

Laboratory Scale Dip-Coating and Vacuum Conversion of Solution Deposited YBCO

**SANDIA NATIONAL LABORATORIES
and
OAK RIDGE NATIONAL LABORATORY**

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Collaborators

- **Sandia Team:**
 - P.G. Clem, J.T. Dawley
- **Oak Ridge Team:**
 - T. Aytug, S. W. Cook, L. Heatherly, H. Hsu, D. M. Kroeger, D. F. Lee, K. J. Leonard, F. A. List, P. M. Martin, M. Paranthaman, S. Sathyamurthy, E. D. Specht, J. Yoo

Funding

- **FY 2003: \$100K (SNL) and \$100K (ORNL)**

FY 2003 Plans

- Develop rapid solvent pyrolysis for the TFA-YBCO dip-coating process
- Demonstrate continuous dip coating and solvent pyrolysis for meter length tapes
- Investigate the conversion of precursor films for a wide range of pressure (nearly vacuum to 1.5 atm)
- Attempt to increase YBCO film thickness on RABiTS substrates toward 2 μm , 200A

OUTLINE

- FY 2003 Results

- Rapid solvent pyrolysis
- Continuous dip-coating on meter lengths

Paul Clem

- Precursor conversion results
- Continuous processing progress

Fred List

- Summary of FY 2003 Results / FY 2004 Plans

- Research Integration



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Motivation

- Chemical solution deposition (CSD) is an attractive method for fabricating continuous YBCO coated conductors.
- Advantages of CSD methods:
 - Fast (10^6 m/yr), low capital cost, and inexpensive precursor cost (< \$1/kA-m) compared to vapor deposition methods.
 - Continuous (reel-to-reel) processing at atmospheric pressure.
- Challenges:
 - MA/cm² quality, YBCO films on biaxially-textured, metallic substrates.
 - Sufficiently thick YBCO layers ($\rightarrow 2 \mu\text{m}$).
 - Reducing organic pyrolysis time, to enable continuous dip-coating.

dip coating → pyrolysis → crystallization → oxygenation

Fluorinated Solution Approaches For CSD YBCO

Primary Issue:

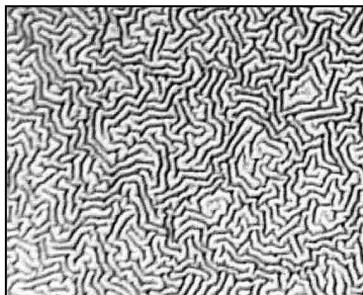
- Trifluoroacetic acid (TFA) based solutions have highly exothermic decompositions in high $p(O_2)$.
 \Rightarrow Requires a slow (1-3 hour) or low $p(O_2)$ pyrolysis.

Question:

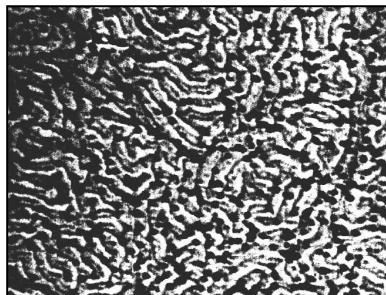
Is it possible to chemically modify precursors to control thermal decomposition and speed up processing?

High Boiling-Point Solvents Smooth Films

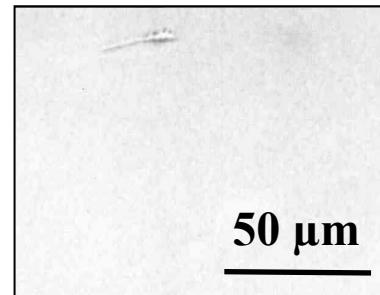
Methanol (TFA)
bp 68°



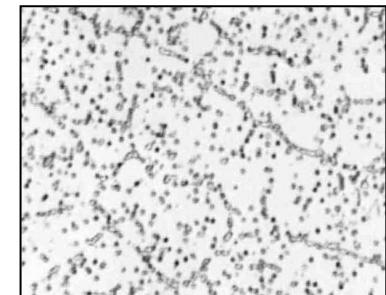
Propanediol
bp 213°



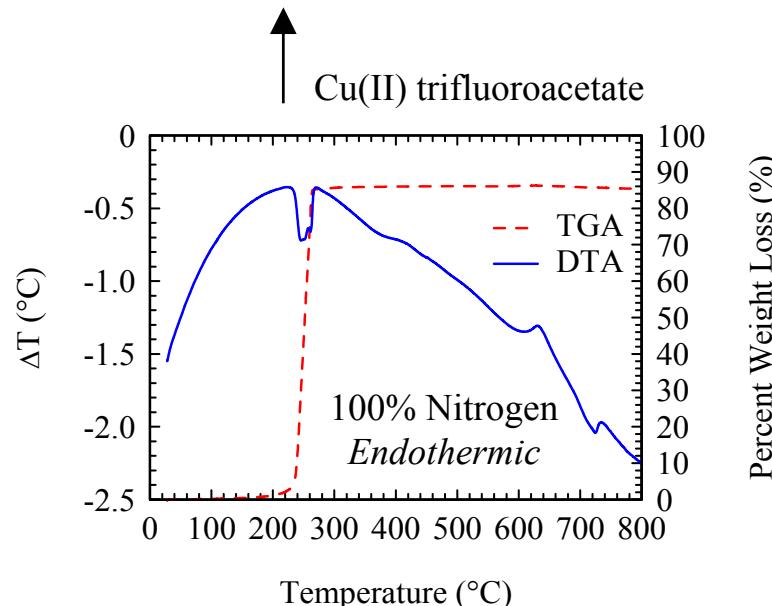
Diethanolamine (DEA)
bp 247°



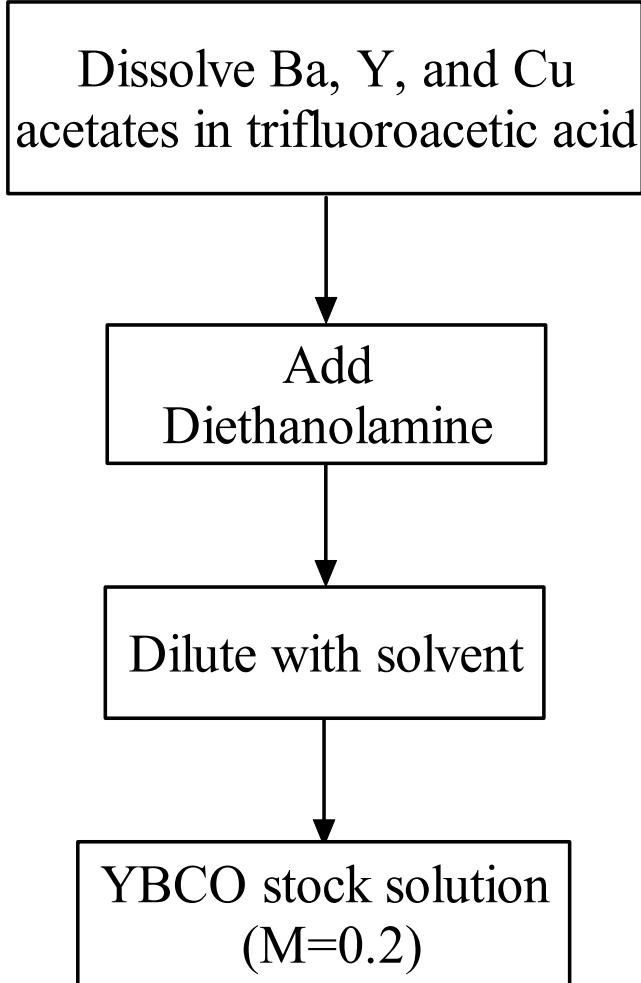
Glycerine
bp 290°



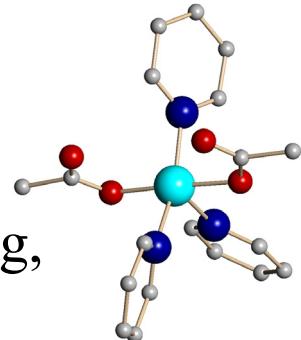
$T_{\text{boiling}} (\text{°C}) \longrightarrow$



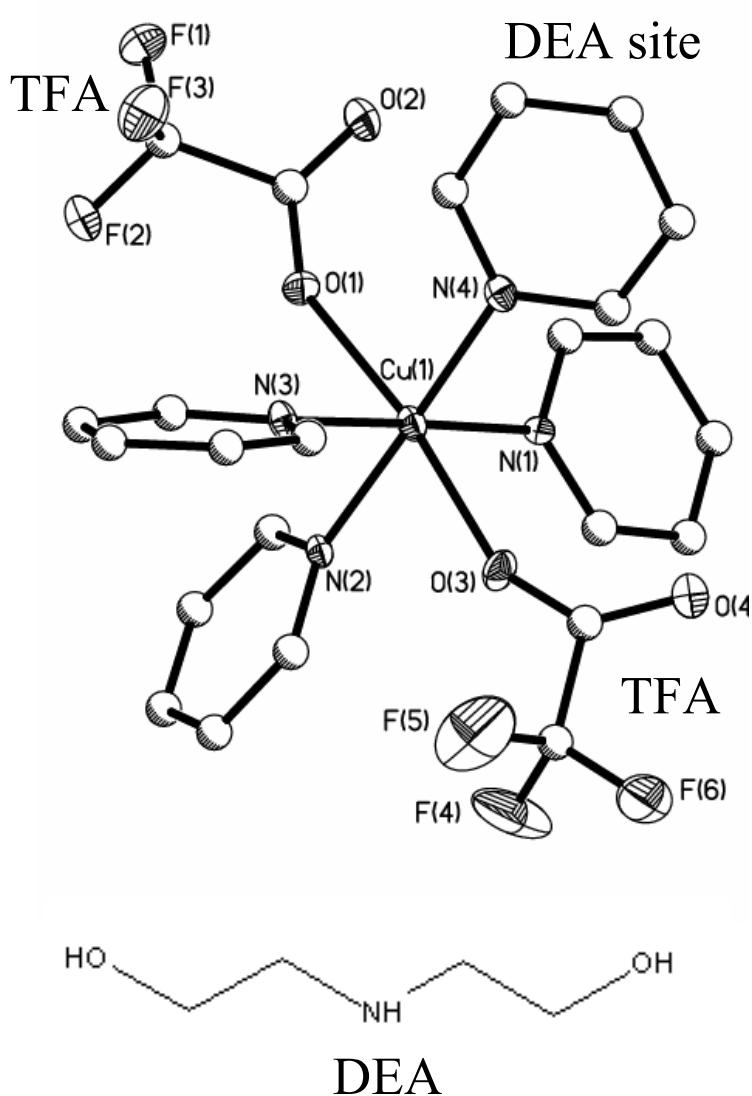
SNL Solution Approach for Fluorinated CSD-YBCO



