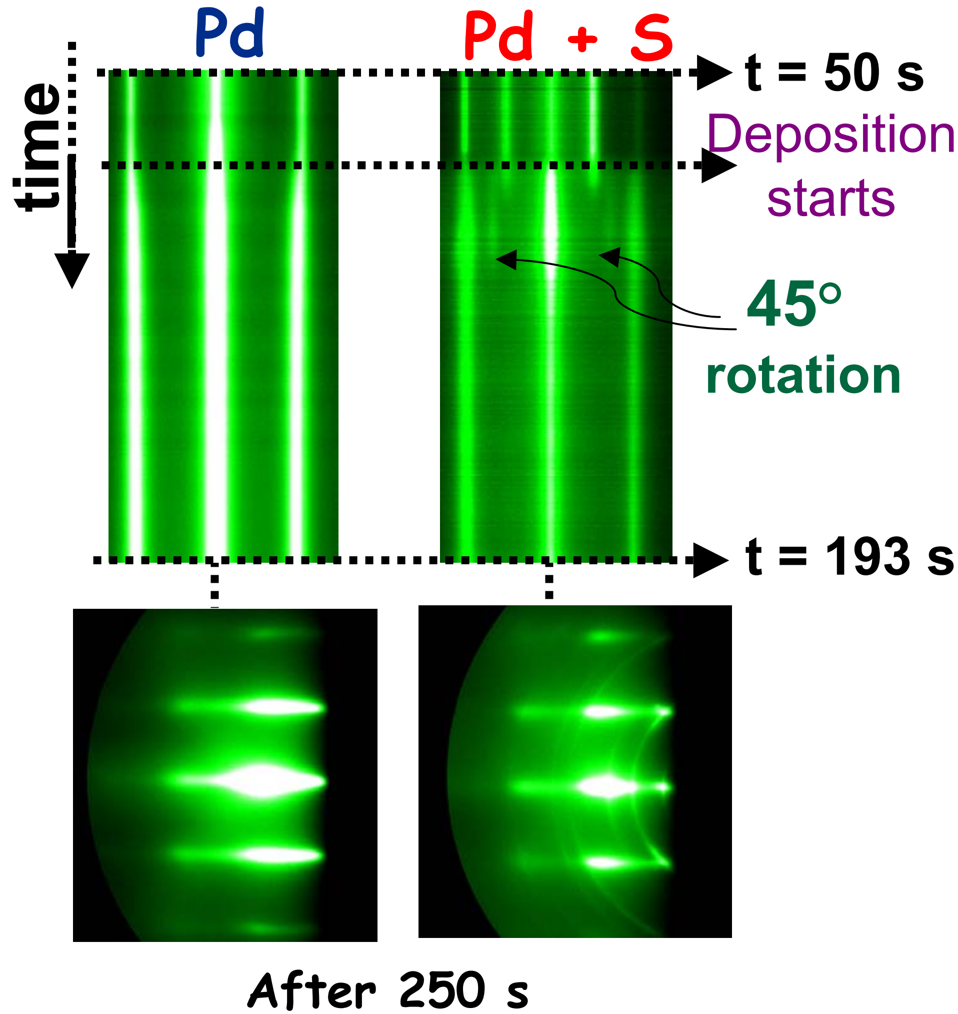
YSZ (111)

Seed Layers That do not Want the S Superstructure: MgO



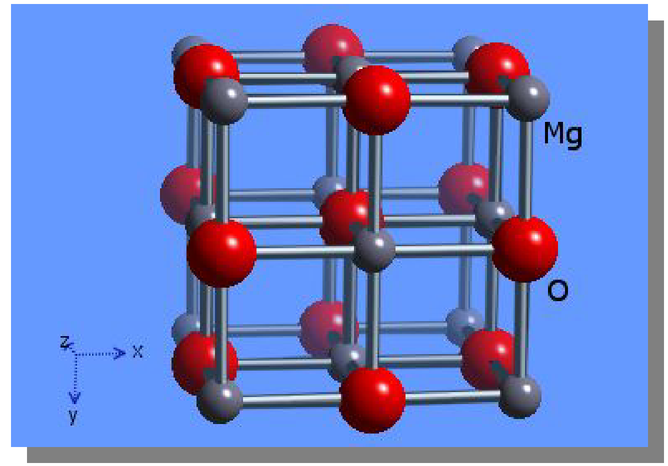
- MgO grows cube on cube on clean Pd
- Initial growth is layer-by-layer
- *c*(2×2)-S disturbs MgO growth



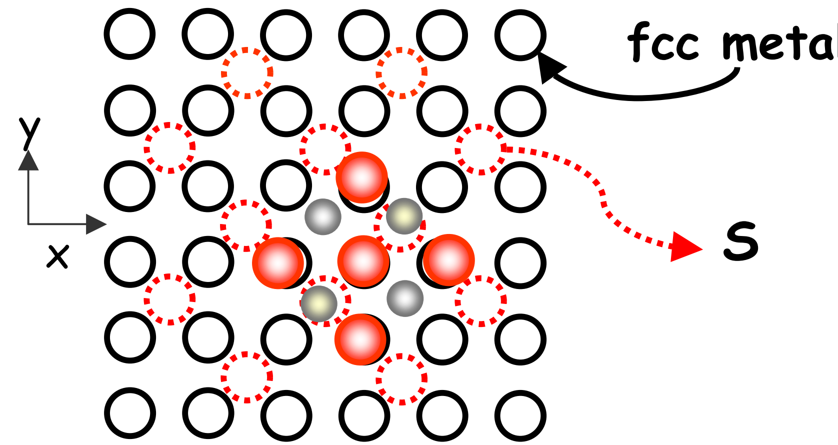


Why does MgO behave differently?

- **Structural differences**
  - No (001) oxygen planes, strong Mg - O bond, no structural vacancies
  - Reported epitaxy on clean Ag
    (S. Schintke et al. Phys. Rev. Lett. 87 (2001) 276801)



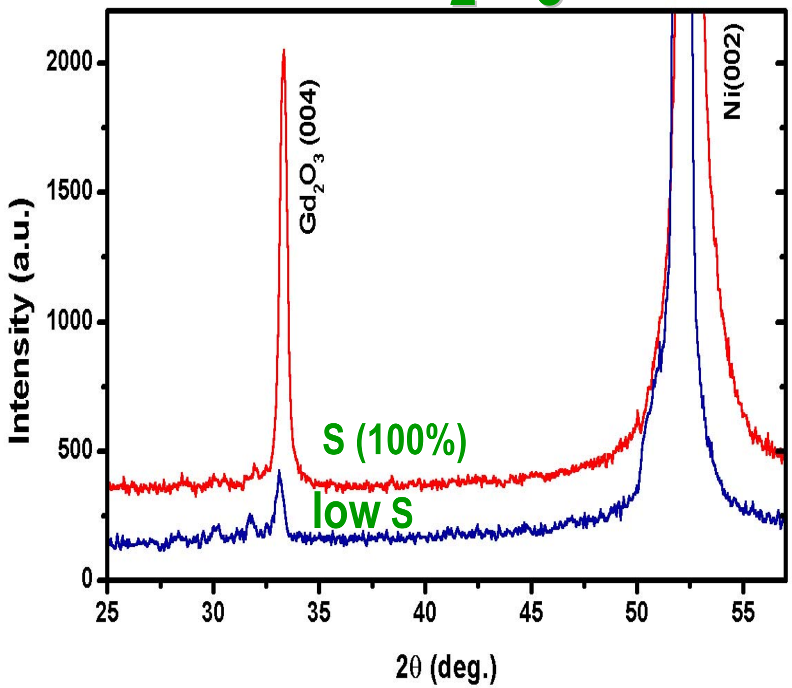
- **Interesting properties of MgO**
  - Good oxygen diffusion barrier
    $D_{MgO}(800°C) \cong 10^{-28}$ cm^2/s
    $D_{STO}(800°C) = 2\times10^{-12}$ cm^2/s
  - Low temperature deposition



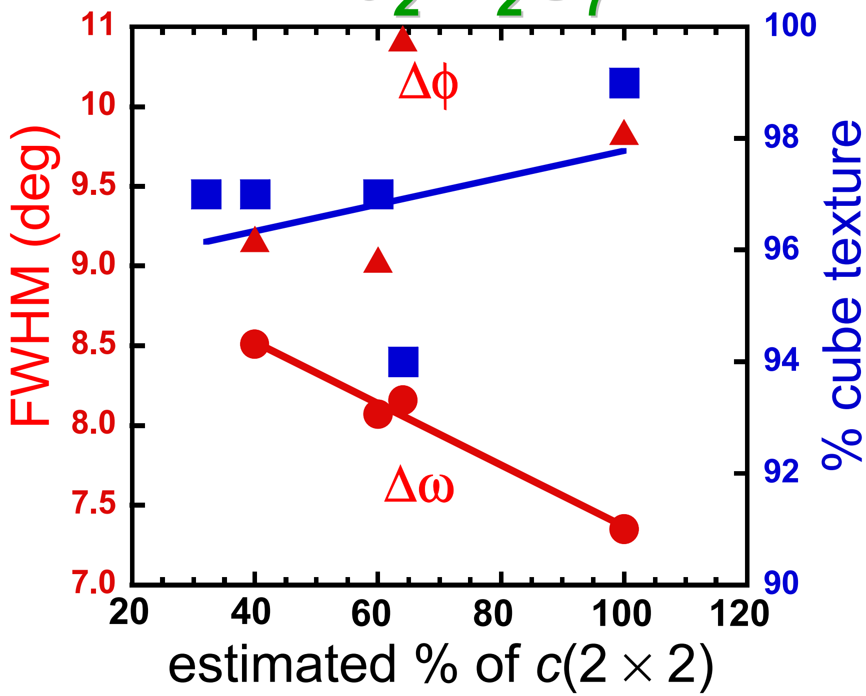
The Effect of S on Solution Buffer Layer Growth

- ***On Ni and Ni-3%W substrates with optimum S (~100 %), buffers with perfect cube texture were reproducibly produced***
- ***On substrates with less S, irreproducible results were obtained***

Gd_2O_3



$La_2Zr_2O_7$



Summary

- *Control of the S superstructure by on-line H_2S exposure has produced consistent epitaxial seed layer deposition at ORNL and AMSC*

- *The study of the influence of S on seed layer epitaxy was extended to a wide range of oxides showing a behavior common to several classes of materials*

- *Not all oxide seed layers want the S template: MgO behaves differently than oxides with fluorite or perovskite structure*

- *Evidence was provided for the importance of S in growth of solution seed layers*

OUTLINE

- **FY 2002 Results:**
  - Studies of sulfur superstructure and influence on epitaxial growth of oxide buffer layers of different structural classes
  - Buffer layers on emerging metal tapes

    Non-magnetic copper and NiCr alloys
  - Single buffer layers for YBCO/RABiTS
  - Cap-buffer-layer development for MgO-based tapes (*LANL* IBAD MgO and *ANL* ISD MgO)
- **FY 2002 Performance and Plans for FY 2003**
- **Research Integration**

Issues Involved in Buffer Layer Deposition on Ni-13%Cr

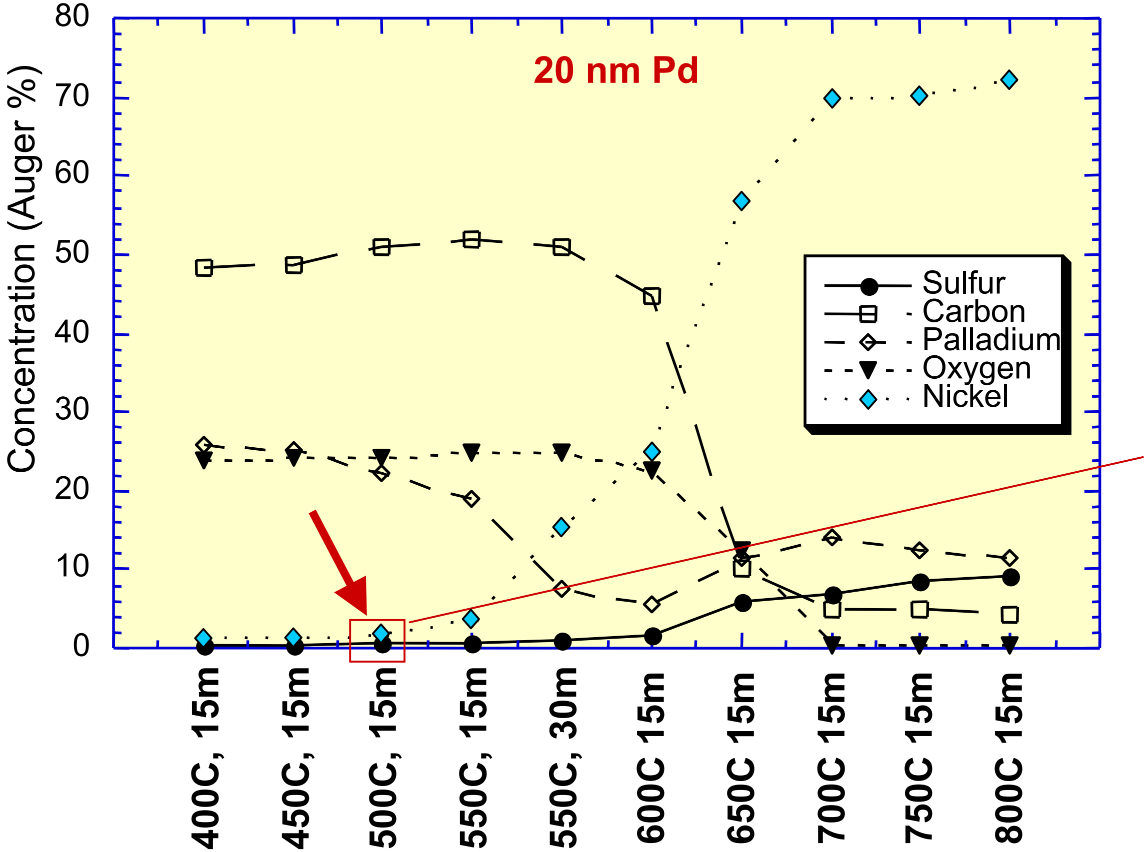
- *c*(2×2)-S superstructure has the same role as in pure Ni

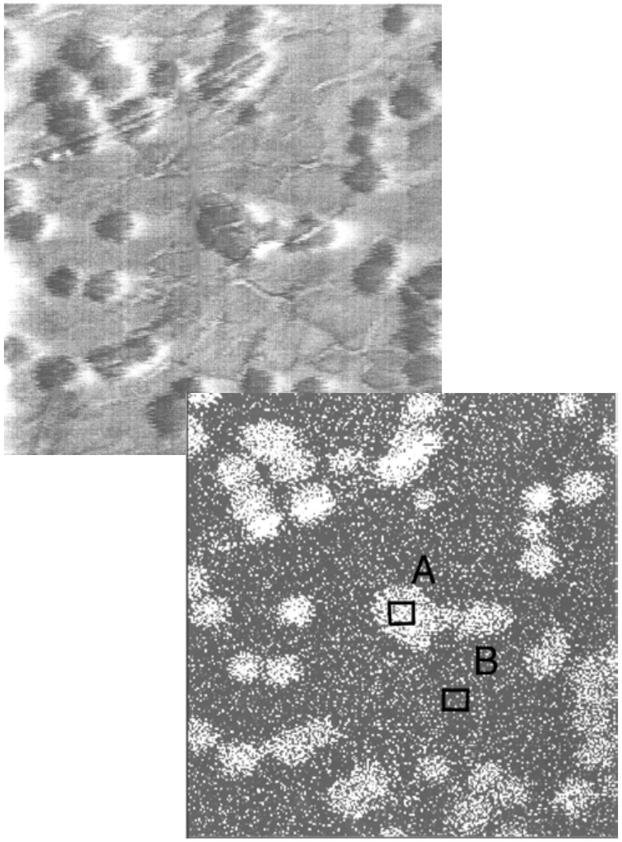
- Cr-O-free surface only stable below $P(O_2)=1.0\times10^{-8}$ Torr
  - YSZ is a viable seed layer but needs UHV
  - J_c = 0.4 MA/cm^2 demonstrated on YBCO/CeO_2(80 *nm*)/YSZ(170 *nm*)/Ni-13%Cr

- Need for a low-deposition-temperature seed layer
  - MgO + Pd overlayer: only if Pd can be thin and no Pd/Ni interdiffusion

Pd/Ni Interdiffusion Studies

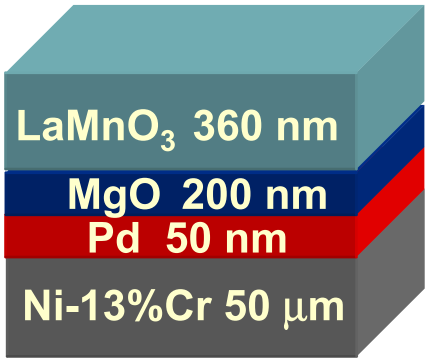
- *Interdiffusion occurs at 500 °C and is dramatic at 600 °C*
- *At T = 400 °C there is no interdiffusion ⇒ Pd film can be thin*

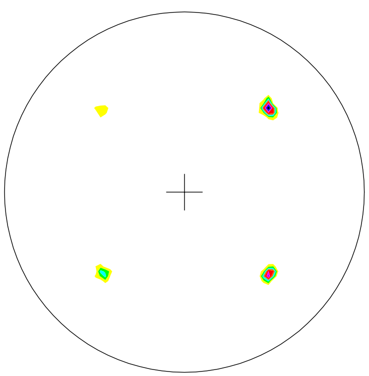




Alternative Architecture for Ni-alloy-Based Conductors

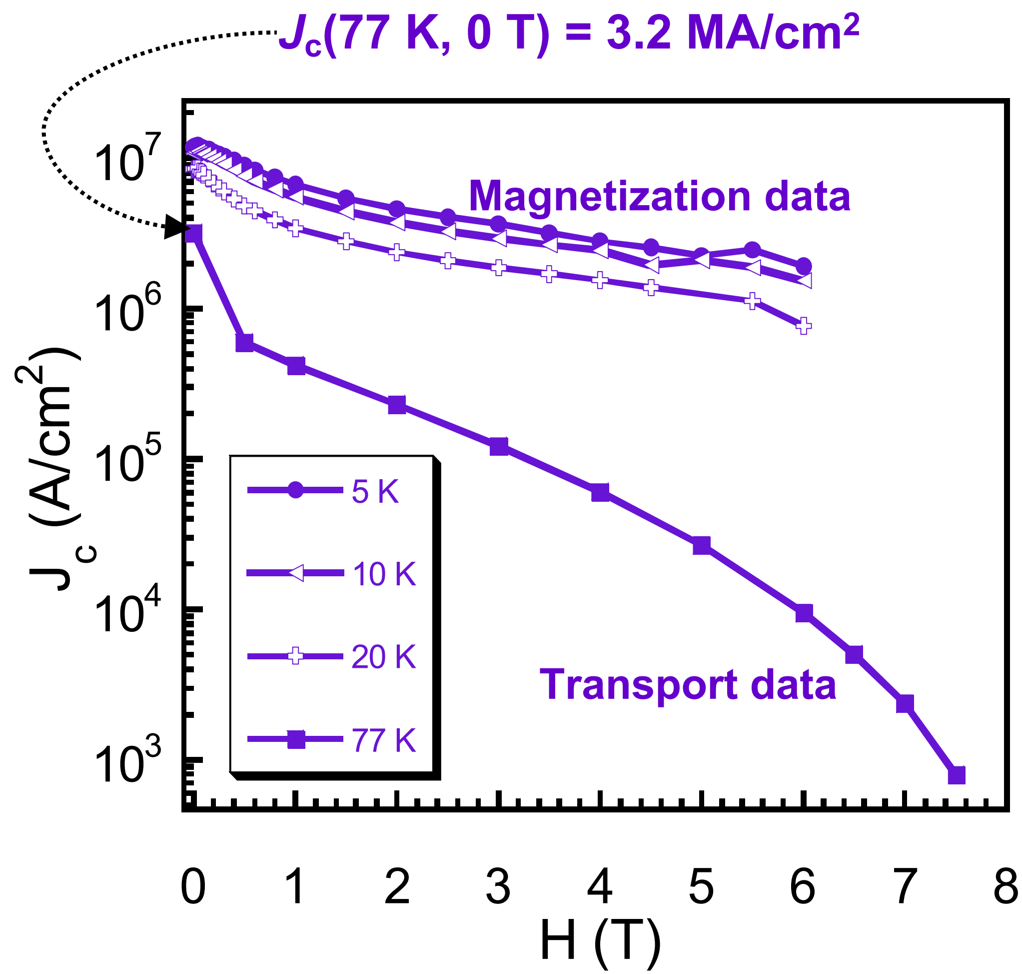
- ***Thin metal layer; no need for sulfurization; low-temperature seed layer deposition***





YBCO (113)

	Δω	Δφ
Ni-13%Cr	4.84°	6.85°
YBCO	2.84°	6.65°



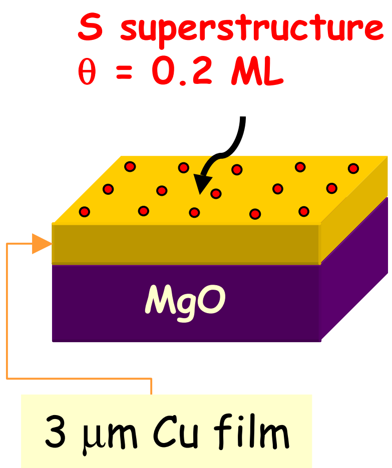
Buffer Layers on Cu

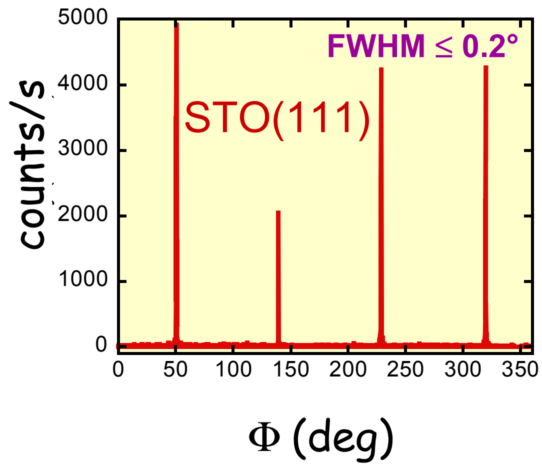
- **Why is Cu interesting?**
  - Inexpensive
  - Low resistivity, no need of stabilizing cap $\Rightarrow$ higher J_E (for totally conducting architectures)
  - Can be strengthened without increasing resistivity

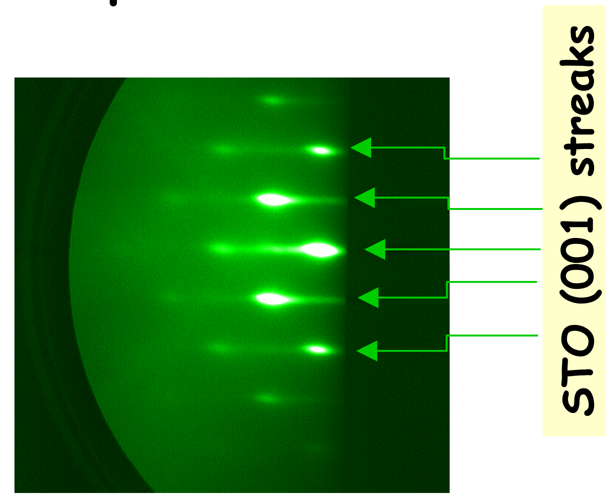
- **Important Issues**
  - Higher thermal expansion than Ni
  - Surface interaction with S different than in Ni
  - Cu-O less self-limiting than Ni-O at high temperatures

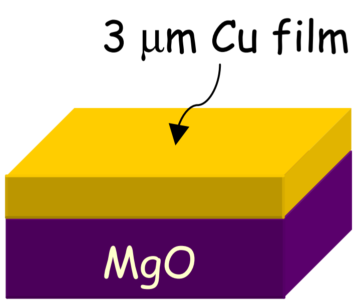
S Superstructures on (001) Cu

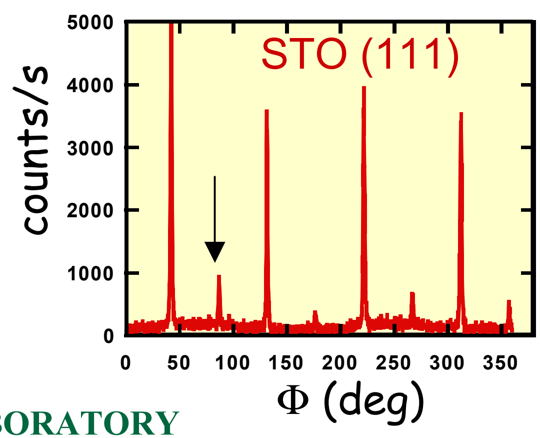
- S forms only a *p*(2×2) superstructure on Cu
- Epitaxy of STO and CeO_2 requires S superstructure

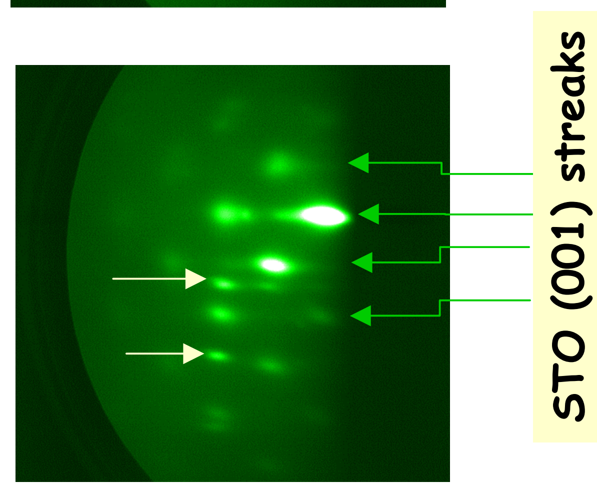








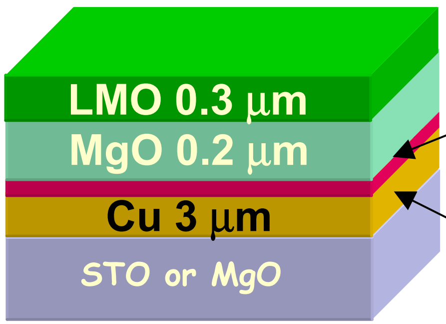




Cu is a Challenging Substrate

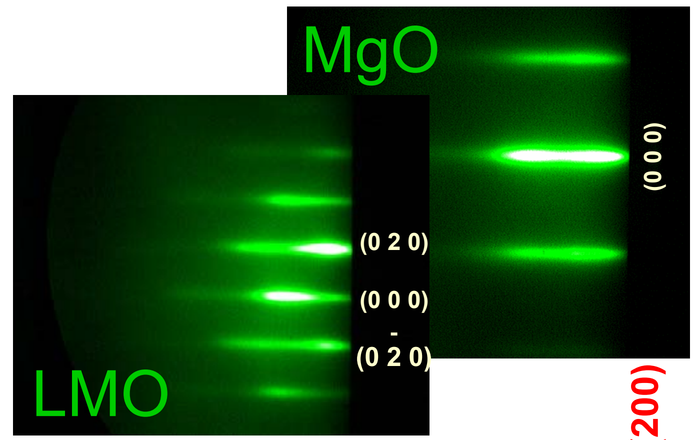
- **The standard architecture is not suitable for YBCO deposition**
  - **disruptive oxidation/delamination**
  - **not a sufficient O/Cu diffusion barrier**
- **Pd, Ag, Ni, Au metal overlayers are not compatible with Cu surface**
  - **surface alloying, orientation other than (001)**
- **Would MgO be a suitable passivating buffer layer?**

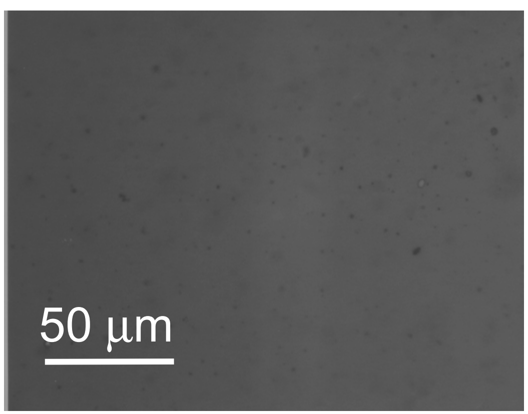
Control Study of Buffer Layers Performance on Cu Epitaxial Films on STO and MgO Substrates



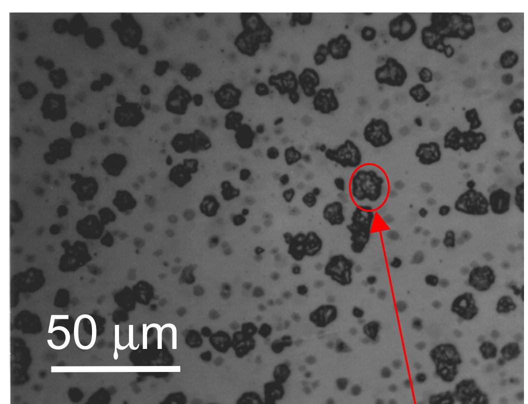
STO nucleation layer, 5 *nm*

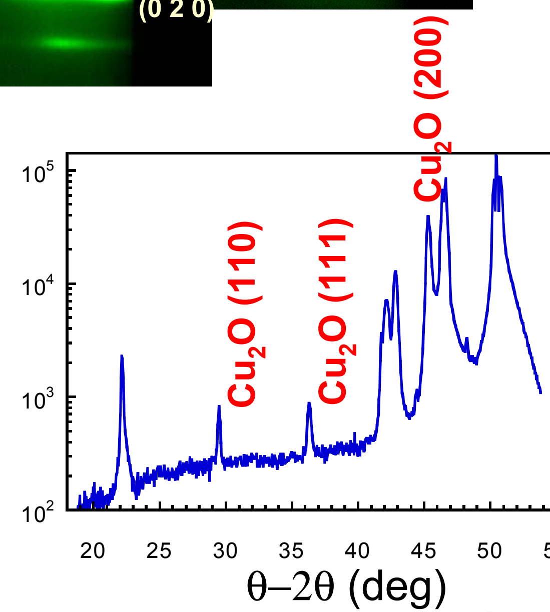
S containing e-beam evaporated films



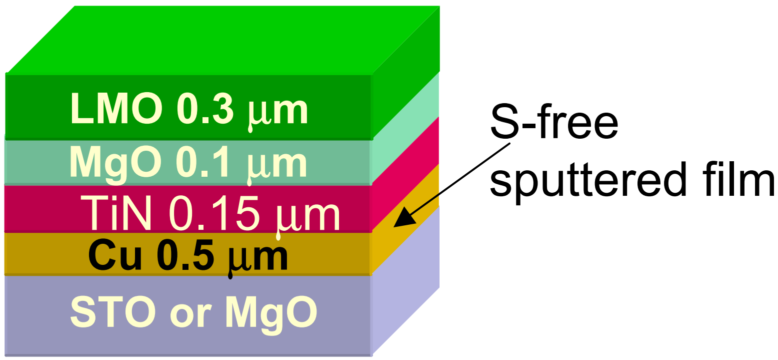


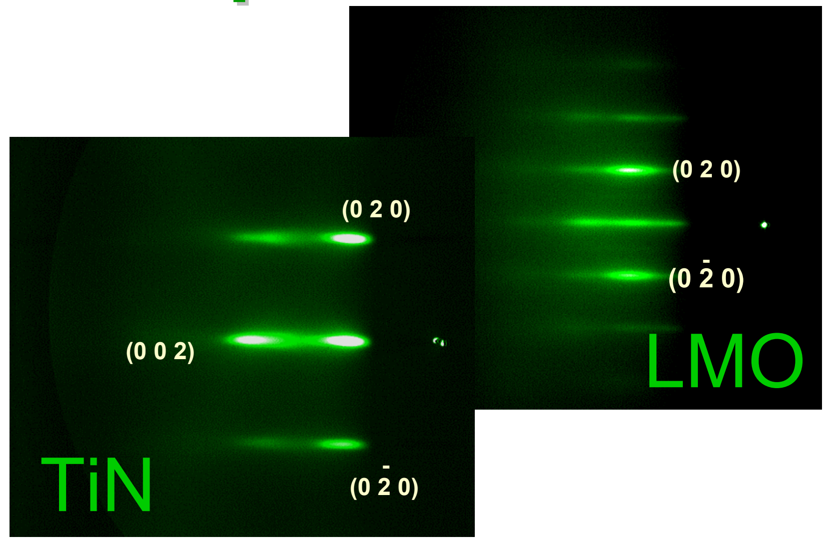
YBCO anneal →

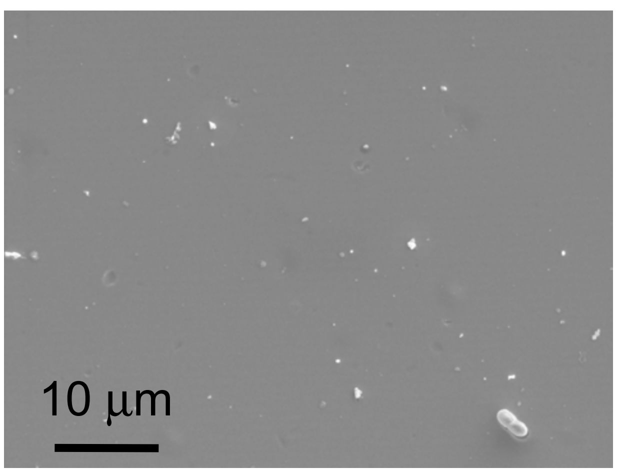




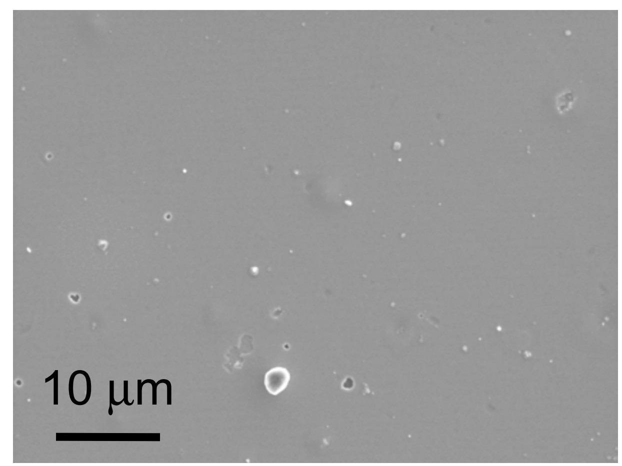
TiN Provides the Cu Diffusion Barrier Needed for YBCO Deposition





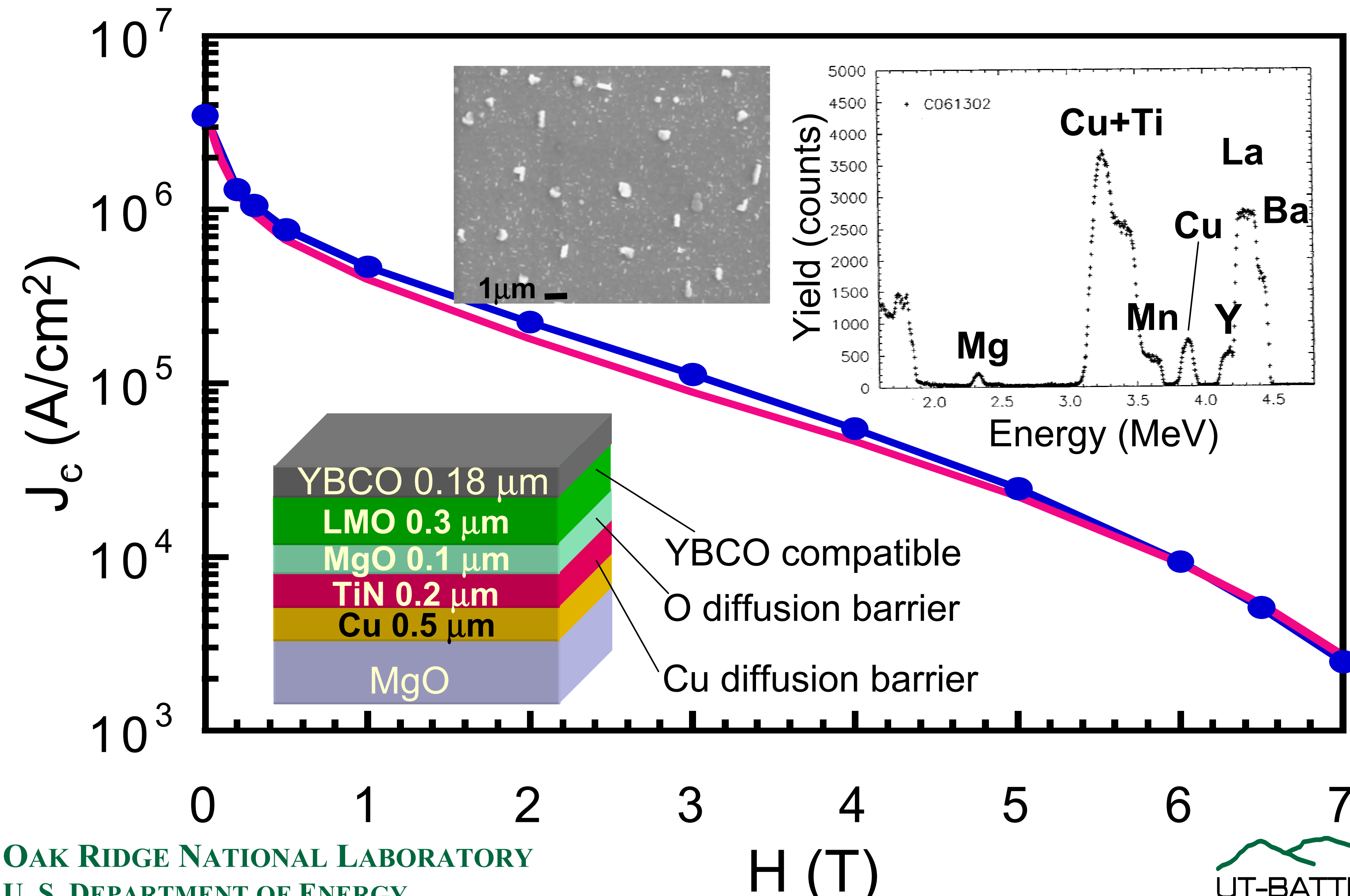


YBCO anneal



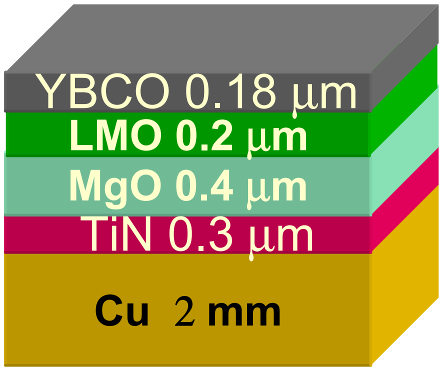
J_c = 3.5 MA/cm² YBCO on Buffered Cu Films