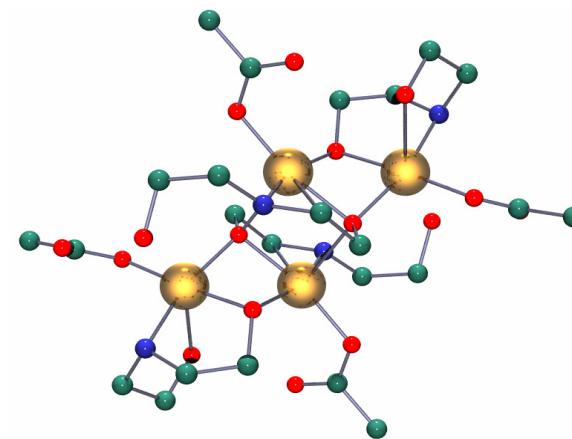
- Previously, diethanolamine (DEA) was found to prevent film buckling during low $p(O_2)$ processing.
- DEA stabilizes the Cu-acetate precursor
 - *Increased solubility*
 - *Reduced volatility*
- DEA likely permits Cu bridging, and forms larger oligomers.
- Increased steric bulk helps reduce volatility and slows decomposition.



XRD Model Structure of DEA-Cu Precursor



- Single crystals of Cu-DEA complexes were isolated and the structure was solved:
 $\text{Cu}(\text{DEA})_4(\text{TFA})_2$.
- The 4 coordinating DEA sites around Cu likely permit bridging and formation of larger oligomeric -Cu-DEA-Cu-DEA-Cu- species.



- Increased bulk slows Cu complex decomposition.

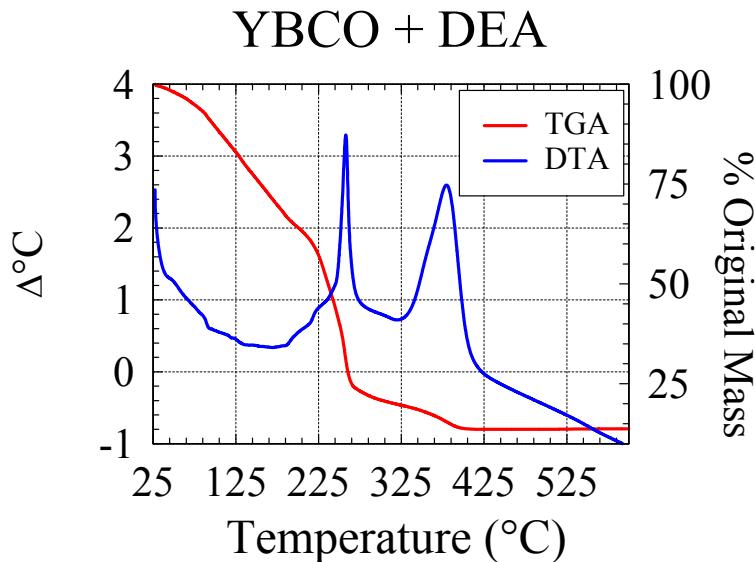
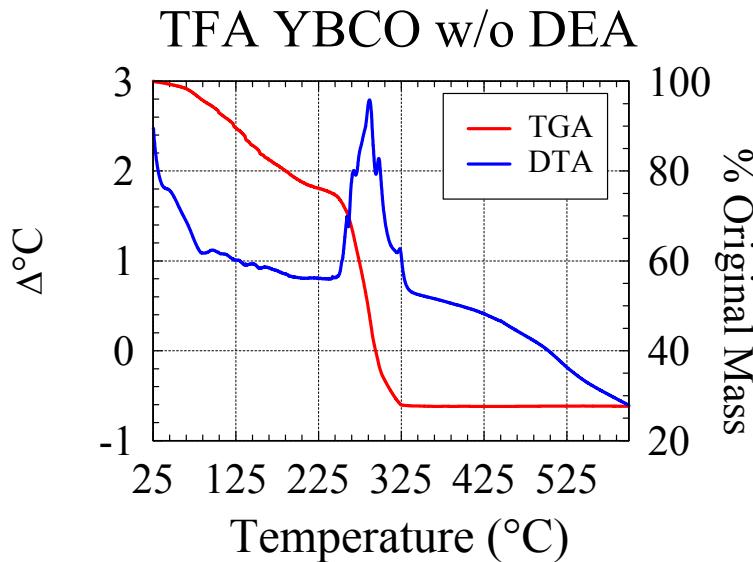


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Thermal Decomposition of Fluorinated YBCO Gels

Test conditions: 3°C/min in air



- DEA addition spreads out precursor decomposition range, compared to use of TFA alone.
- The two stage decomposition preserves film integrity.
(no cracking, buckling, or porosity development)

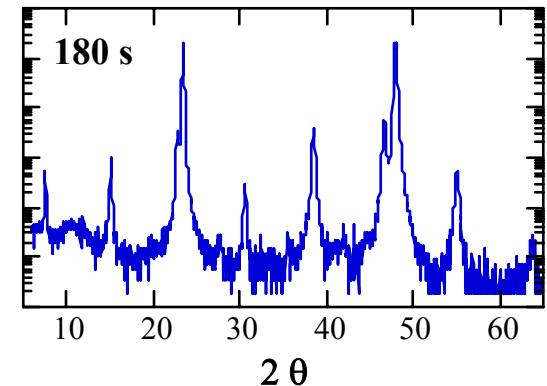
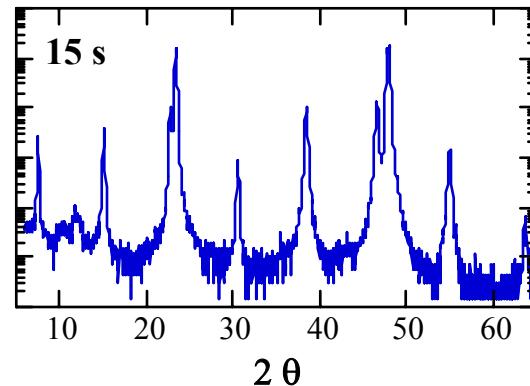
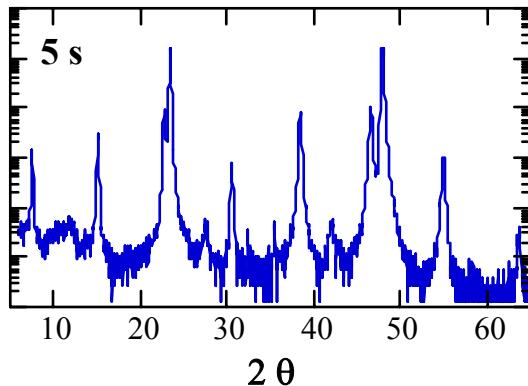
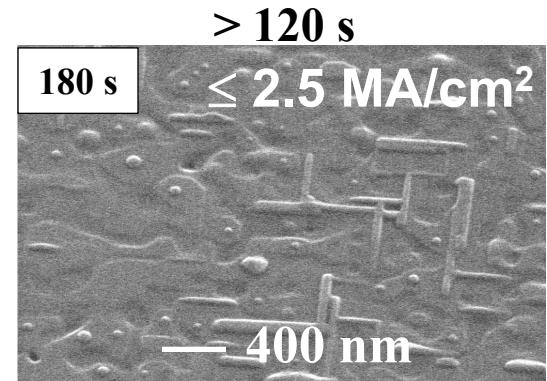
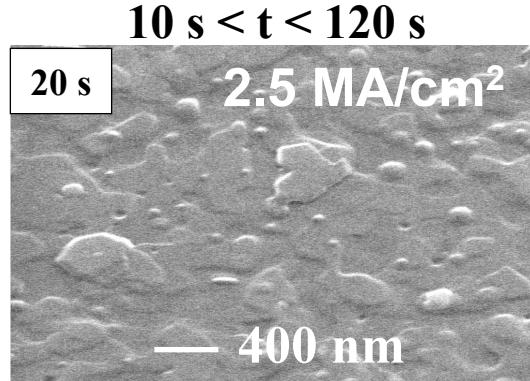
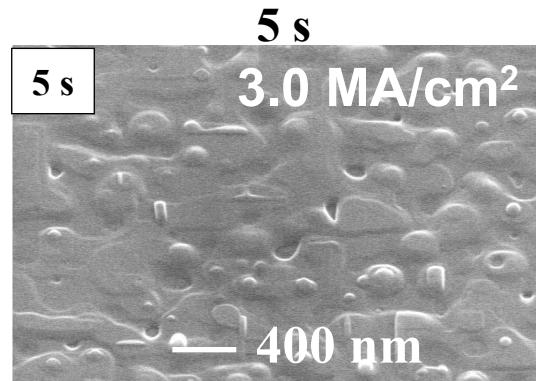


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Morphology and Phase Development of DEA-YBCO Films on LaAlO₃

A broad pyrolysis time window exists between 10 and 120 seconds @ 325 °C.



High J_c but voids and
secondary phases
(→ Incomplete pyrolysis?)