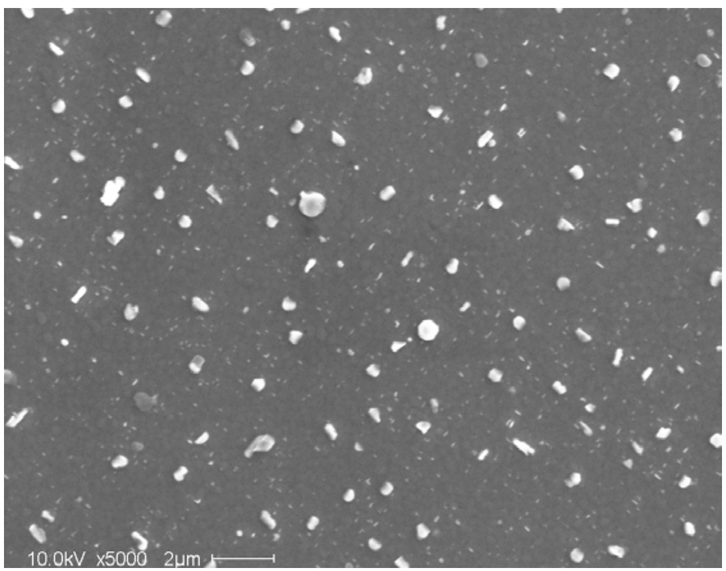
- *clean interfaces after YBCO deposition, non detectable Cu-O/Ti-O*

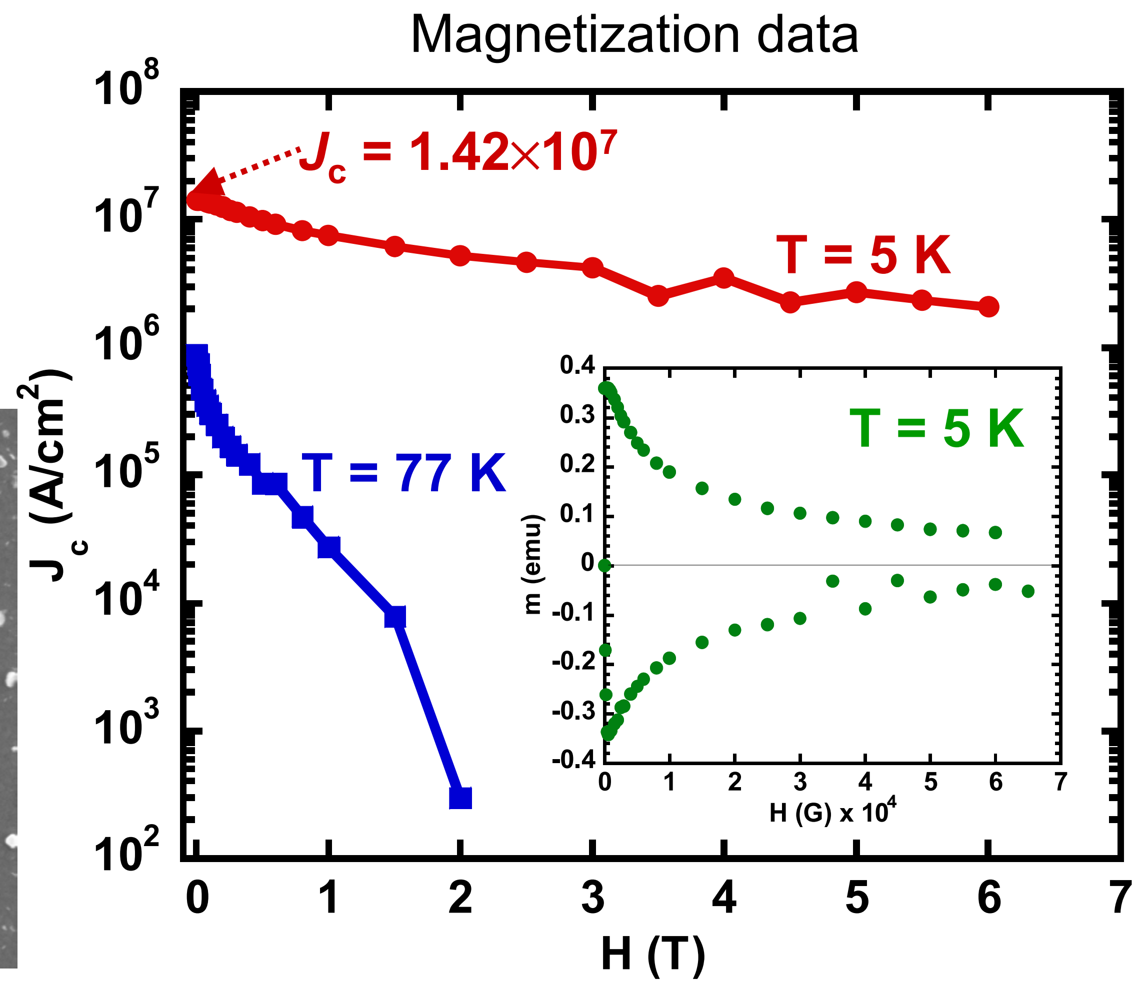


High J_c YBCO on Buffered Single Crystal Cu

- Dense, crack-free microstructure







Summary

- *A RABiTS architecture that uses MgO and $LaMnO_3$ with no need for sulfurization gives J_c = 3 MA/cm^2 Ni-13%Cr substrates*

- *Study of Cu surface has highlighted differences in S adsorption/segregation and seed layer nucleation as compared to other fcc metal surfaces*

- *High J_c was demonstrated for the first time on Cu using TiN as Cu diffusion barrier*

OUTLINE

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  - Studies of sulfur superstructure and influence on epitaxial growth of oxide buffer layers of different structural classes
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    Non-magnetic copper and NiCr alloys
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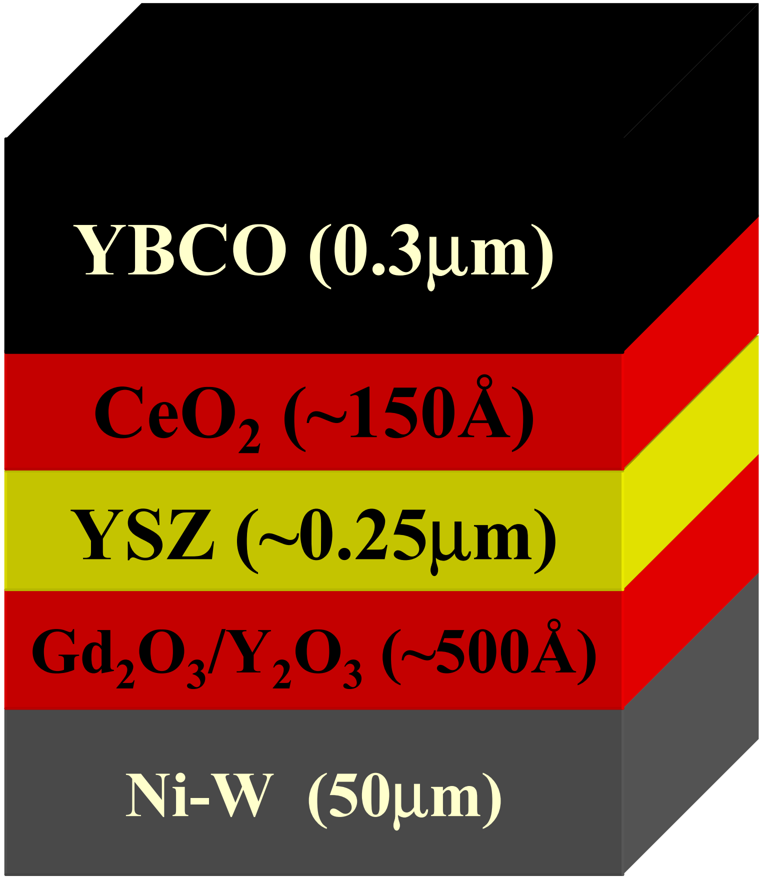
- **FY 2002 Performance and Plans for FY 2003**
- **Research Integration**

RABiTS process with a standard architecture



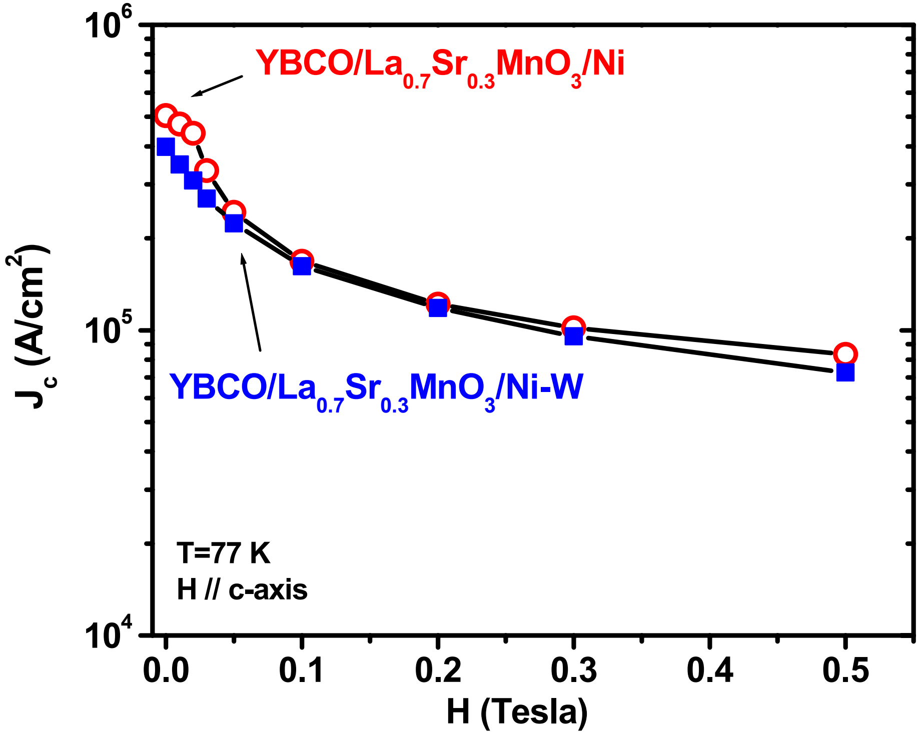
- YBCO by ex-situ BaF_2/TFA process or PLD (0.2 μm)

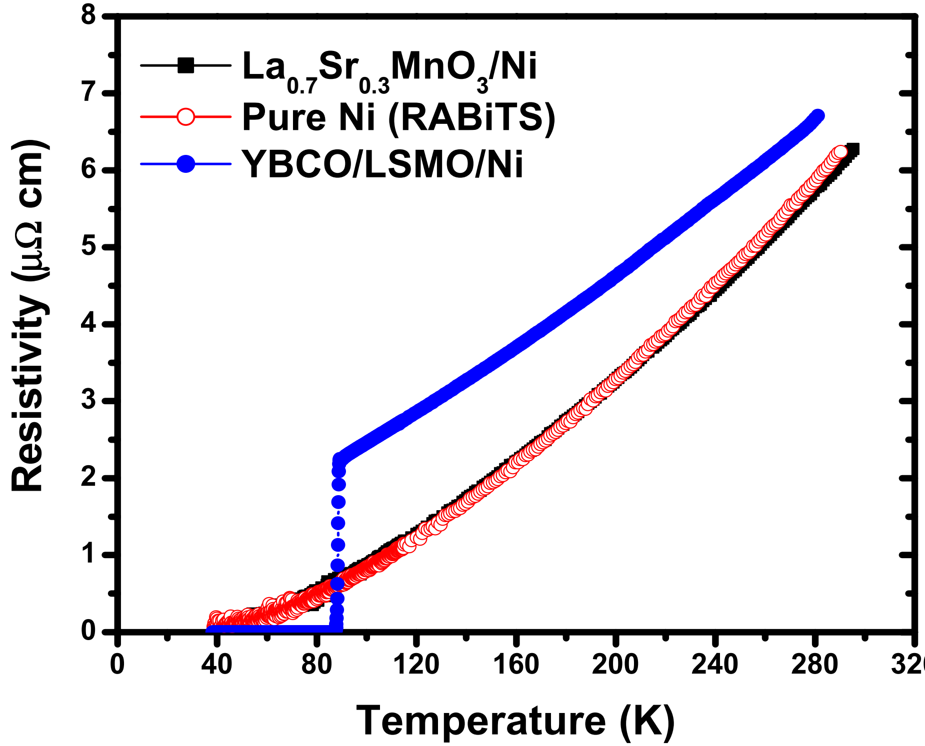
  Best J_c 2.0 x 10^6 A/cm^2 at 77 K
- Barrier and cap layers by rf sputtering
- Seed layers by e-beam or dip-coating

Objective: To develop a simple alternative buffer architecture
Candidates: $LaMnO_3$ (LMO); $La_2Zr_2O_7$ (LZO)
Techniques: rf sputtering and solution process

Developed a Conductive *YBCO/ $La_{0.7}Sr_{0.3}MnO_3$ /Ni* Multilayer Architecture

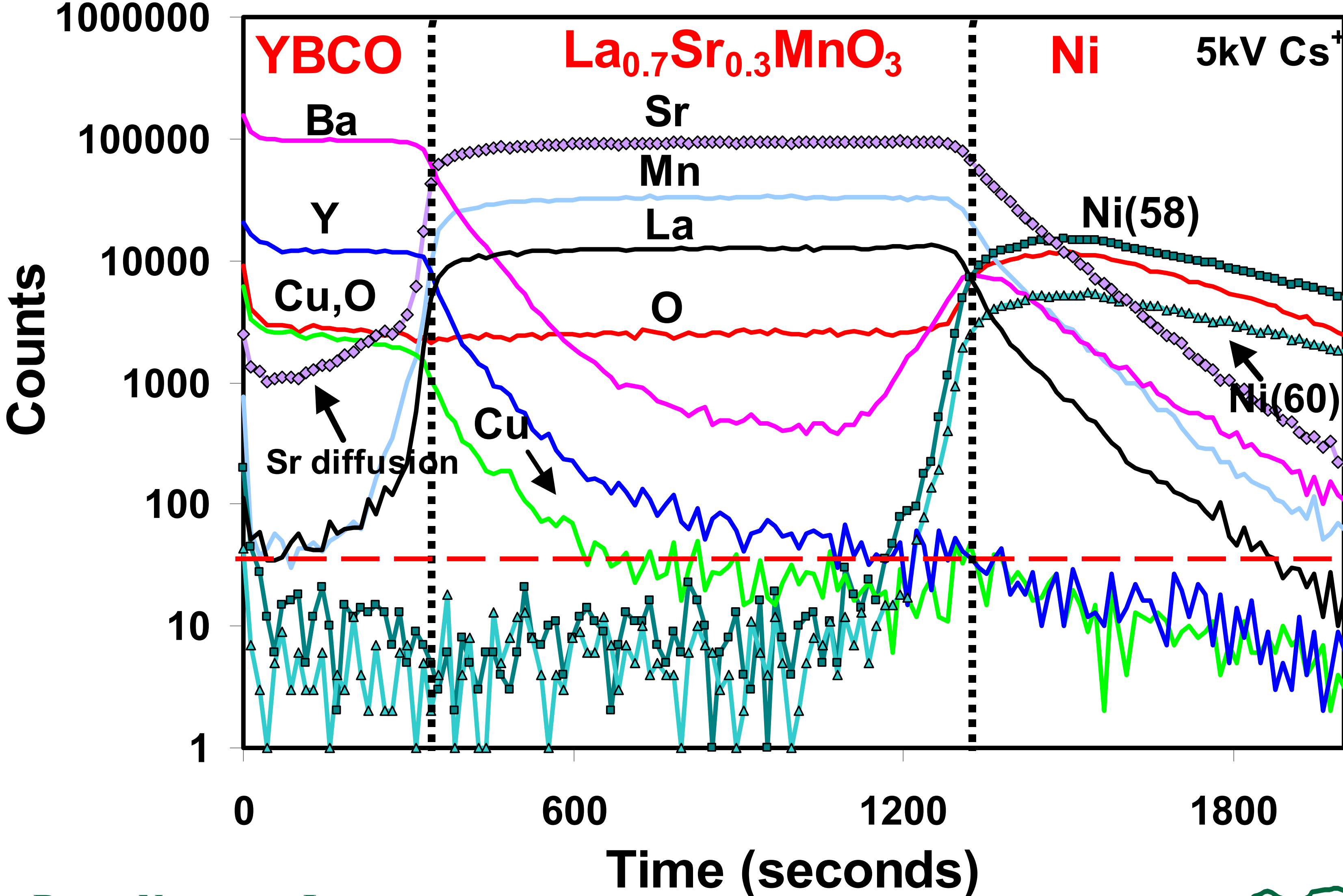
- YBCO (PLD); $T_c = 88$ K
- $J_c = 0.5x10^6$ A/cm^2 @ 77 K
- Good electrical coupling with Ni.
- Overall low net resistivity (≈ 7 μΩ-cm), *but* four-terminal res. indicates some contact barrier





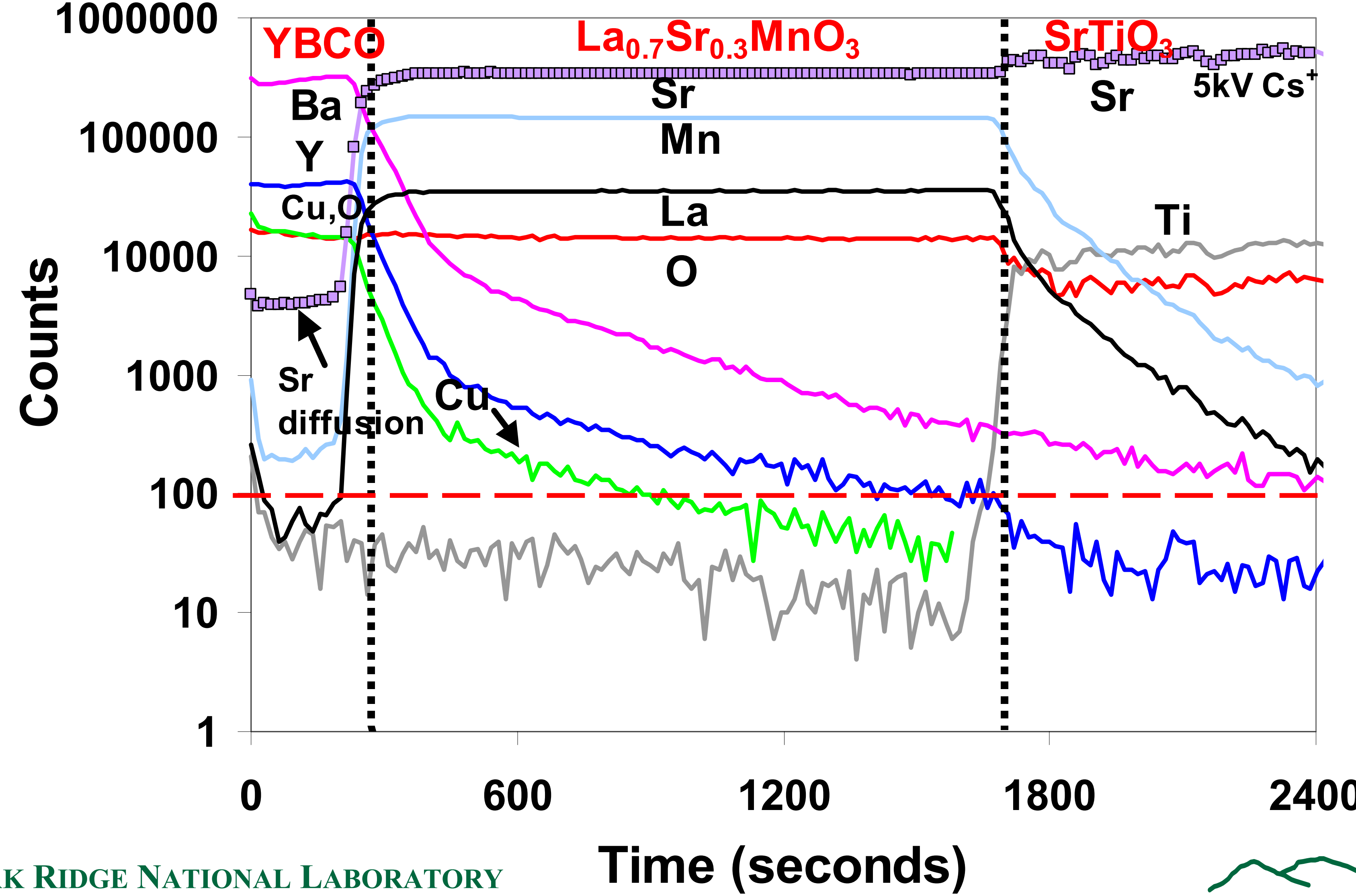
Ref.: T. Aytug et al., Appl. Phys. Lett. 79, 2205 (October 2001)

SIMS depth profile analyses indicated a low level Sr contamination of YBCO, from the LSMO layer on Ni

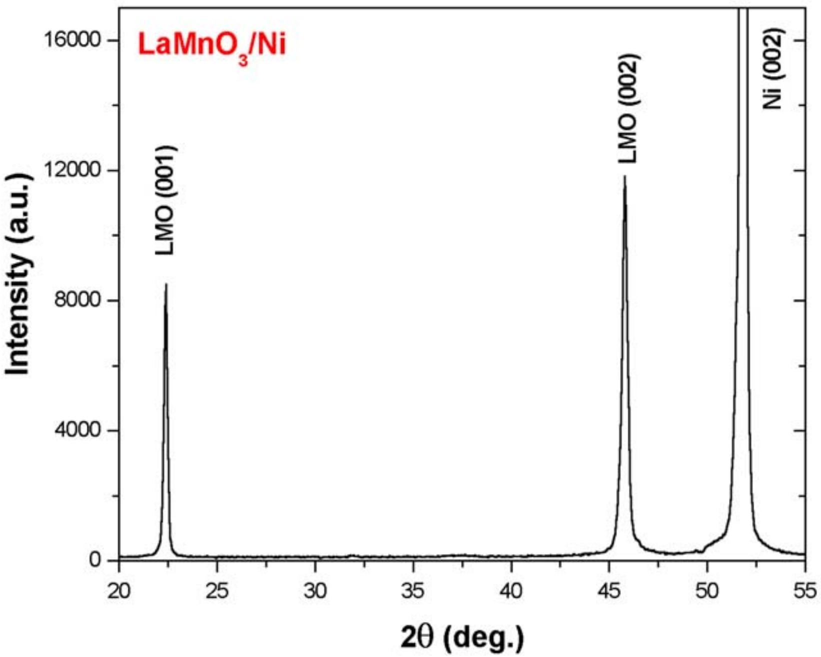


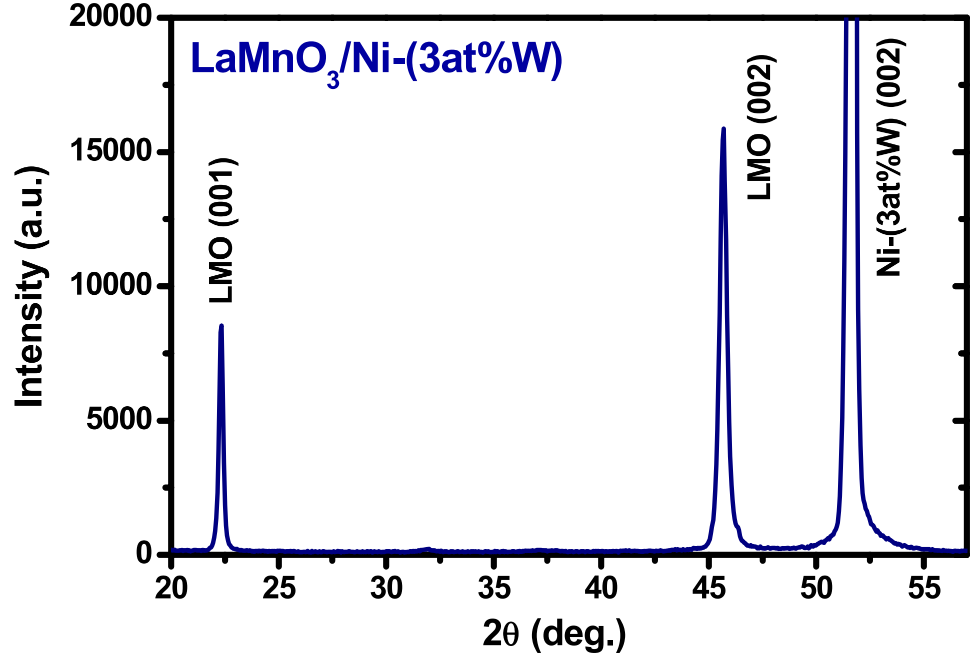
R.E. Erickson (3M)

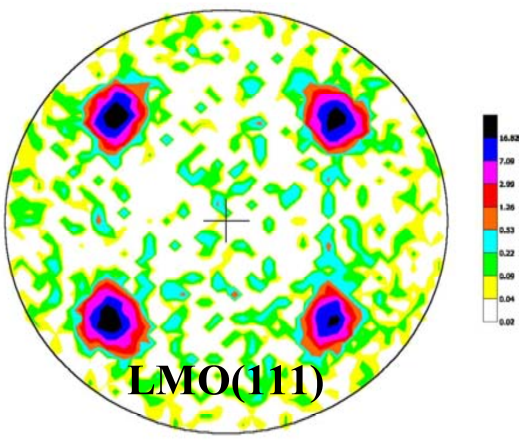
SIMS depth profile analyses indicated a low level Sr contamination of YBCO, from the LSMO layer on STO

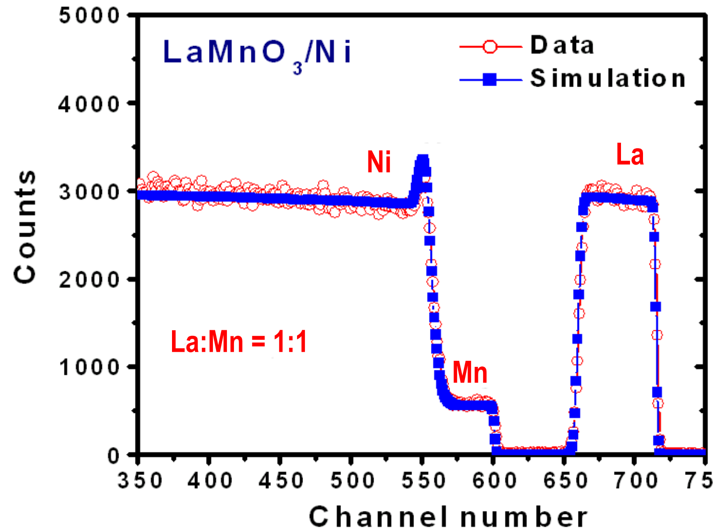


Textured LMO layers were deposited on both Ni and Ni-W substrates using rf sputtering

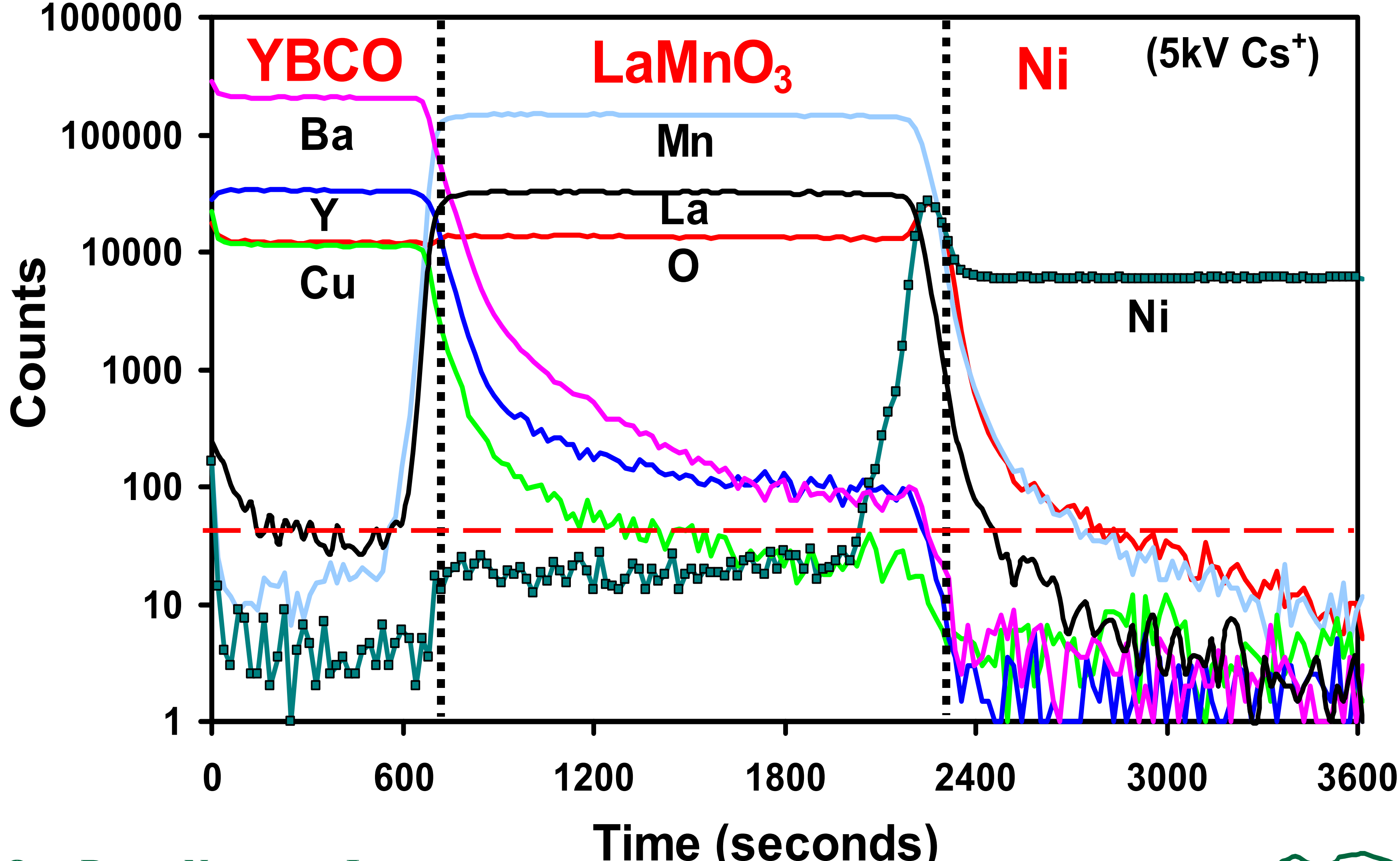




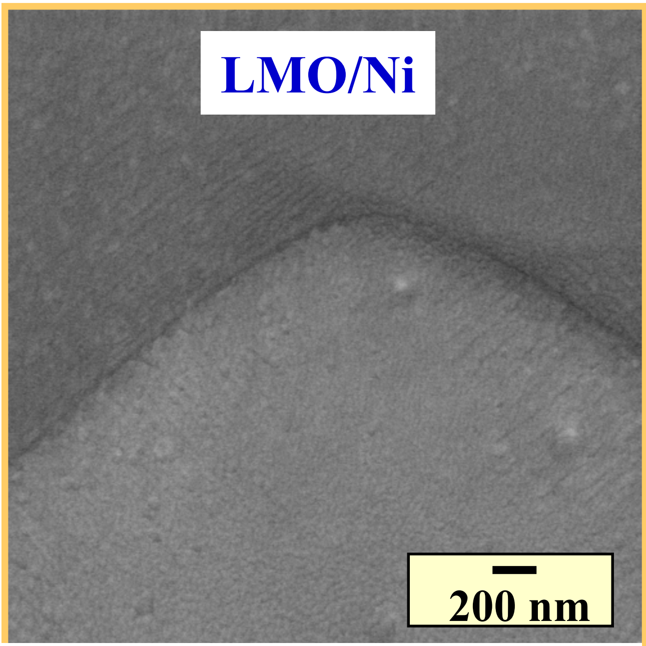


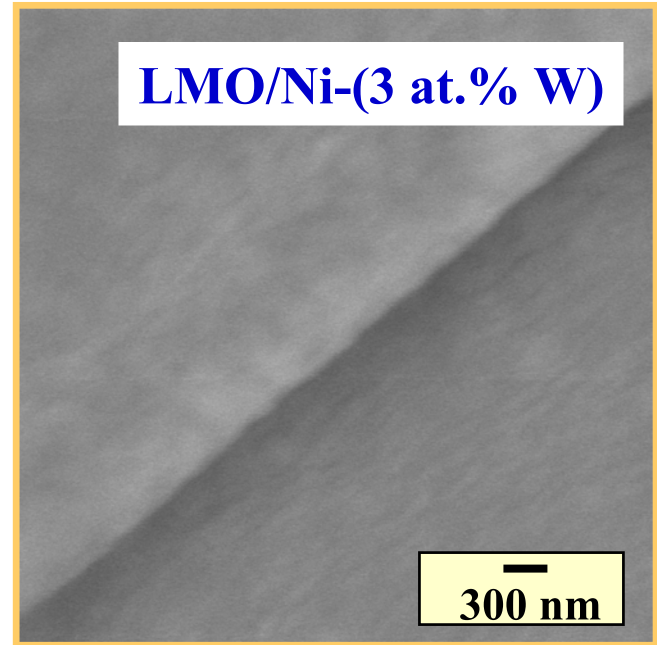


SIMS depth profile analyses indicated no contamination of both YBCO (from LMO) and LMO (from Ni) layers