Good morphology
Excellent *c*-axis
alignment

a-axis grain onset

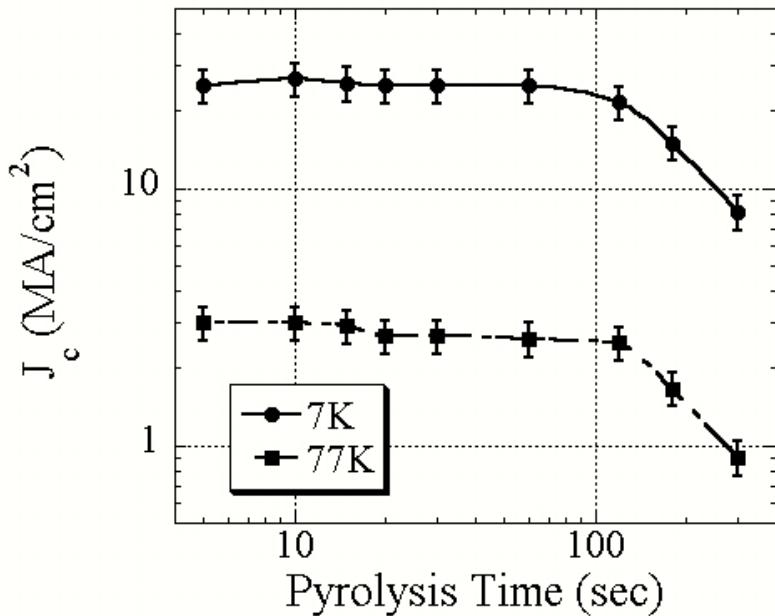


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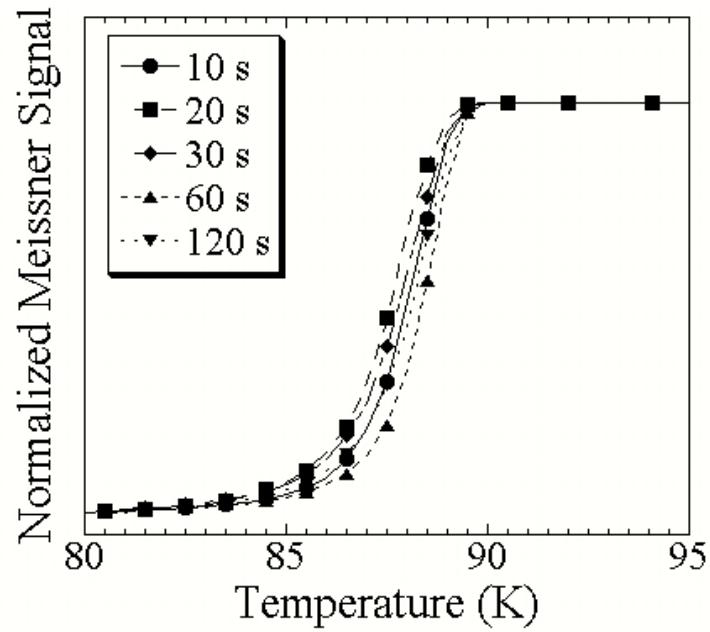
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Film Properties vs. Pyrolysis Time

J_c (77 K) > 2.5 MA/cm² for films within the optimized window.

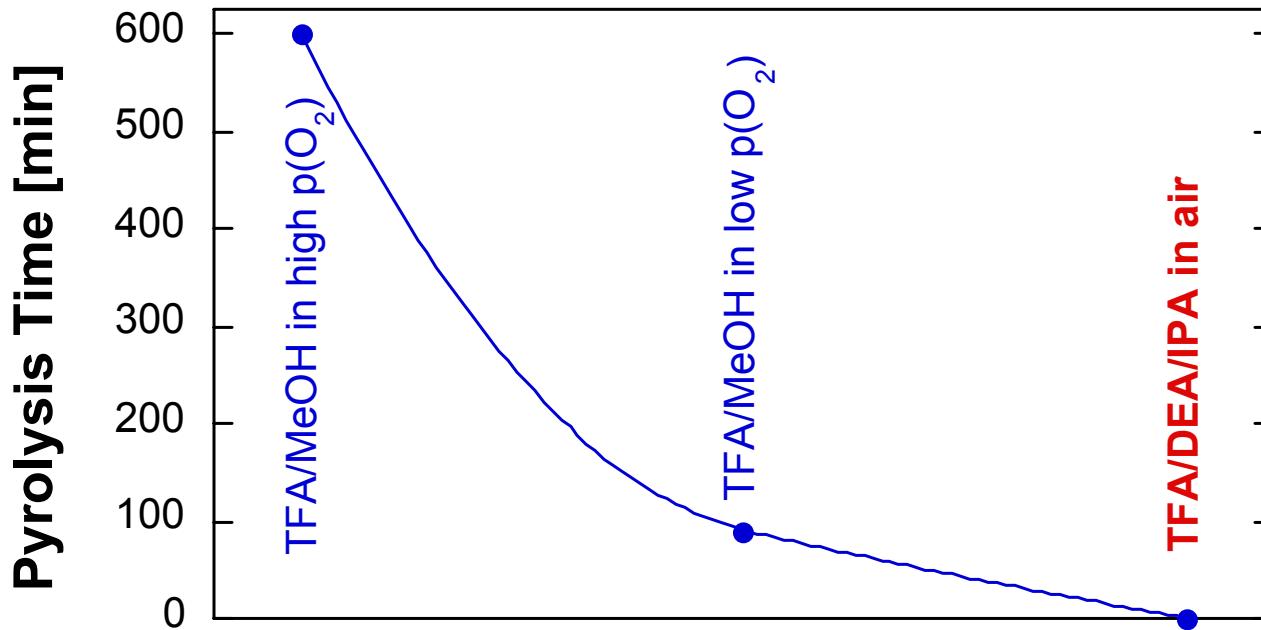


T_c is similar (89K) for films within the optimized window.



Benefit of New DEA-YBCO Chemistry

Pyrolysis time reduced from >1 hour → 20 seconds



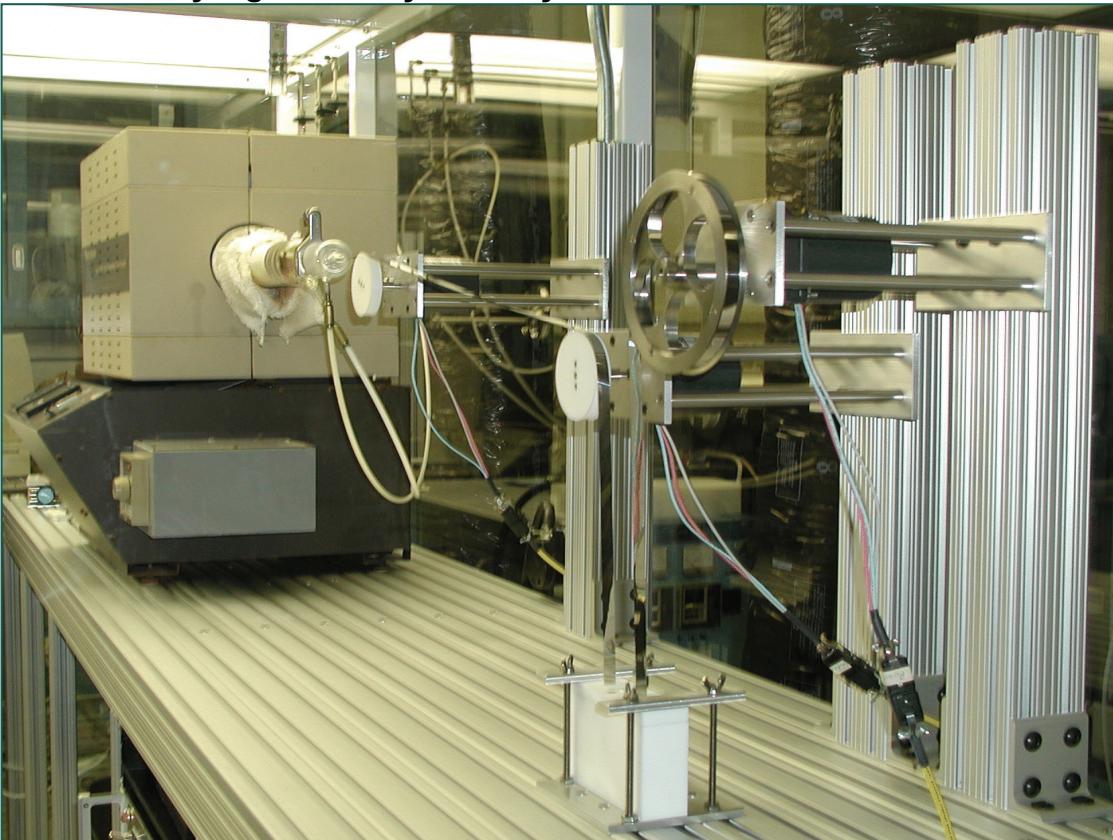
Both coating speed and pyrolysis of “SanDEA” YBCO precursors are now non-factors for chemical solution deposition methods

Furnace length needed for dip coating at 2.5 cm/s (790 km/y)

1 hour pyrolysis: *90 meters*
20 second pyrolysis: 50 cm

Continuous dip coating of SanDEA-YBCO on RABiTs at ORNL's ACCI

T. Aytug, S. Sathyamurthy, F. A. List, M. Paranthaman



Reel to reel, continuous dip coating at 90 m/h (2.5 cm/s)