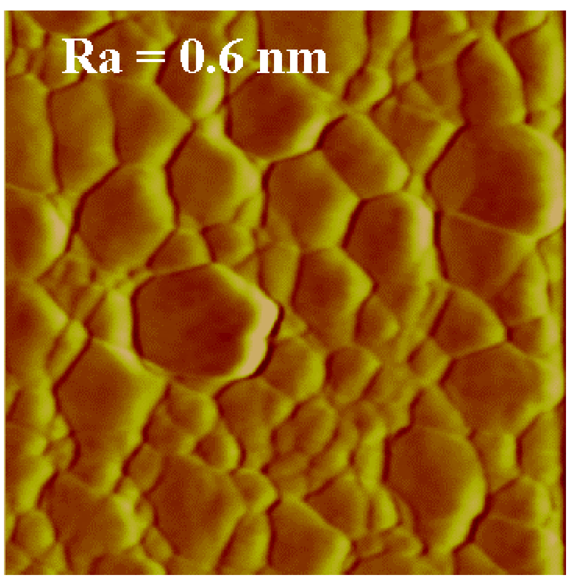


Smooth microstructure of *$LaMnO_3$* Buffers





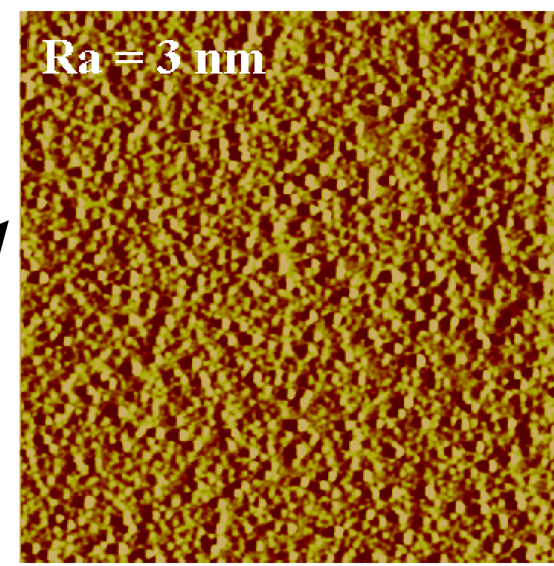
Z
5 nm



1 μm

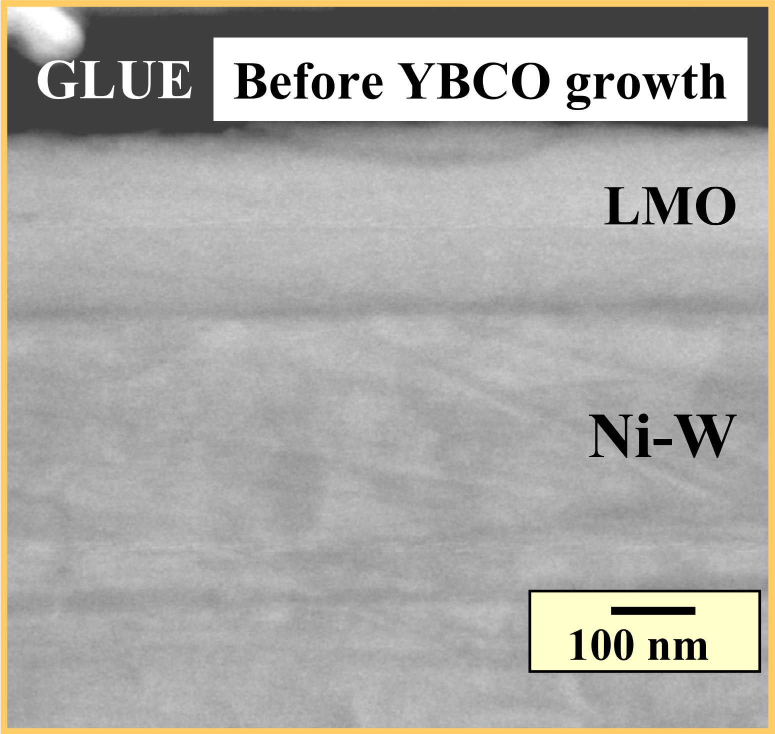
LMO/Ni-(3 at.% W)

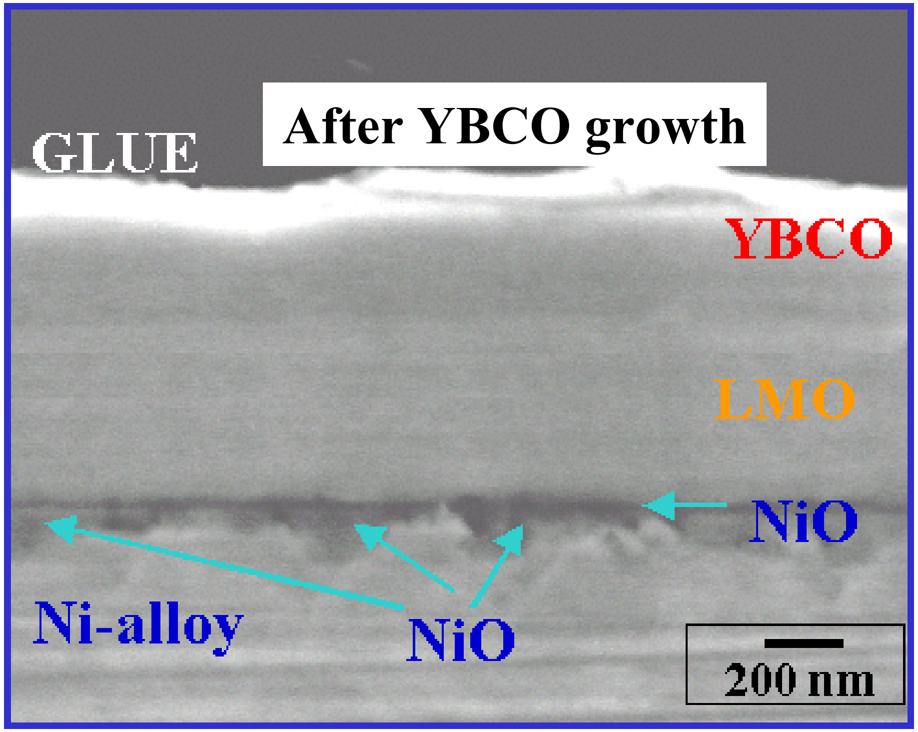
Z
10 nm



10 μm

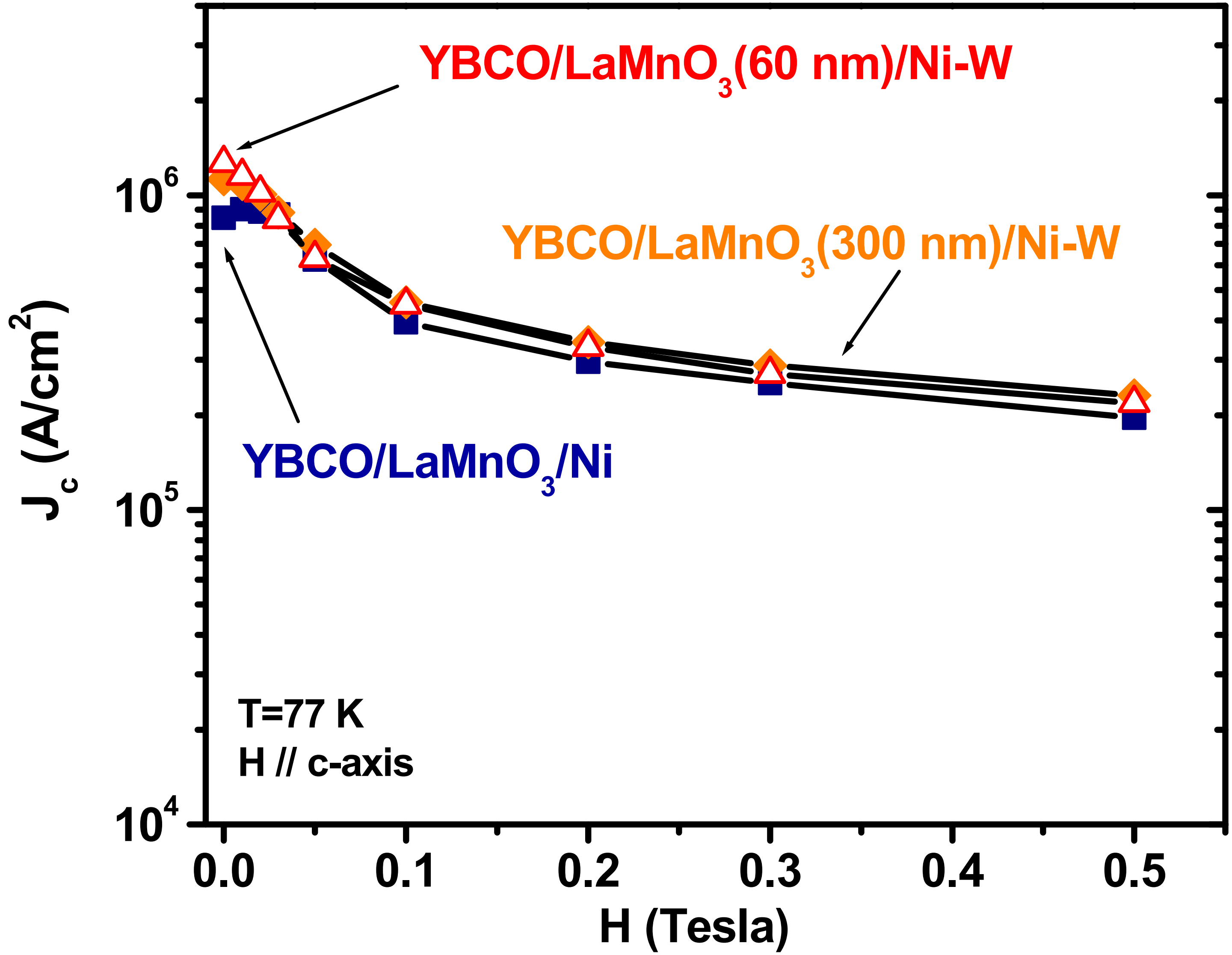
Cross-section images of YBCO/*LaMnO$_3$* on *Ni-W*



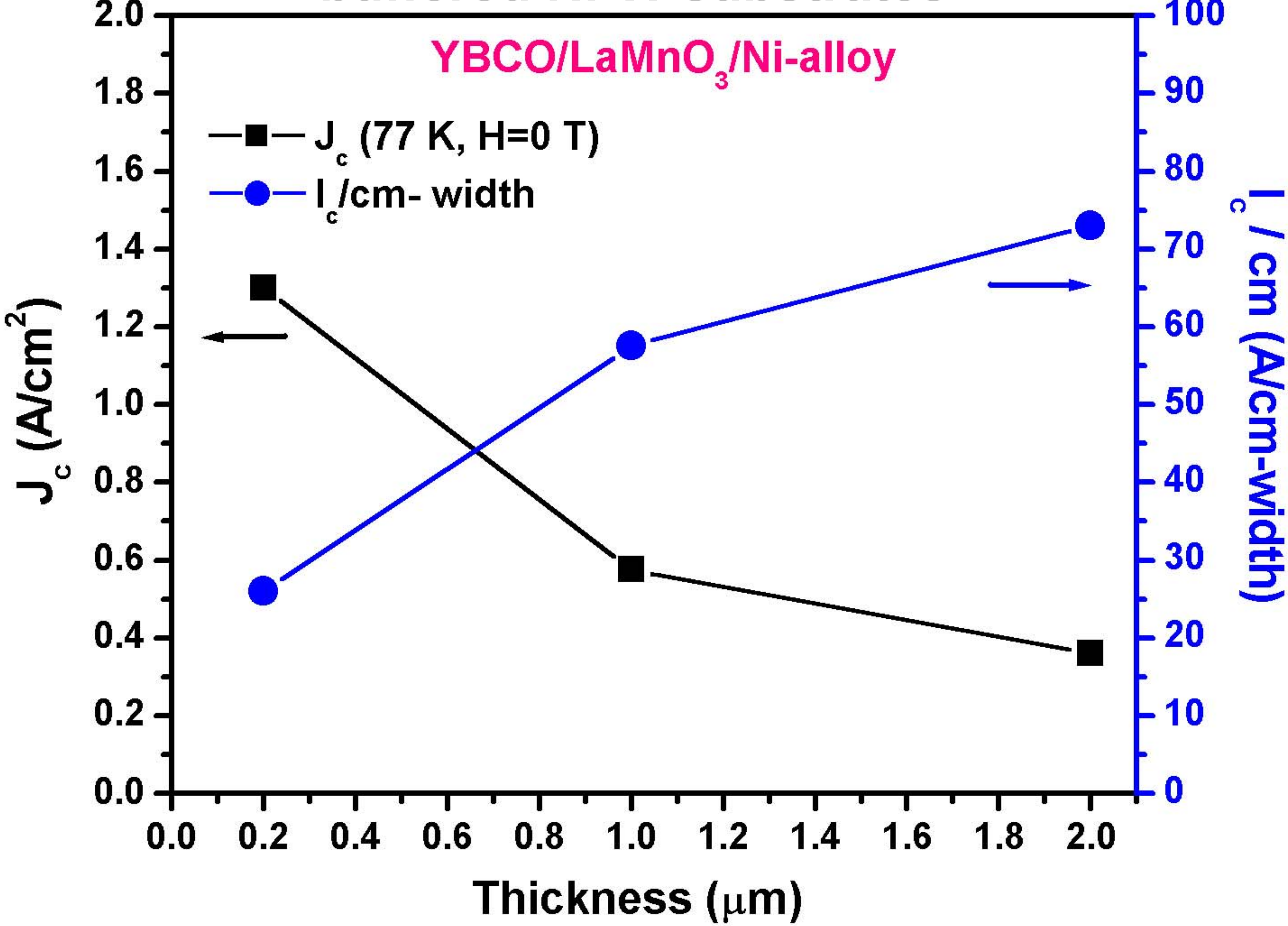


- NiO is formed at the LMO/Ni interface during the YBCO growth
- Ni diffusion is contained at the LMO layer
- LMO/YBCO interface is clean

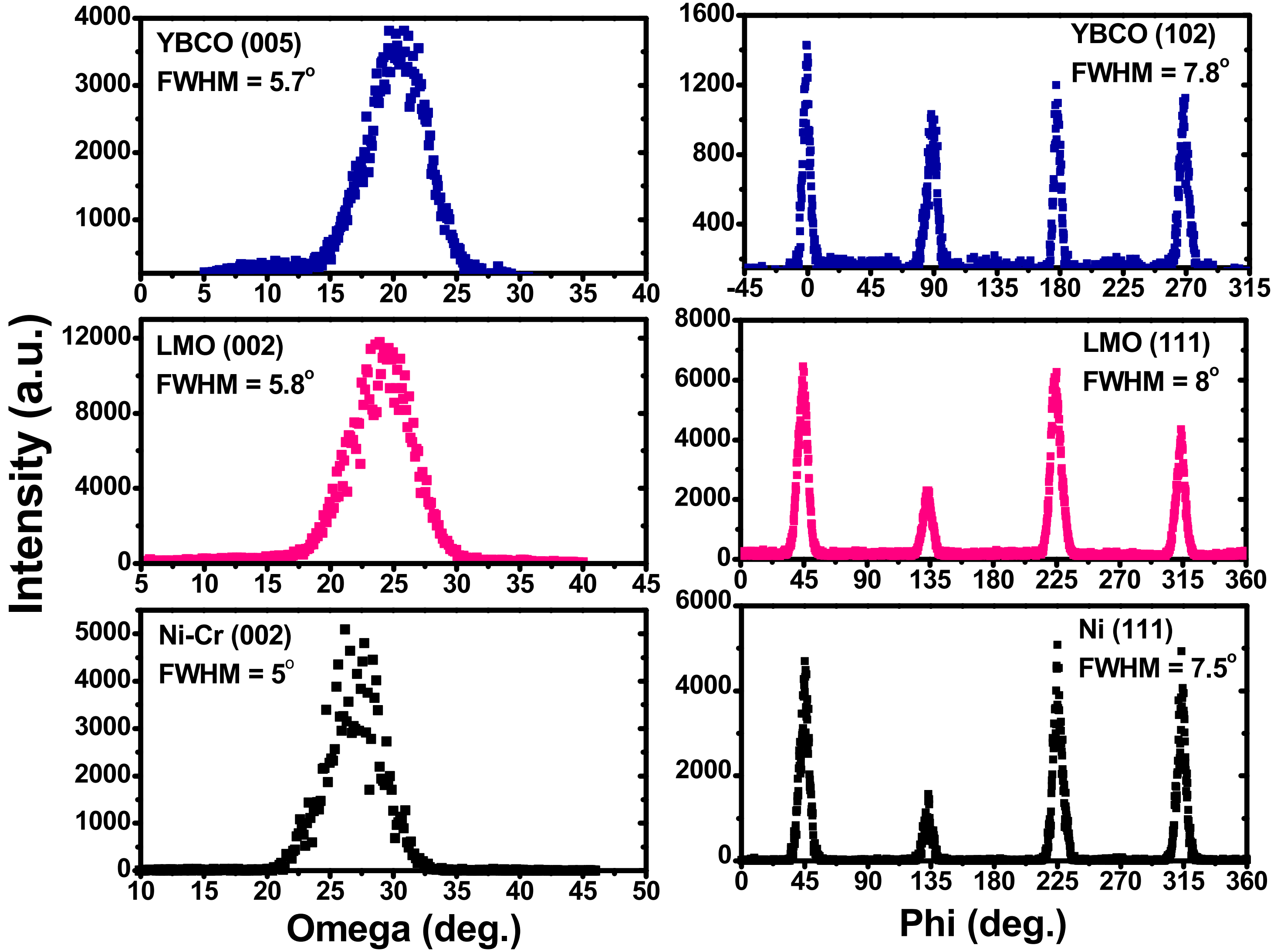
PLD was used to grow YBCO films (0.2 μm) with a J_c of over 1 MA/cm² on LMO buffered Ni and Ni-W substrates



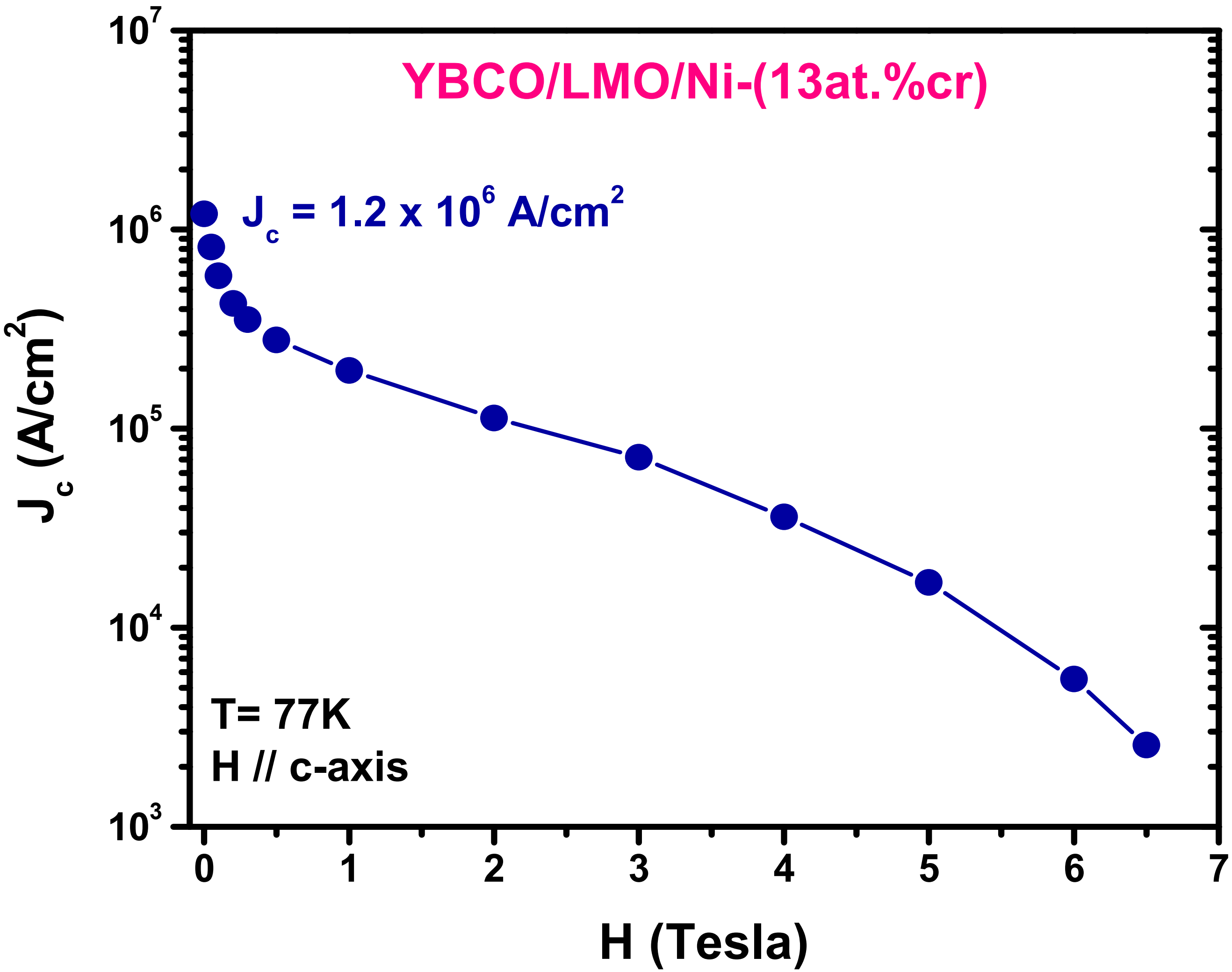
PLD was used to grow thick YBCO films on LMO (300 nm) buffered Ni-W substrates

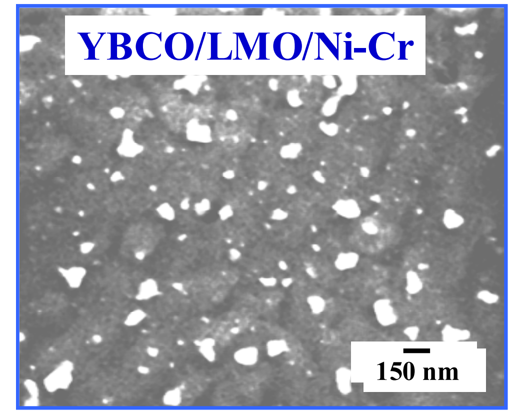


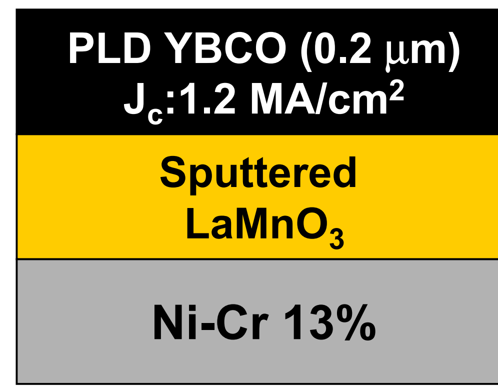
Highly textured YBCO and $LaMnO_3$ buffers were grown on strong, non-magnetic Ni-Cr 13% substrates



YBCO films with a J_c of 1.2 MA/cm^2 on LMO buffered non-magnetic Ni-Cr 13% substrates using PLD

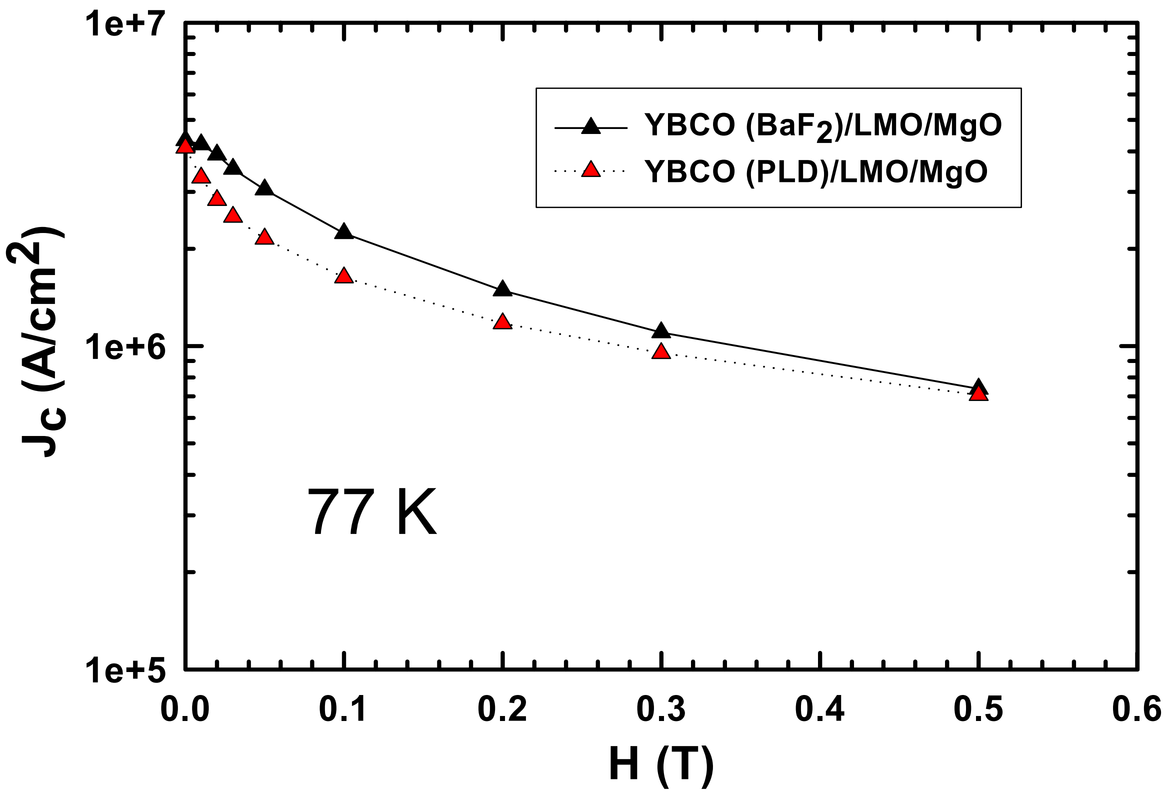




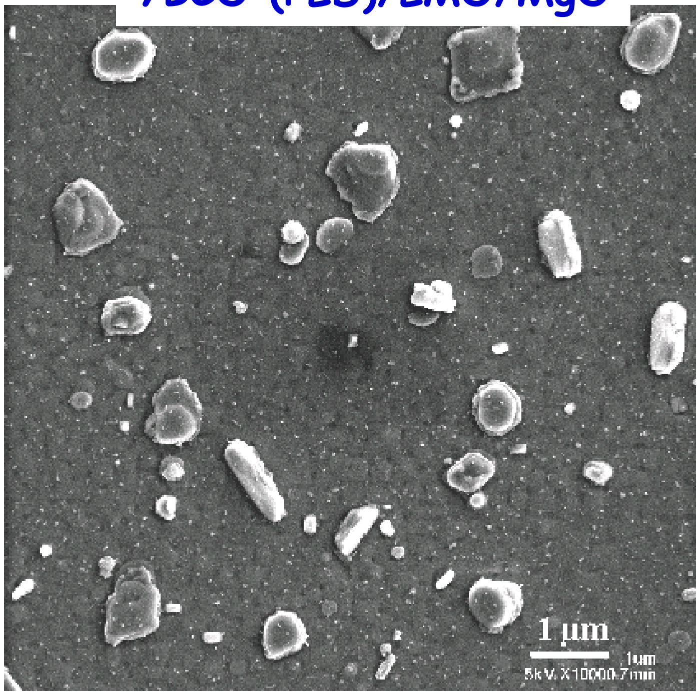


$LaMnO_3$ Buffers for non-RABiTS based YBCO Coated Conductors

Demonstrated the compatibility of LMO buffers on MgO single crystal substrates by growing YBCO films with a J_c of over 4 MA/cm^2 using both PLD (0.2 μm) and Ex-situ BaF_2 (0.3 μm) processes



YBCO (PLD)/LMO/MgO



Terry Holesinger (LANL)

- Highly dense YBCO films were produced
- LMO is also compatible with BaF_2 precursors

An Oak Ridge – Los Alamos collaboration produced excellent results on IBAD MgO

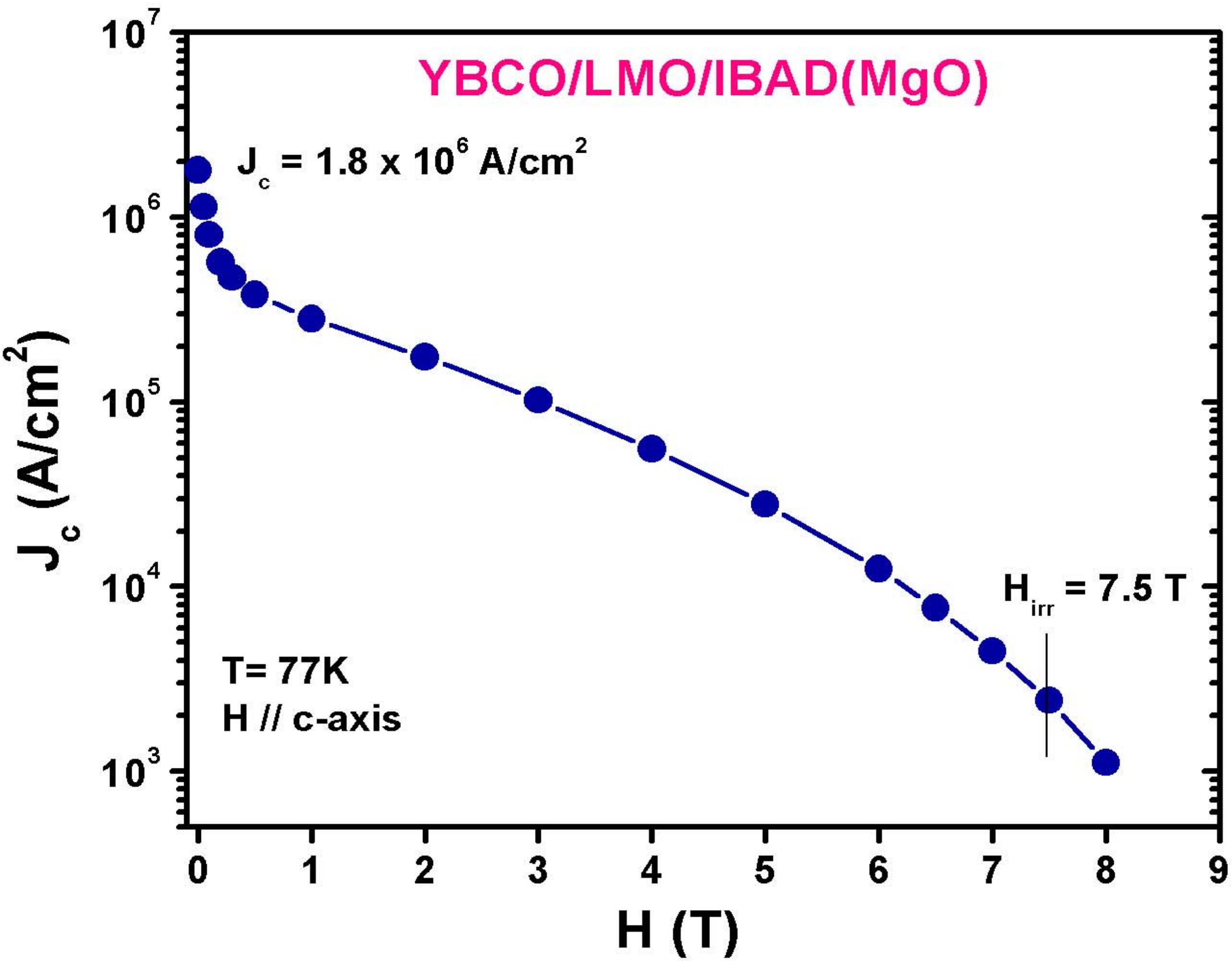
- Los Alamos sent high-quality IBAD MgO samples to Oak Ridge
- Oak Ridge sputtered a $LaMnO_3$ buffer layer on the MgO
- The samples were returned to Los Alamos for PLD YBCO

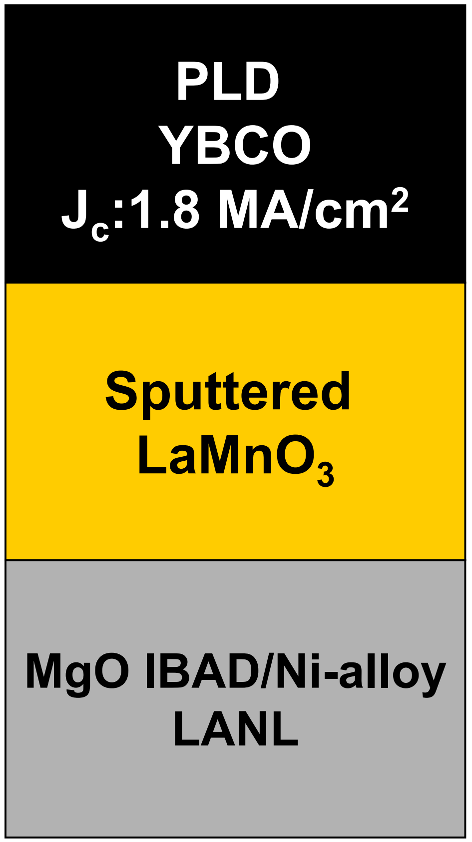
Result:

- YBCO texture – 5.2° FWHM (in-plane); 1.8° FWHM (out-of-plane)
- YBCO thickness – 1.65 μm
- J_c (75 K, self-field, two bridges) – 1.3 and 1.5 MA/cm^2
- **Equivalent I_c – 230 A/cm-width**

This performance is comparable to the best single-layer results achieved by Los Alamos on IBAD MgO, and at several institutions on IBAD YSZ

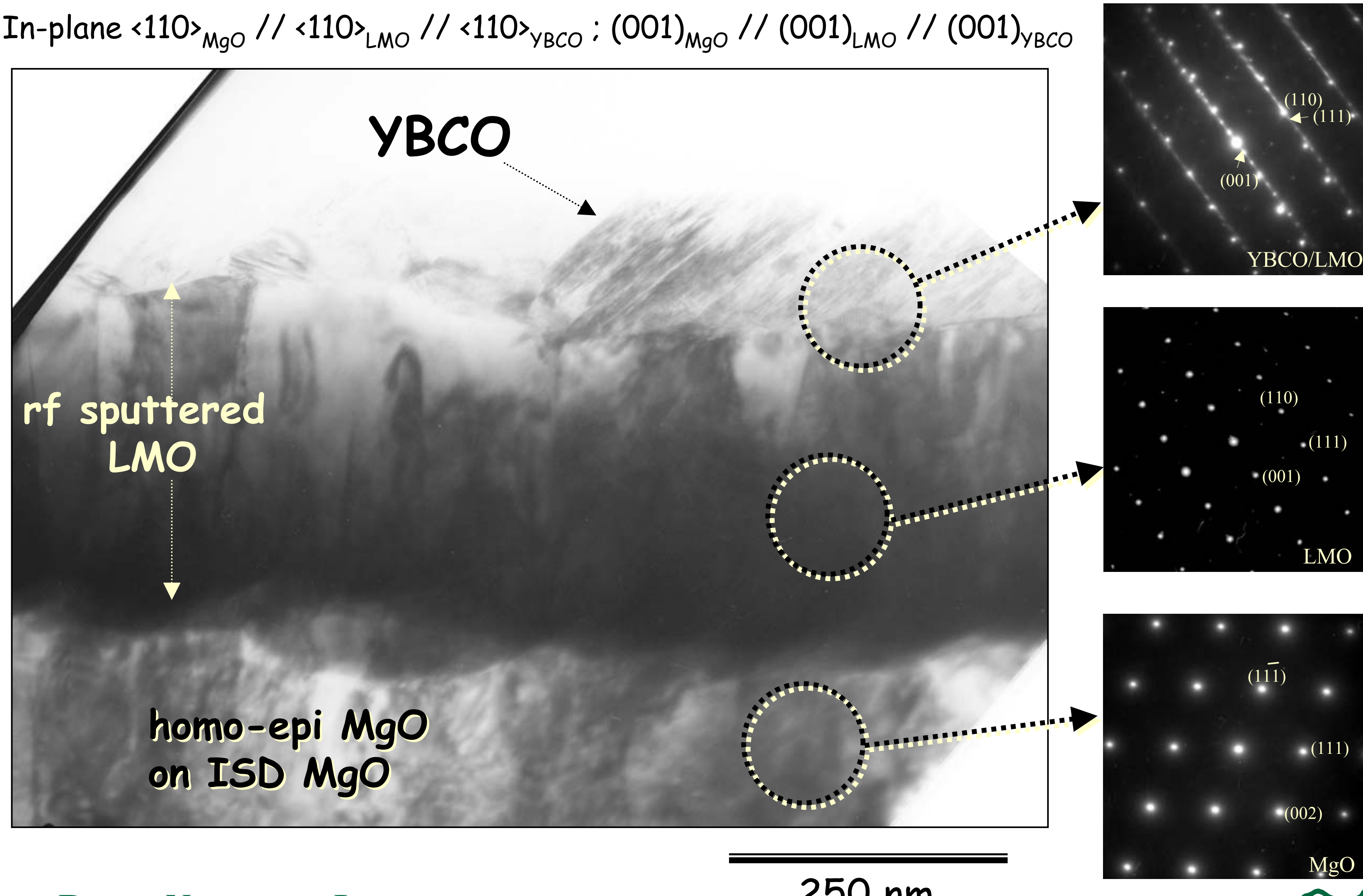
Demonstrated the growth of YBCO films (0.2 μm) with a J_c of 1.8 MA/cm^2 on *ORNL*-$LaMnO_3$ buffered *LANL*-IBAD MgO Buffers at ORNL