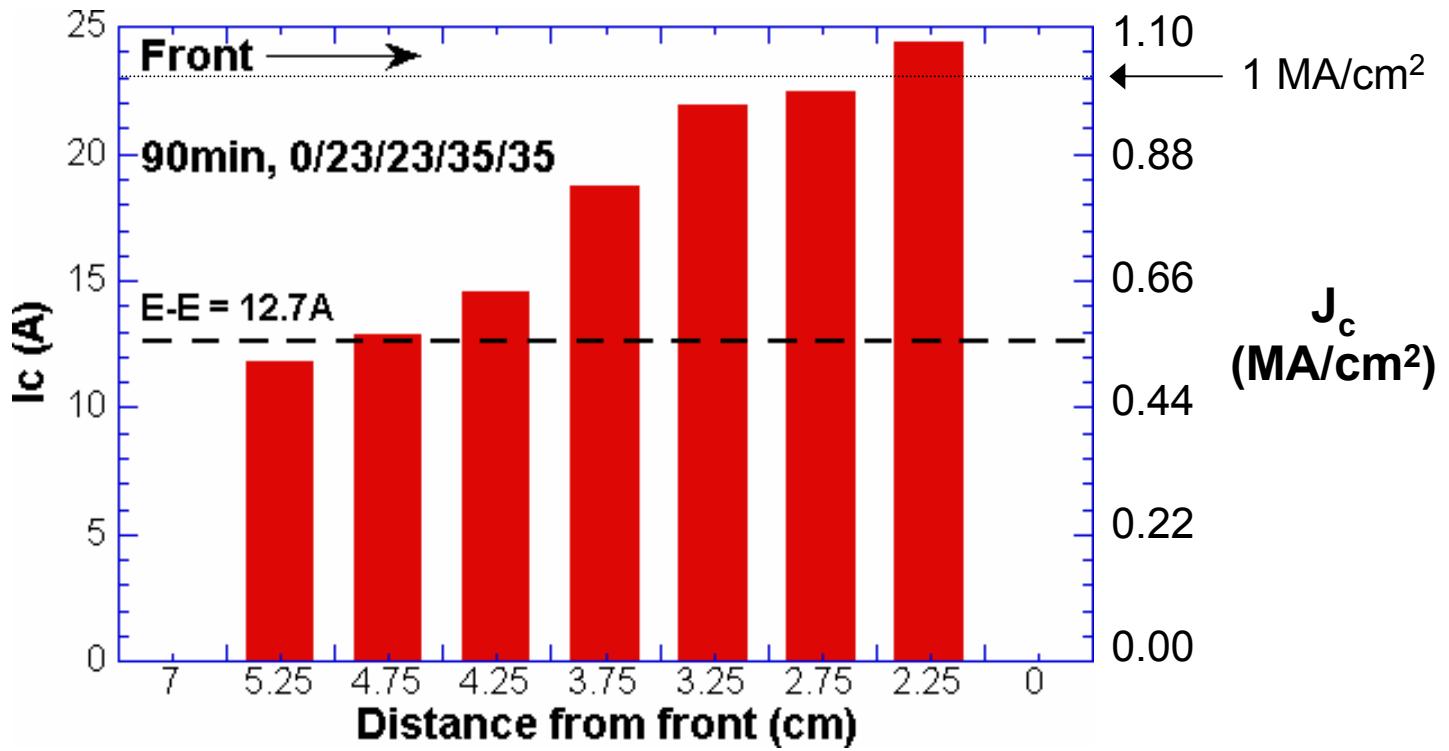
Continuous pyrolysis of 20 seconds in 50 cm hot zone

1 meter of YBCO precursor: 40 seconds

Meter Length Conversion of YBCO

D. Lee, M. Paranthaman (ORNL), J. Dawley, P. Clem (SNL)

3 meters of $0.23\mu\text{m}$ and $0.5\mu\text{m}$ SanDEA YBCO
continuously coated at ORNL on RABiTS.



Initial sample conversion J_c (77 K) = 1.06 MA/cm 2

End-to-end J_c = 0.55 MA/cm 2

Best static J_c = 1.2 MA/cm 2 on CeO $_2$ /YSZ/Y $_2$ O $_3$ /Ni-W

ORNL Thick Film Conversion of SanDEA YBCO

Two methods investigated for thicker ($\rightarrow 2 \mu\text{m}$) YBCO:

- 1) Thicker single layer precursors (0.25 μm , 0.5 μm , 0.75 μm)
- 2) Multilayering (multipyrolysis, single crystallization)

Single layer thickness processes developed to date:

<u>composition</u>	<u>thickness</u>	<u>best Jc</u>	<u>best Ic</u>
SanDEA 25	0.23 μm	1.2 MA/cm ²	25 A/cm
2x SanDEA 25	0.5 μm	1.1 MA/cm ²	55 A/cm
SanDEA 75	0.7 μm	0.58 MA/cm ²	41 A/cm
3x SanDEA 75	2.1 μm	under test	under test

Key questions:

- Can pyrolysis furnace design be improved?
- What are optimum conversion conditions for TFA YBCO?
- Are kinetics the same as for evaporated BaF₂ YBCO?

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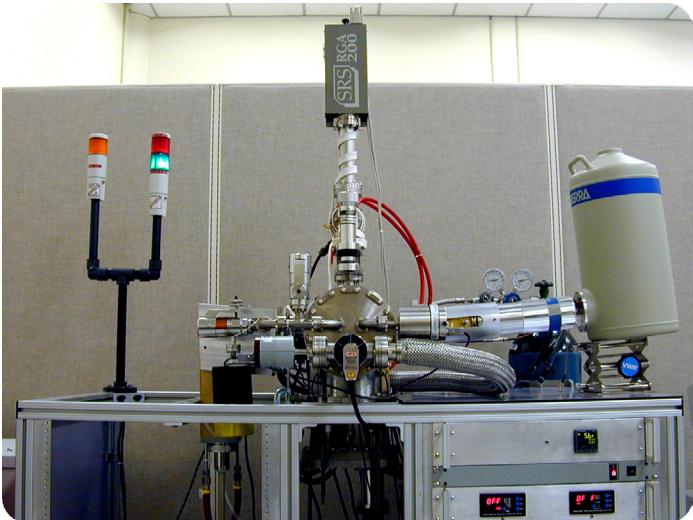
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TFA precursor conversion has been conducted in each of three conversion systems.

Low-Pressure System

$P_{\text{total}} \sim 0.1 \text{ Torr}$
in-situ XRD



Atmospheric Pressure System

$P_{\text{total}} \sim 1000 \text{ Torr}$
reel-to-reel



Reduced-Pressure System

$P_{\text{total}} \sim 100 \text{ Torr}$
variable gas flow

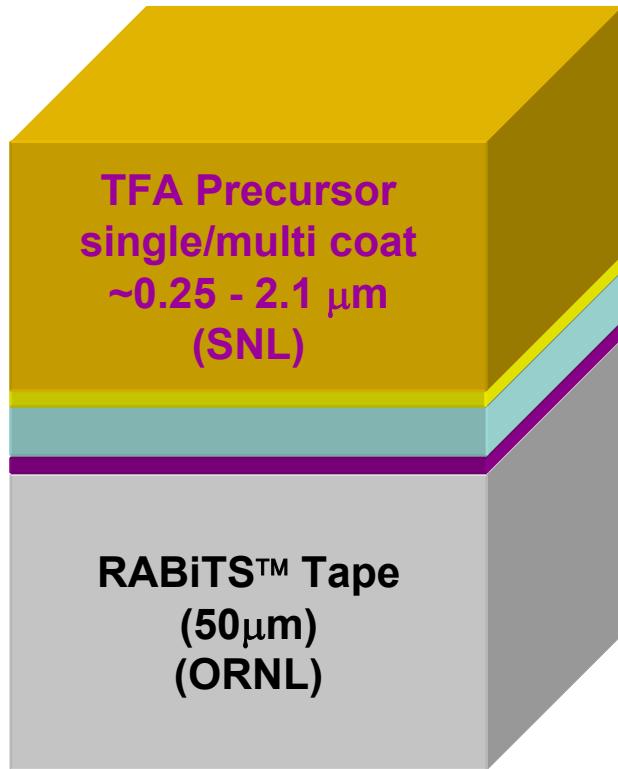


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For conversion studies, TFA precursors were compared to those deposited by e-beam co-evaporation (PVD).

~ 40 TFA samples



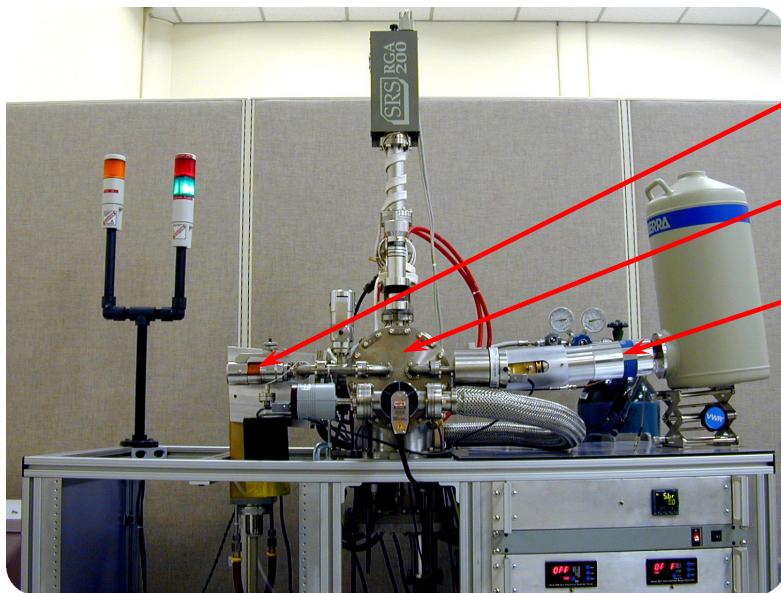
109 PVD samples



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The low-pressure conversion system is equipped with *in-situ* x-ray diffraction to follow crystalline phase development .