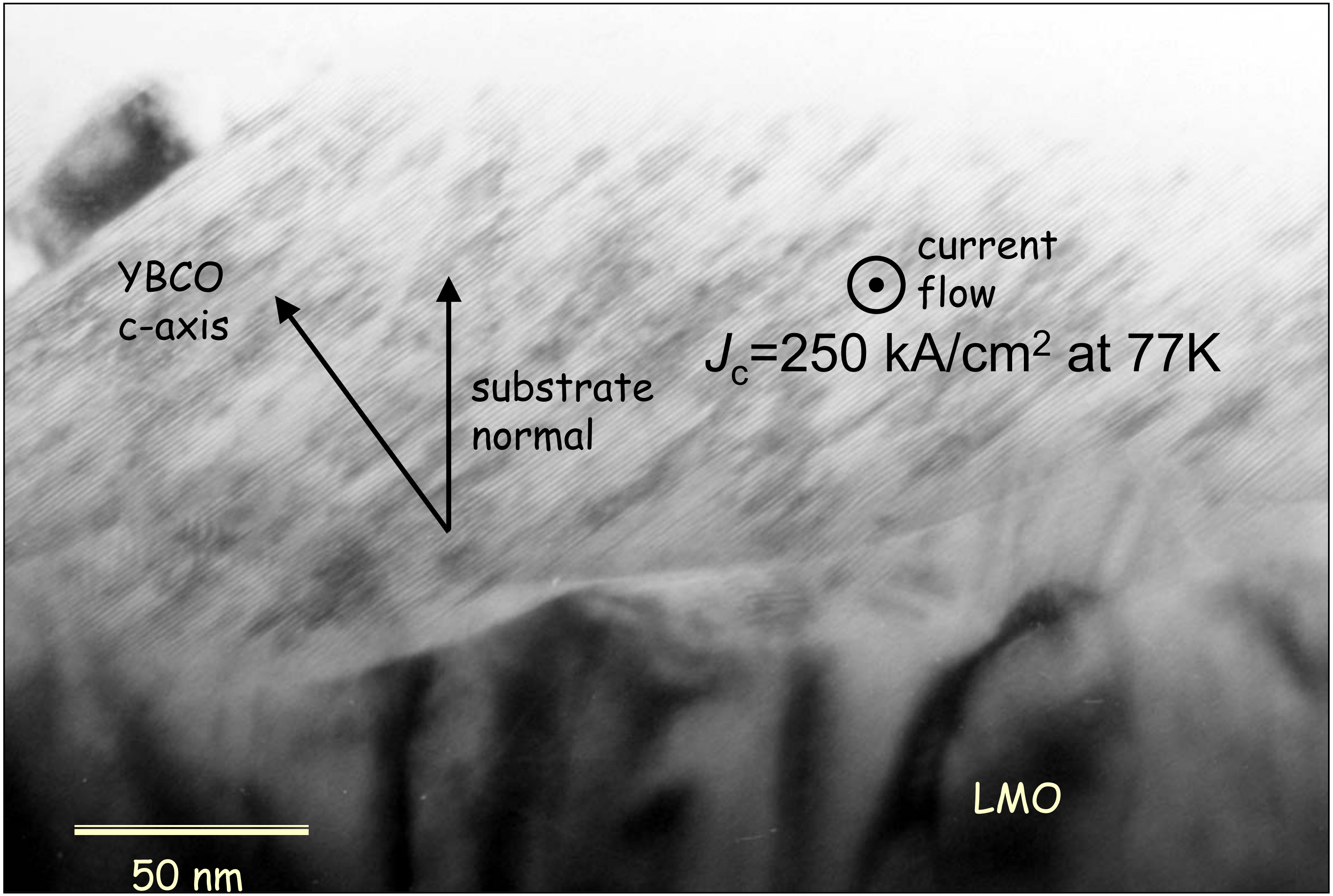
An Oak Ridge – Argonne collaboration resulted in demonstration of the "cube-on-cube" growth of YBCO (ORNL)/LMO (ORNL)/MgO-ISD (Argonne)

In-plane <110>$_{MgO}$ // <110>$_{LMO}$ // <110>$_{YBCO}$; (001)$_{MgO}$ // (001)$_{LMO}$ // (001)$_{YBCO}$



Dean Miller, ANL

YBCO *c*-axis inclined ~36° from substrate normal
But, current conduction in basal planes



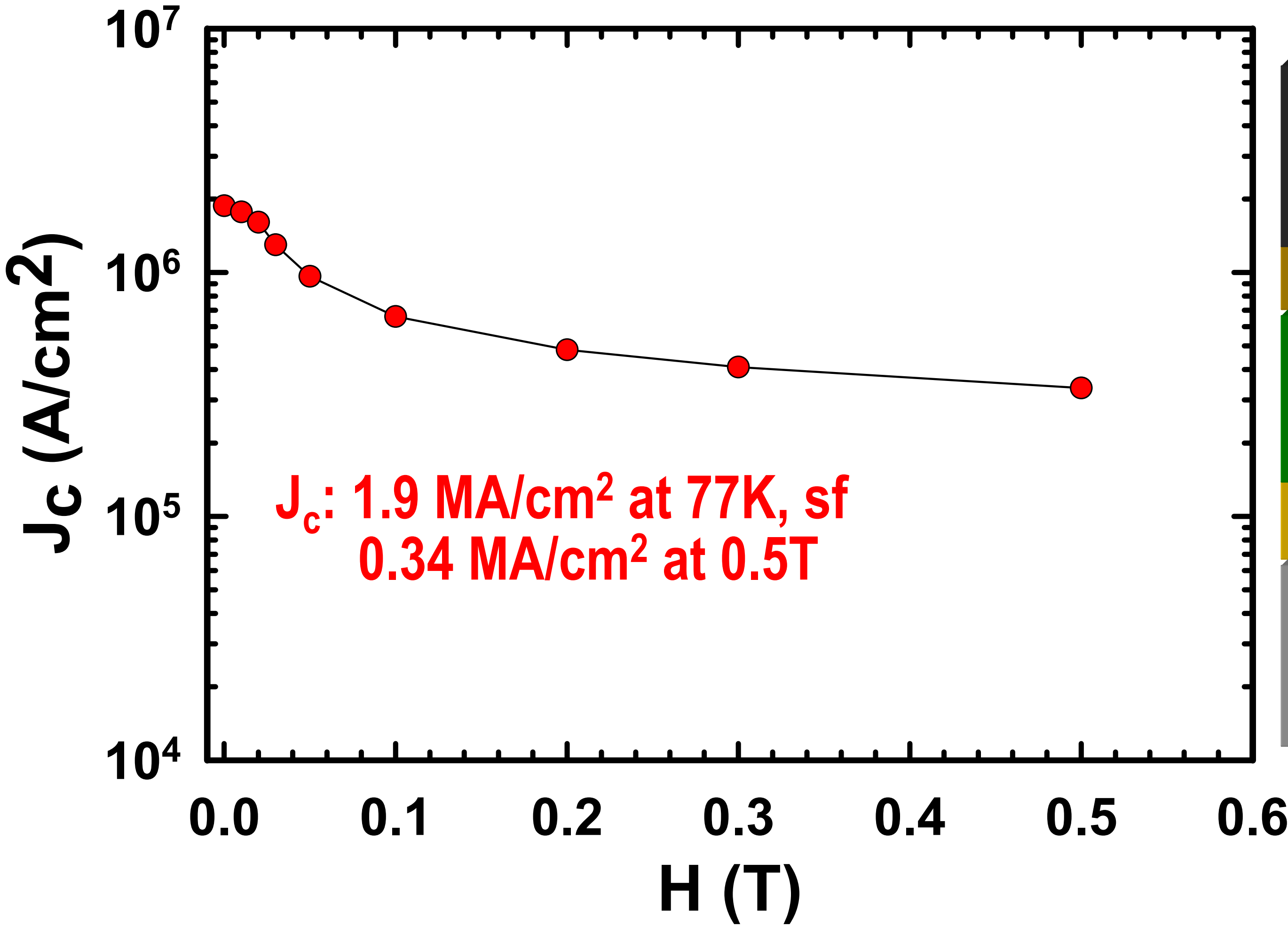
Dean Miller, ANL

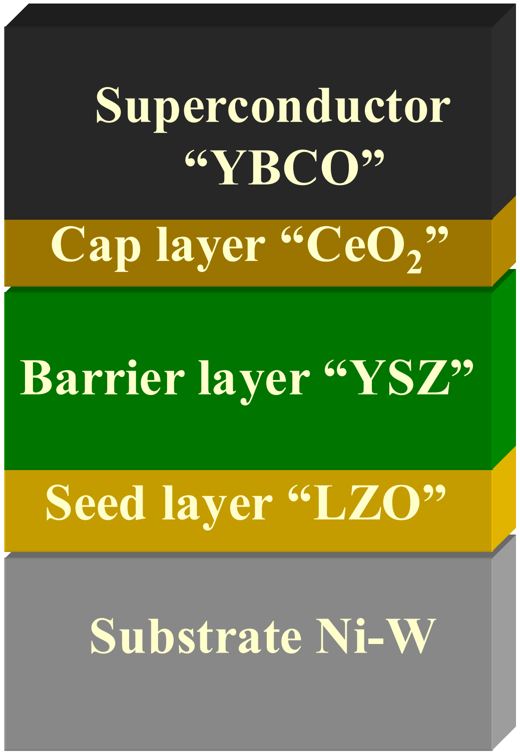
Summary

- $LaMnO_3$ layer has been identified as an excellent seed layer, Ni diffusion barrier layer, and a cap layer (PLD YBCO)
- YBCO films with a J_c of 1.2 MA/cm^2 were obtained on LMO buffered non-magnetic Ni-Cr 13% substrates
- High J_c YBCO films were produced on LMO buffered- MgO IBAD or ISD substrates

Solution based $La_2Zr_2O_7$ (LZO) Buffers

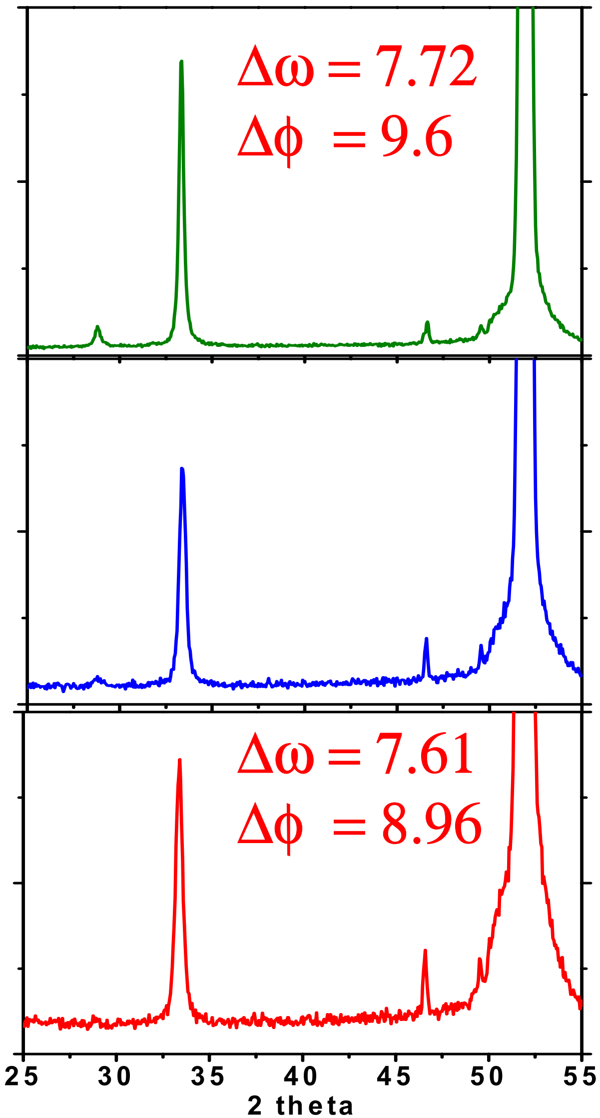
LZO seeds on Ni-3%W substrates yielded high current density YBCO films grown by PLD (FY 2001)





The performance of solution LZO seed layers approach that of e-beam Y_2O_3 seed layers

X-ray and microstructure of all solution LZO layers



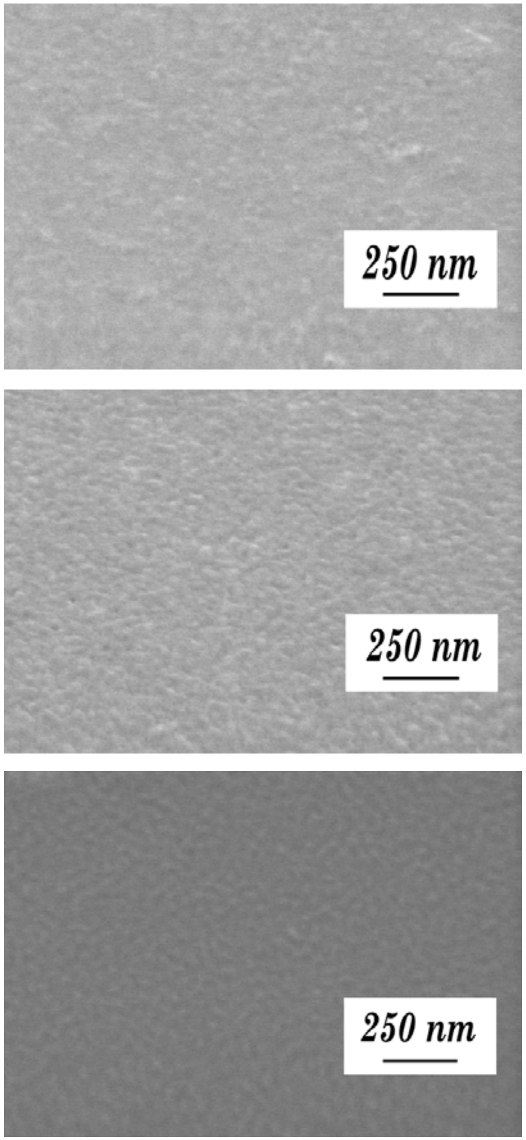
LZO coat 3

LZO coat 2

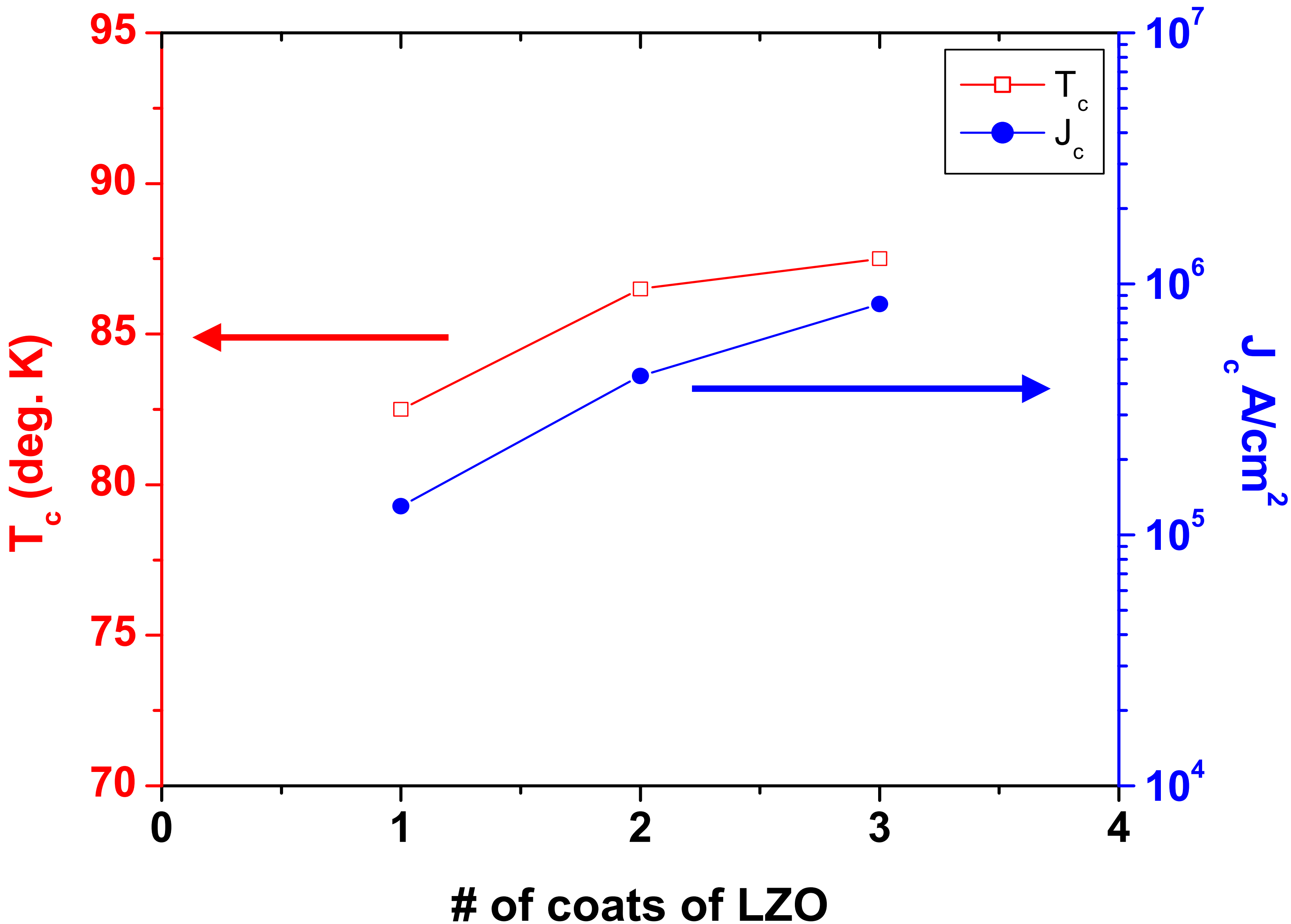
LZO coat 1

Nickel

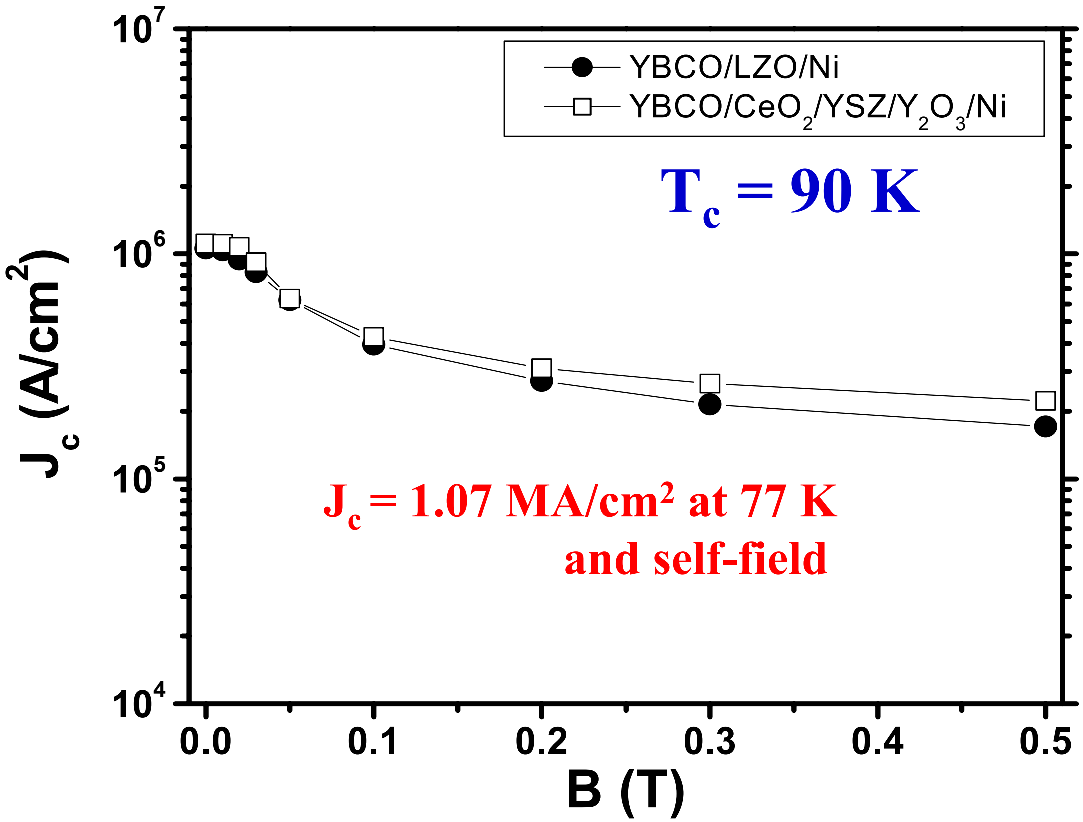
$\Delta\omega = 7.73$, $\Delta\phi = 9.2$



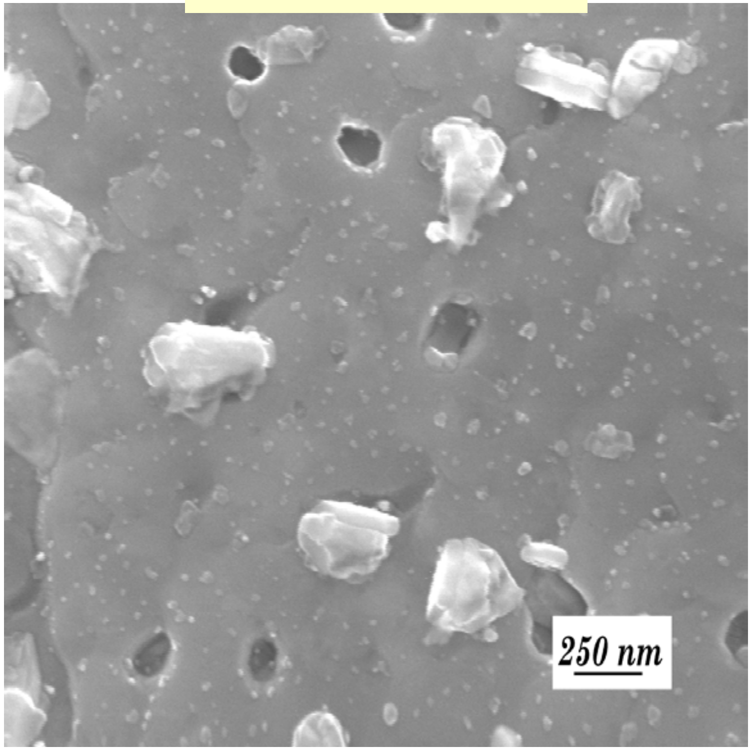
T_c and J_c data on PLD grown YBCO films (0.2 μm) on all solution LZO buffered Ni substrates



YBCO films (0.2 μm) with a J_c of over 1 MA/cm^2 have been grown on all solution 60 nm thick LZO buffered Ni substrates using PLD

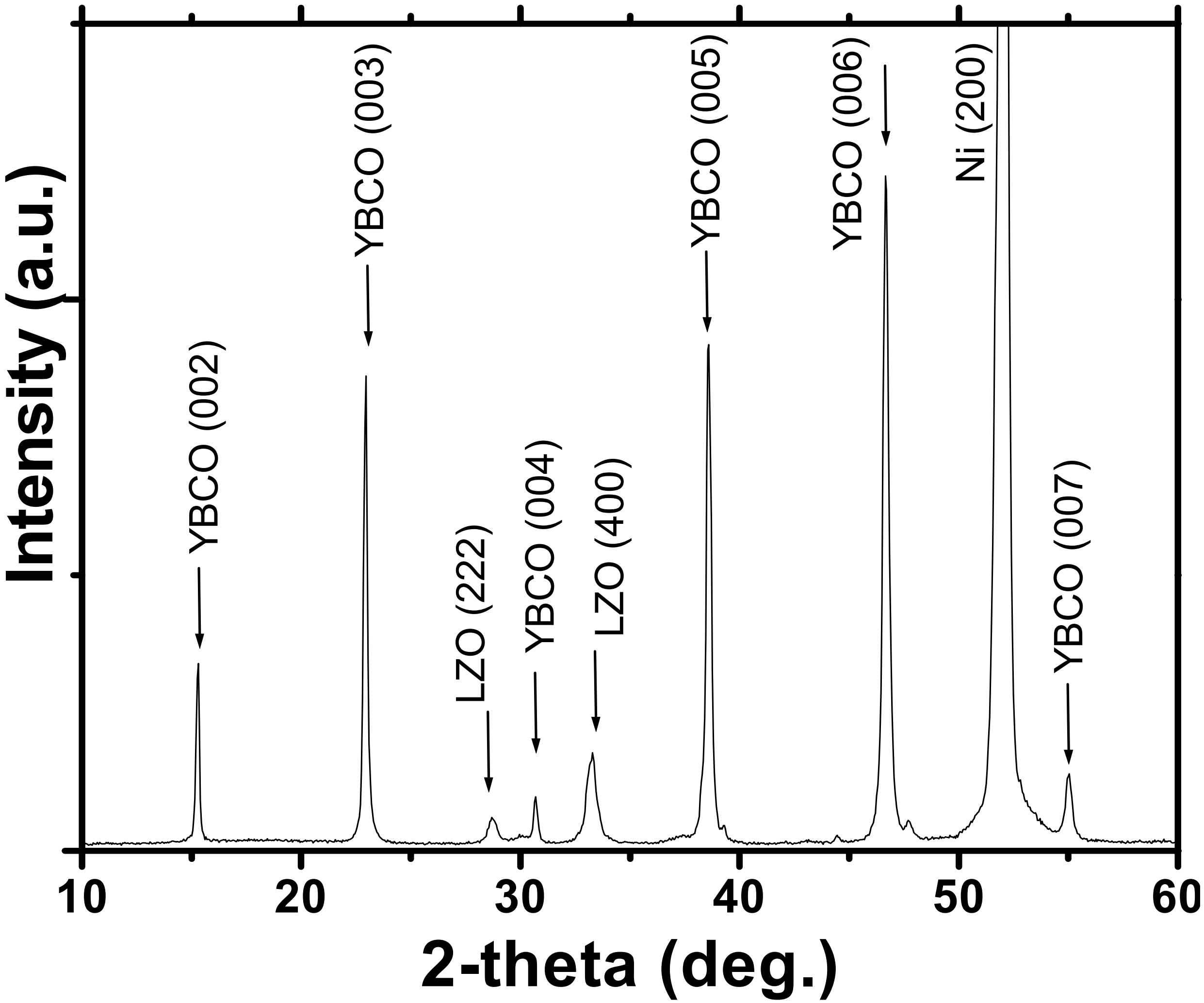


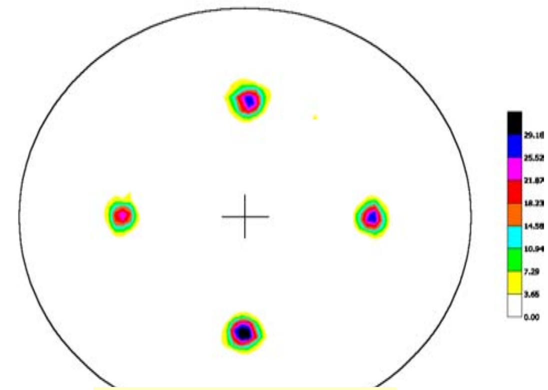
YBCO/LZO/Ni



The performance of single solution buffer layers approach that of our standard three-layer architectures

Highly aligned YBCO films (0.2 μm) have been grown on all solution 60 nm thick LZO buffered Ni-W substrates using PLD

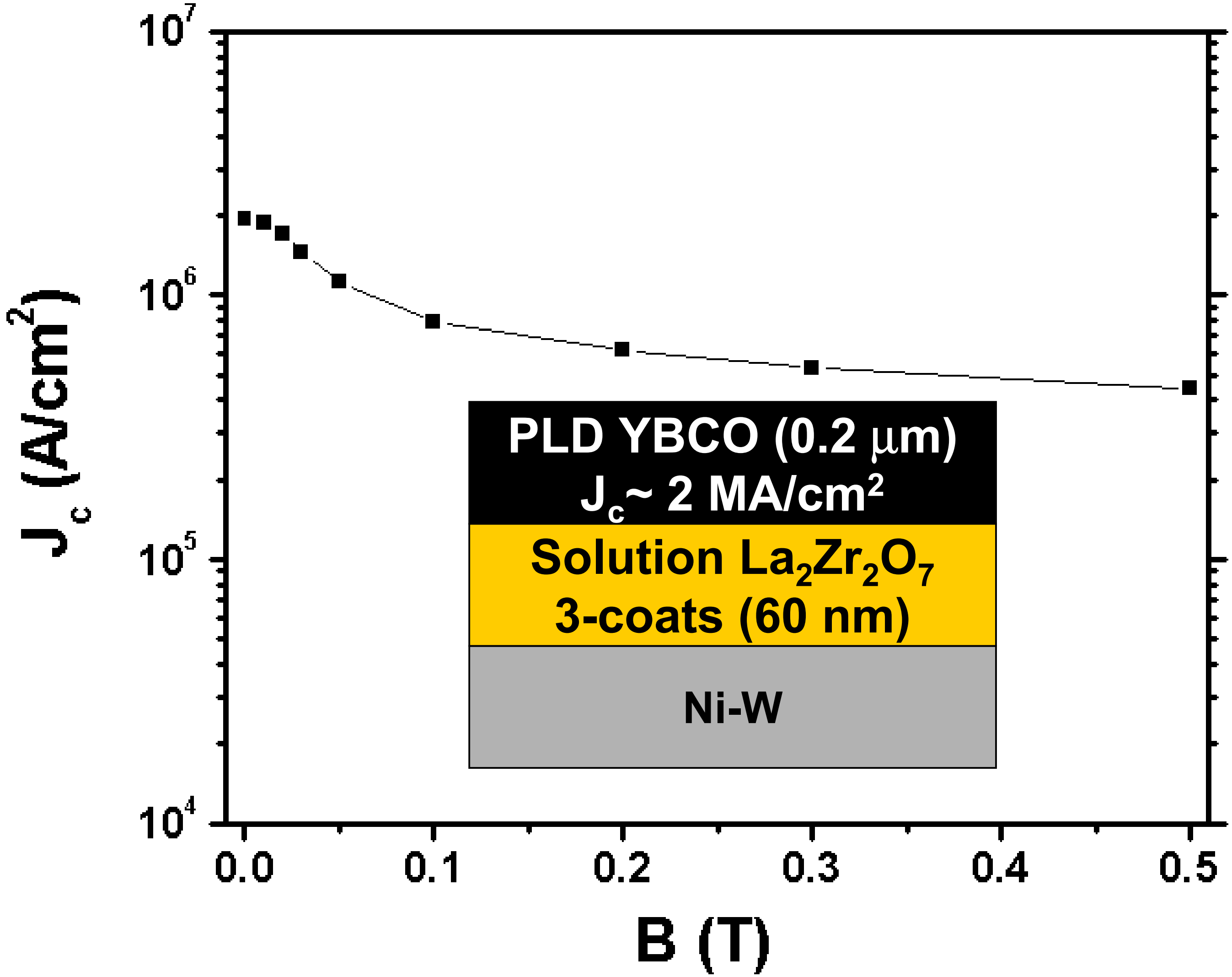




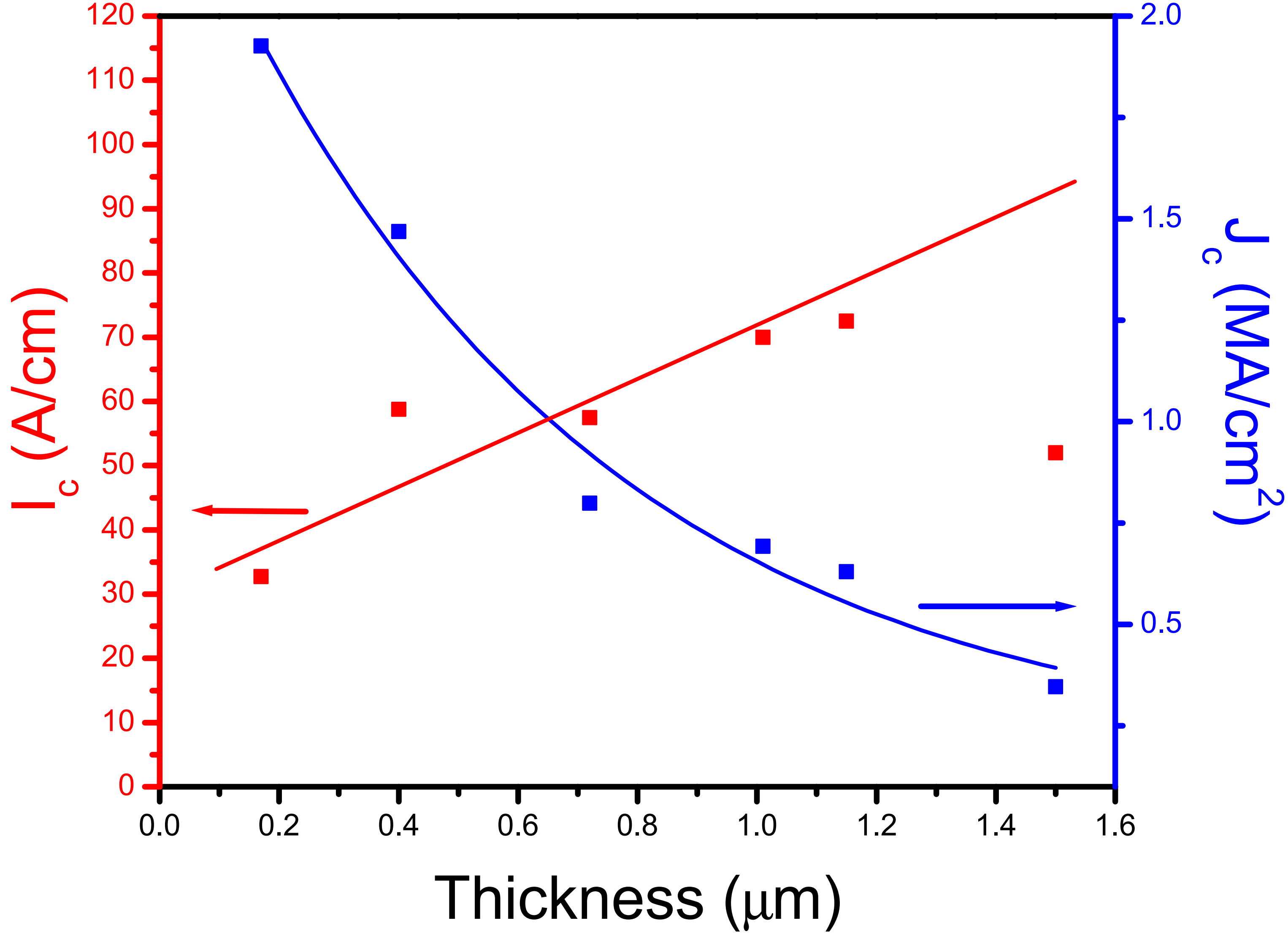
YBCO (103)

	Δω	Δφ
Nickel (deg)	5.7	7.65
YBCO (deg)	6.8	9.3

All Solution-grown Single Buffer Layer Yielded 2 MA/cm^2 YBCO Conductor on Ni-W substrates



Thick PLD YBCO films on all solution LZO (60 nm) buffered Ni-W substrates



Summary

- LZO has been identified as an excellent Ni diffusion barrier layer
- YBCO films with a J_c of 2 MA/cm^2 were produced on all solution LZO buffered Ni-W substrates
- Efforts are being made to make long lengths of LZO layers

FY2002 Performance and FY2003 Plans

FY2002 Plans

- Optimize sulfur treatment to demonstrate consistent epitaxial seed layer deposition
- Optimize buffer layers on metal alloy substrates
- Investigate single buffer-layers for YBCO/RABiTS

FY2002 Performance

- ✓ Process conditions for superstructure formation identified
- ✓ Effects on epitaxial growth of vapor deposited and solution-grown oxides determined
- ✓ Growth models proposed for epitaxy of different structural classes
- ✓ Significant tech transfer to industry
- ✓ Buffer architectures found for growth of YBCO on Ni-13%Cr and Ni-3%W
- ✓ Solution-based $La_2Zr_2O_7$ single buffers developed on Ni-W and Ni tapes
- ✓ Sputtered $LaMnO_3$ single buffers developed on Ni, Ni-W, and Ni-Cr tapes

New Task(s) Added in FY 2002

FY2002 Plans (cont'd)

- **Initiate development of buffer layers for YBCO coatings on copper alloys**

- **Develop cap-buffer layers for MgO-based tapes, in collaboration with *LANL* (IBAD MgO) and *ANL* (ISD MgO)**

FY2002 Performance

✓ **High-J_c films have been deposited by PLD on buffered copper films and single crystals**

✓ ***High-J_c* YBCO have been deposited by PLD on buffers of ORNL $LaMnO_3$ on LANL and ANL MgO-buffered alloy tapes**

FY2003 Plans

- ***Research and develop faster, potentially lower cost, and simpler RABiTS buffer-layer architectures that are compatible with ex-situ BaF_2 or MOD YBCO processes***
  (collaboration with SNL and AMSC)

- ***Continue fundamental studies of epitaxial growth on textured non-magnetic substrates, including copper and copper alloys (collaboration with U. Florida, AMSC, SUNY Buffalo and North Carolina State)***

- ***Develop suitable buffer architectures on IBAD-MgO and ISD-MgO substrates for compatibility with ex-situ YBCO (collaboration with LANL and ANL)***

- ***Develop viable high-rate processes to fabricate high-quality thick buffer layers by solution deposition***

Research Integration

- **Five CRADA teams working with ORNL staff to develop science base for buffer layers for coated conductors**
  3M Company; American Superconductor Corp.; MicroCoating Technologies; Neocera, Inc., Oxford Superconducting Technology

- **Collaborations with universities and other labs**
  U. Wisconsin; U. Kansas; U. Florida; ANL; LANL; SNL

- ***Information/expertise transfer:***
  - ***>30 publications and presentations, >20 issued patents related to RABiTS technology***
  - ***WEB posting of Annual Report and presentations from this meeting***