Low-Pressure Conversion System

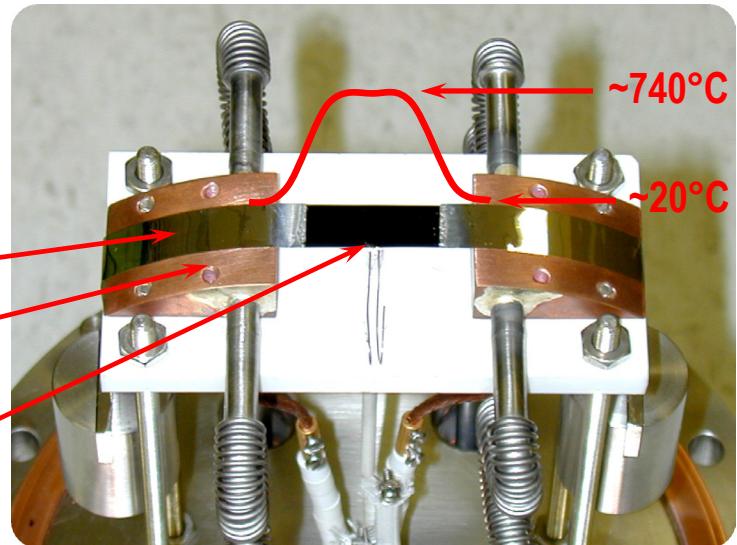
Nickel Leader
Water Cooled Cu Electrode
Precursor Sample (1x3 cm)

X-ray Source

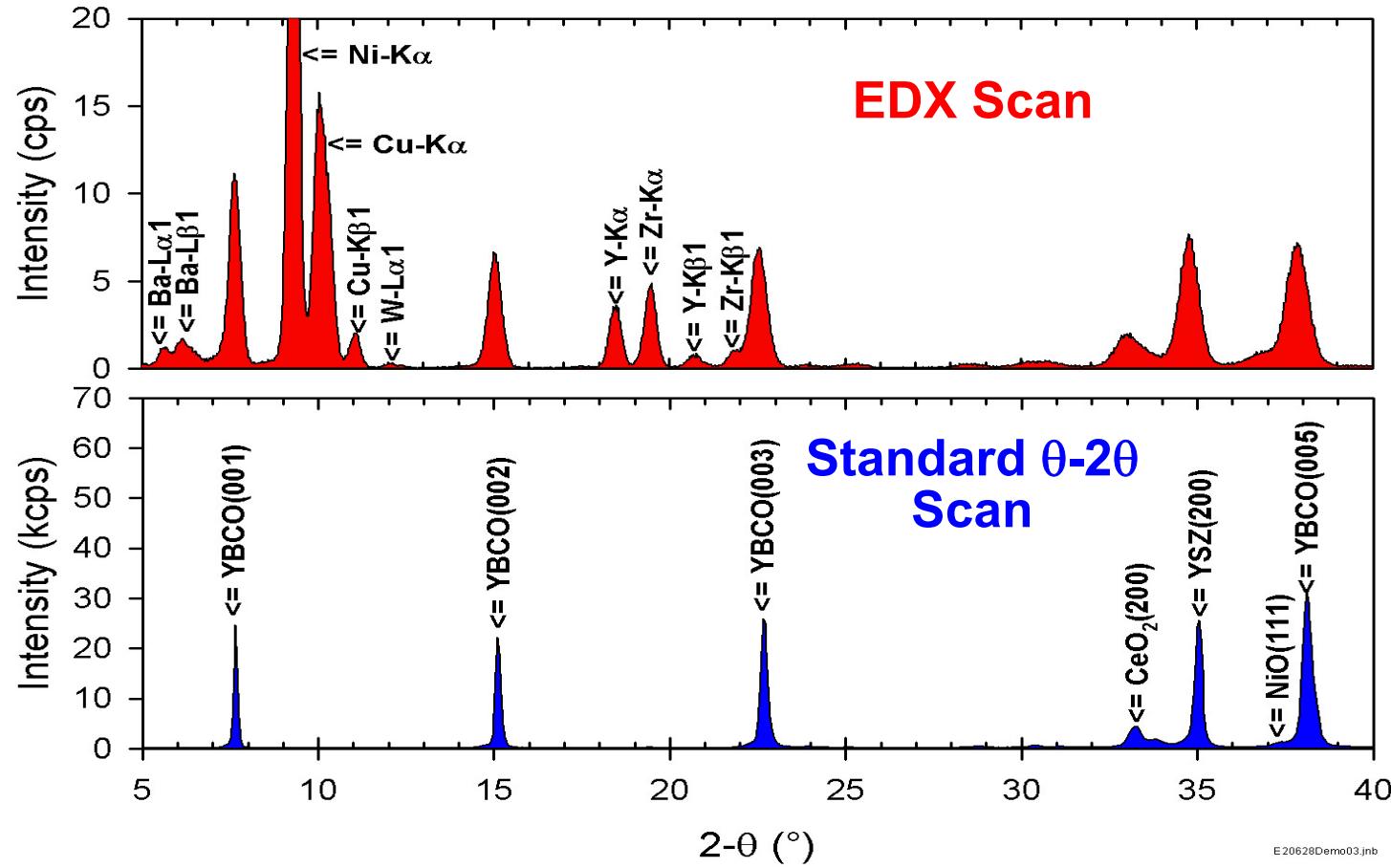
Reaction Chamber (5×10^{-8} Torr base)

X-ray Detector

Sample Holder



X-ray data is collected using an energy dispersive detector at rates up to ~4 scans/min.



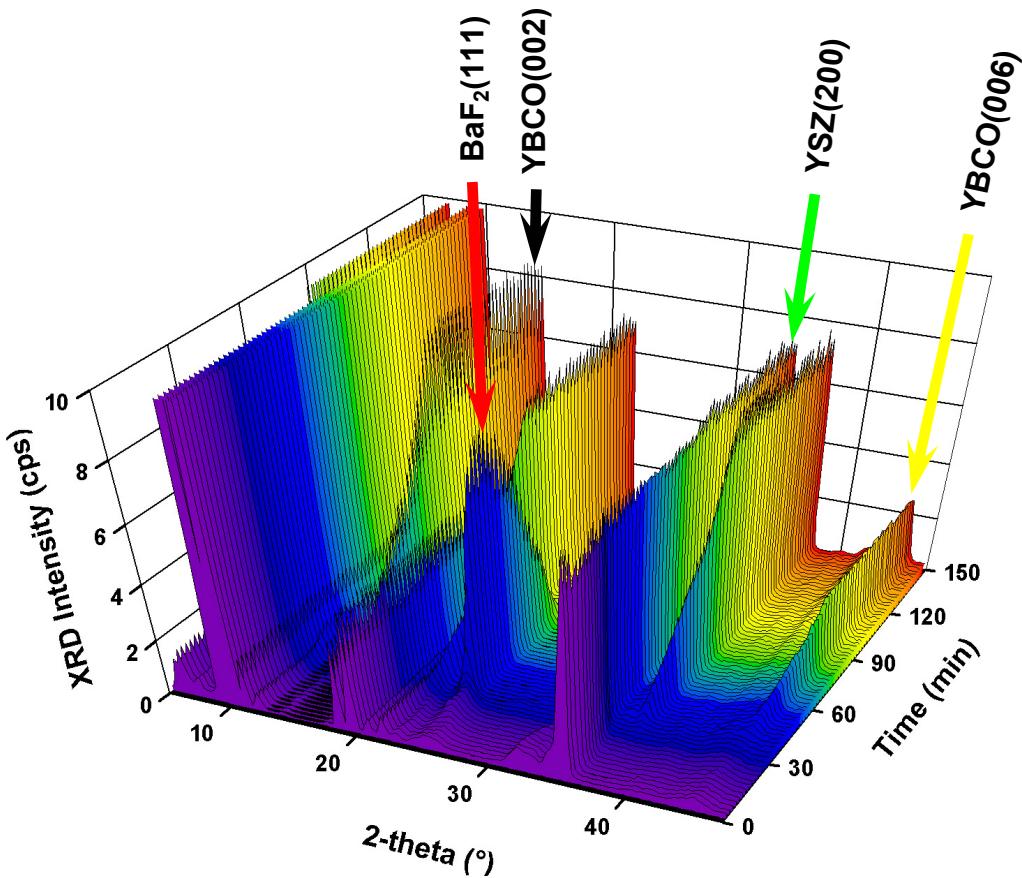
E20628Demo03.inb



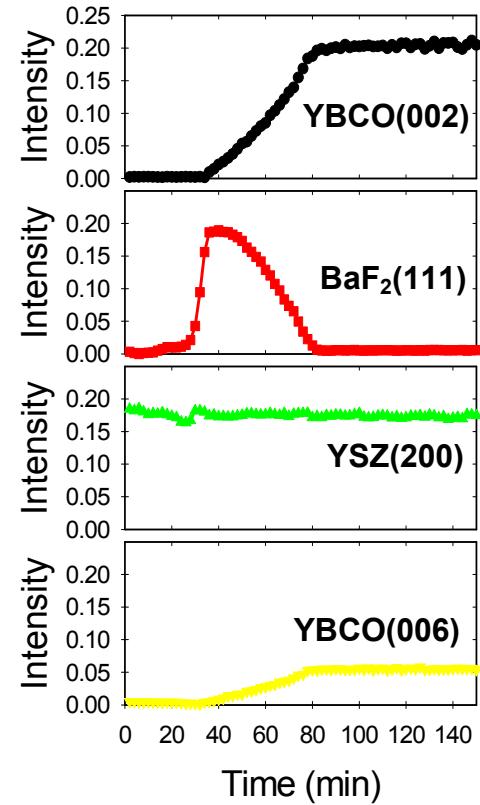
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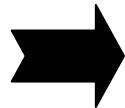
From a family of scans, peak scans are generated for specific crystalline phases.



Family of Scans



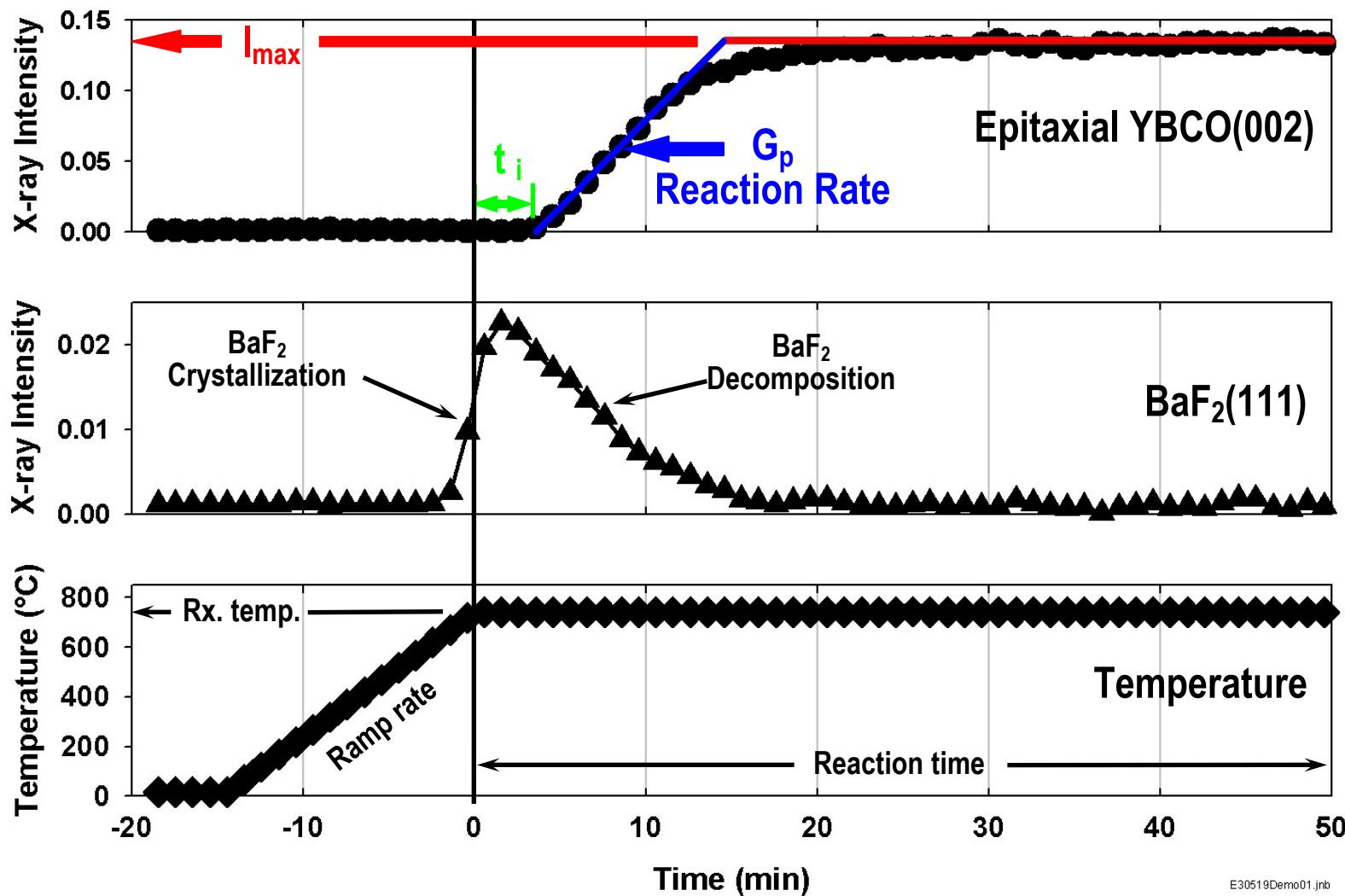
Peak Scans



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From peak scans, details of conversion kinetics are determined.

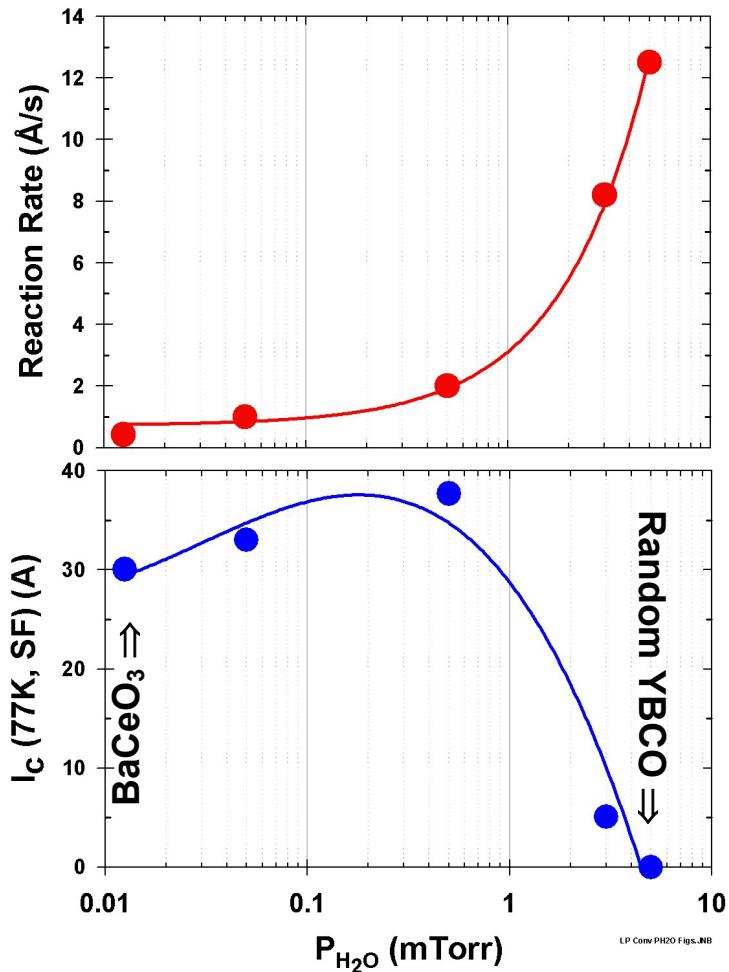
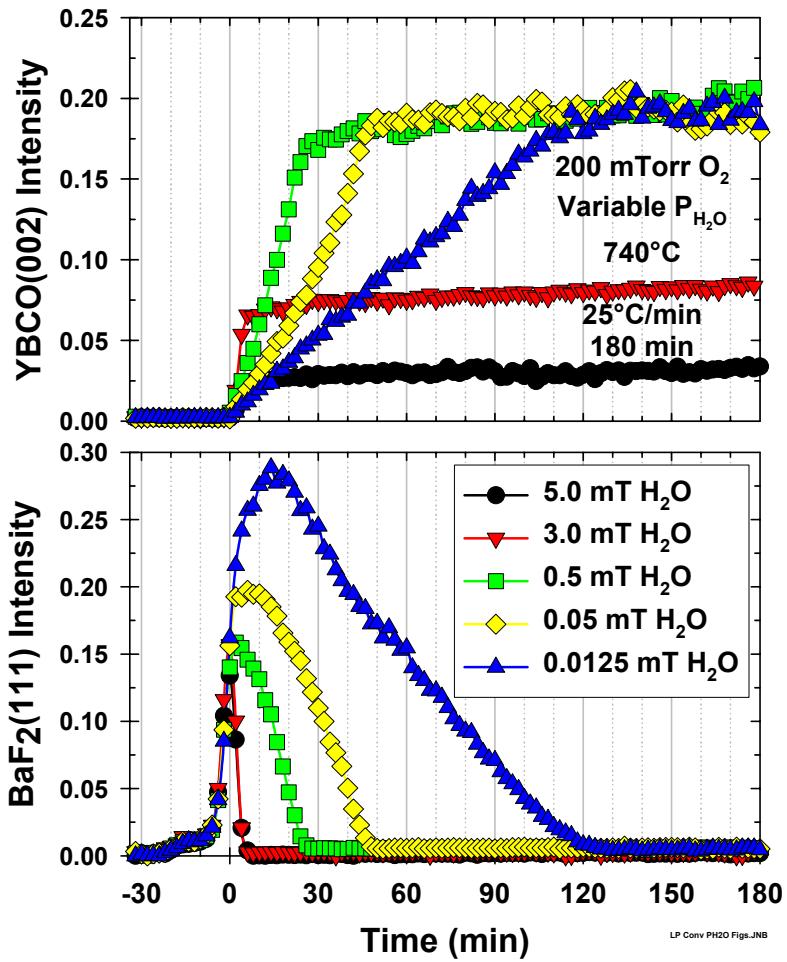


E30519Demo01.jnb

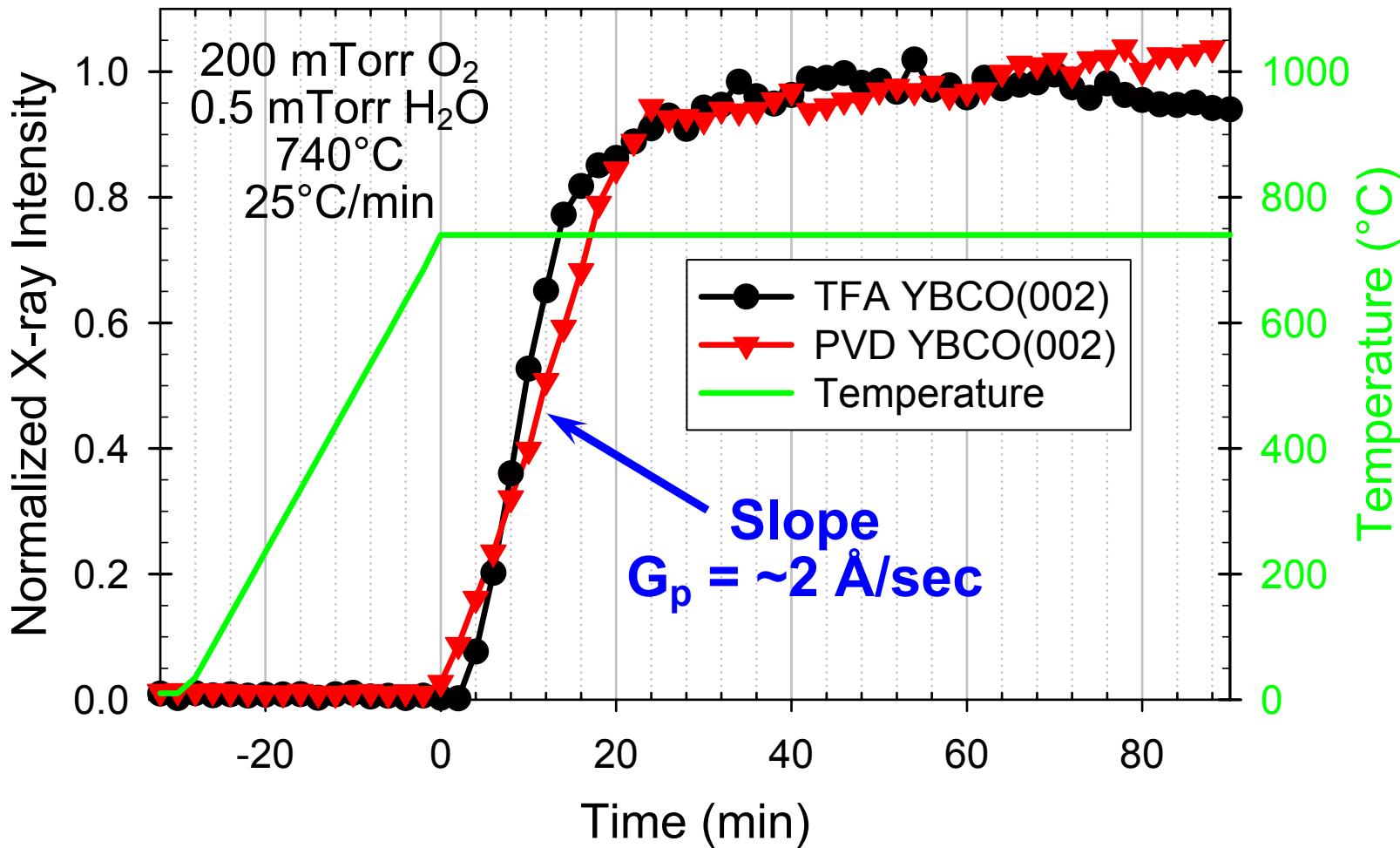
Low-pressure conversions of precursor have been conducted for a range of process parameters.

- Oxygen partial pressures (P_{O_2}) $1 \Leftrightarrow 1000$ mTorr
- Water partial pressure (P_{H_2O}) $0.01 \Leftrightarrow 300$ mTorr
- Reaction temperature $620 \Leftrightarrow 820$ °C
- Ramp rate $0.5 \Leftrightarrow 1000$ °C/min
- Reaction time $2 \Leftrightarrow 480$ min

The reaction rate (G_p) for thin (~0.3 μm) PVD precursor increases with $P_{\text{H}_2\text{O}}$.



For conversion conditions optimized for thin PVD precursor, G_p is similar for TFA and PVD precursors.

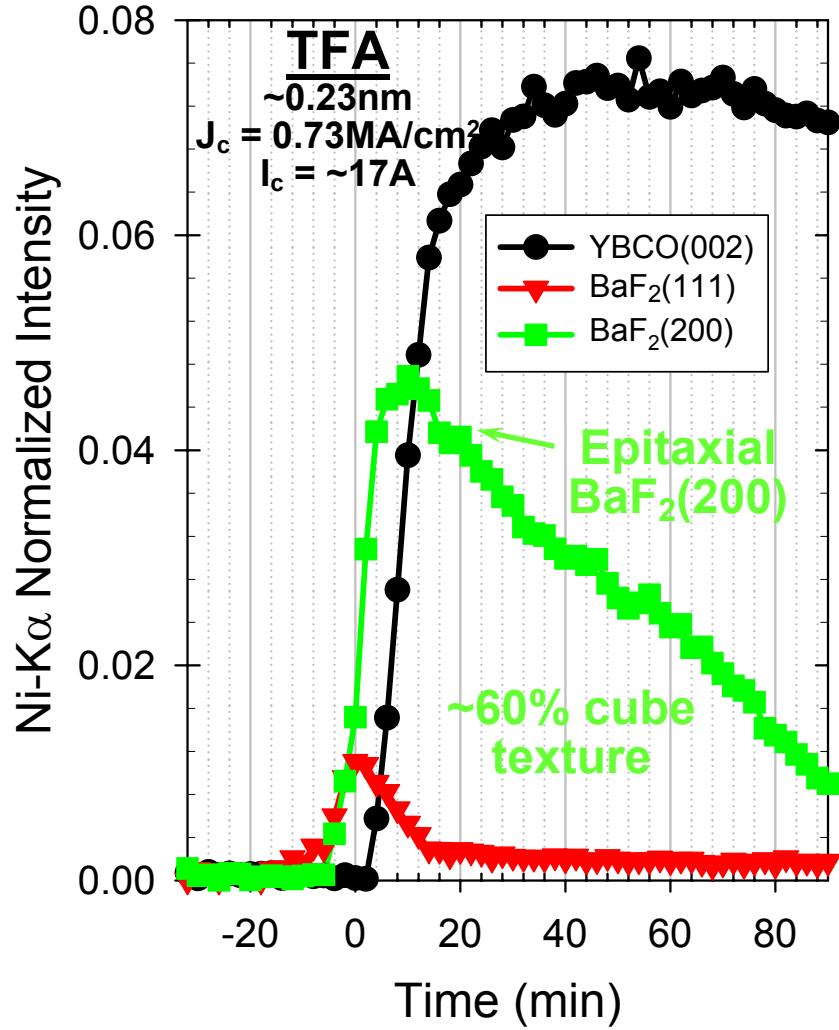
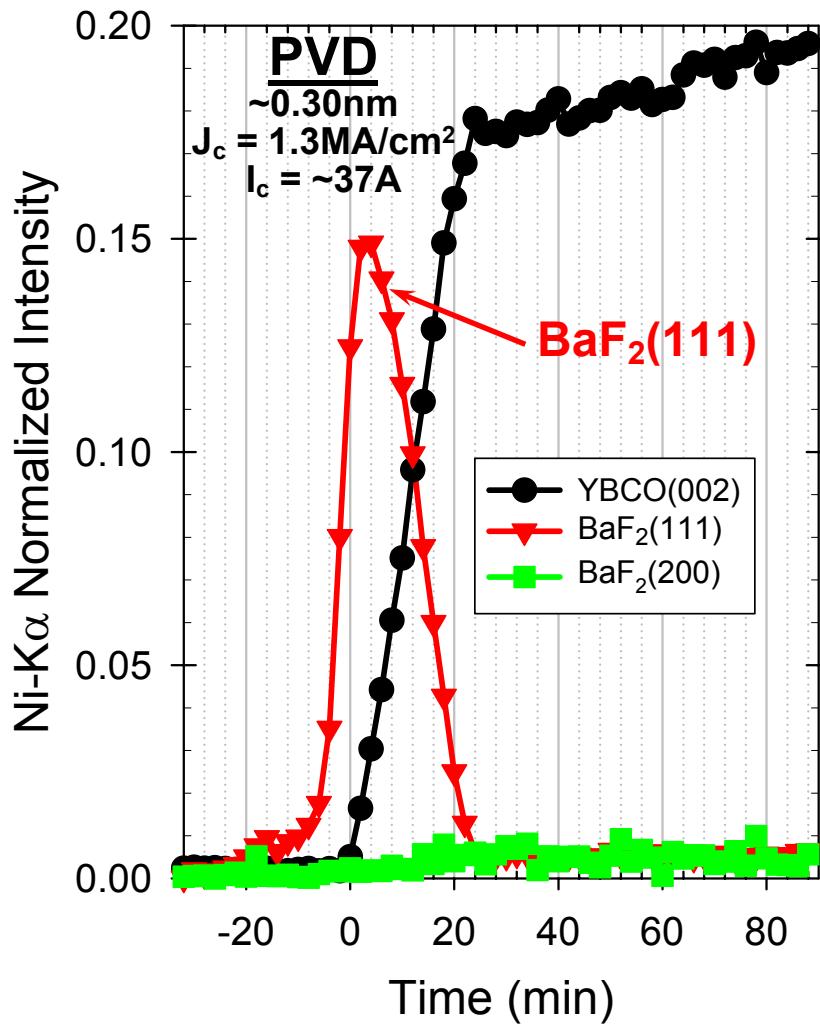


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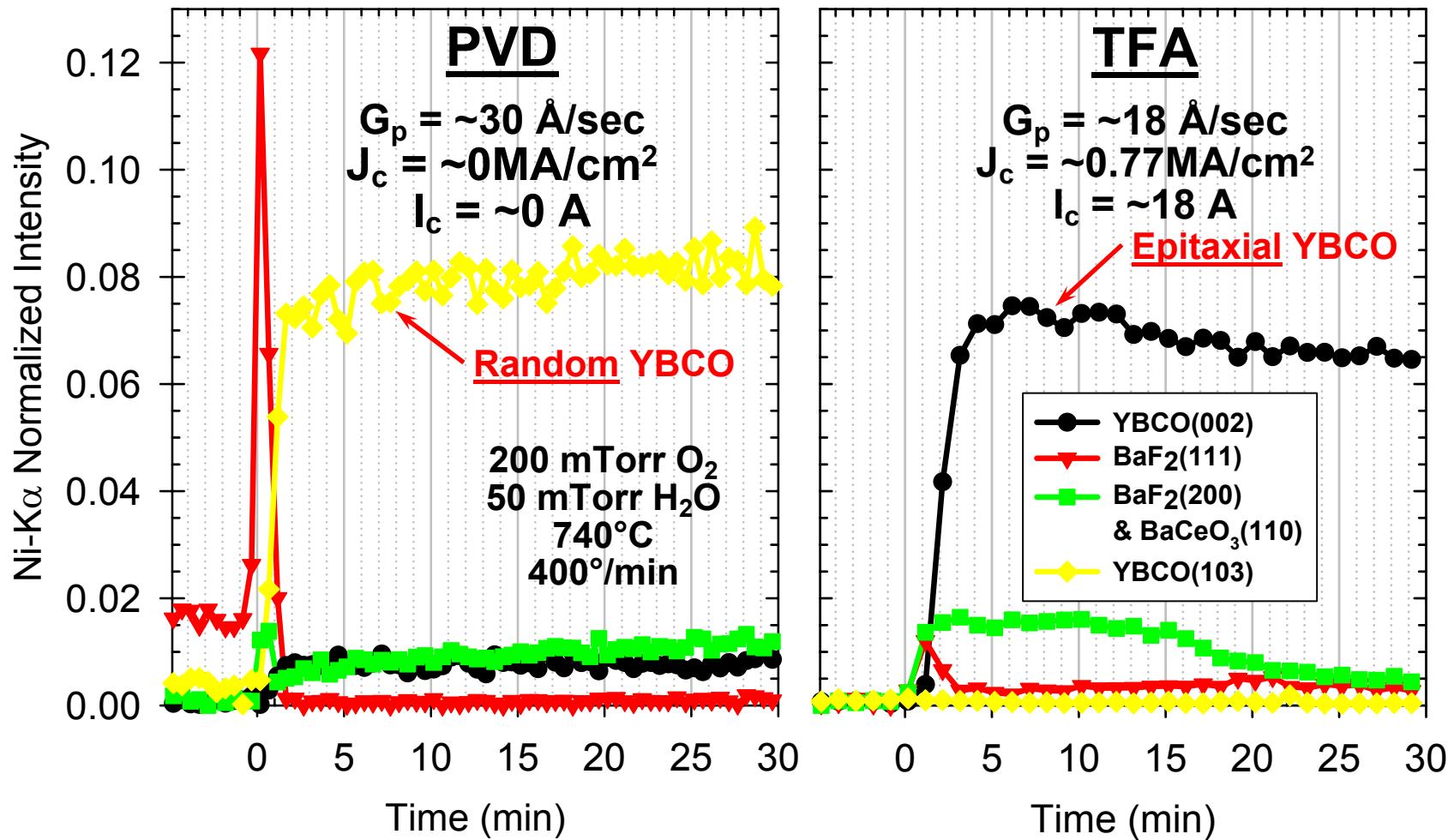
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However, crystalline phase development is distinctly different for PVD and TFA precursors.



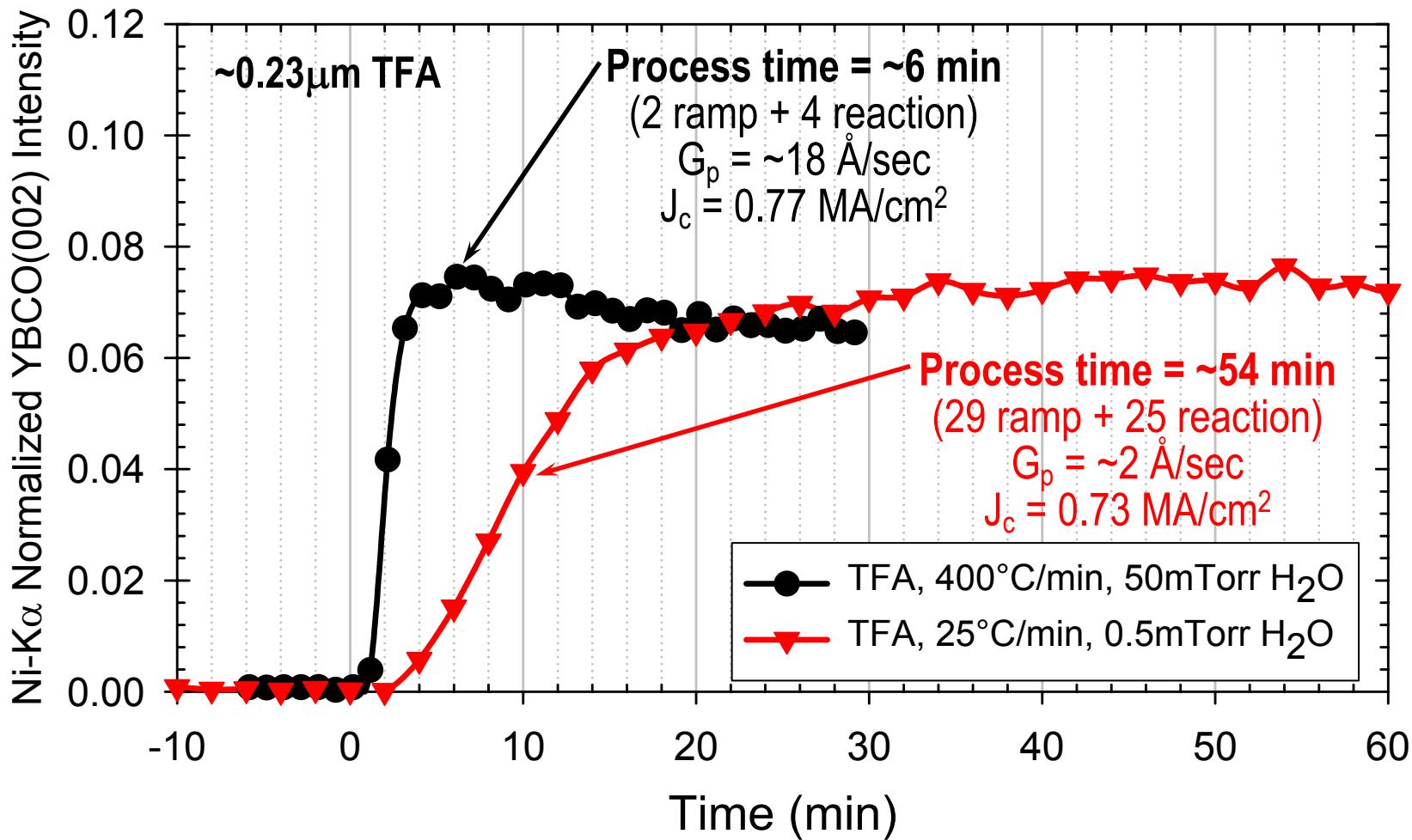
Higher G_p 's for both PVD and TFA precursors are obtained using higher P_{H_2O} & higher ramp rate.



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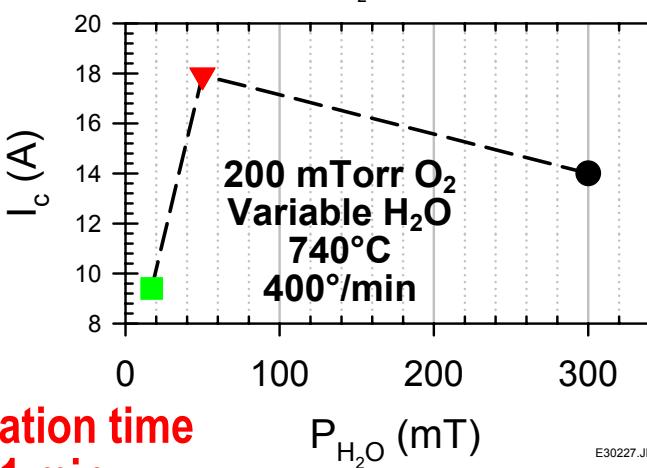
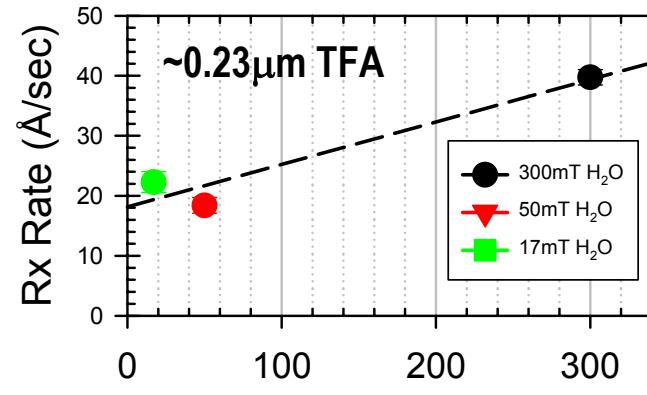
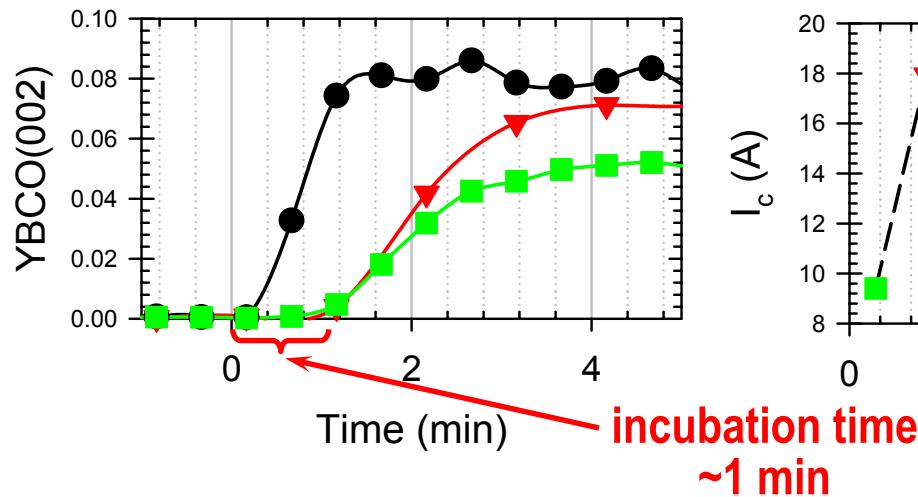
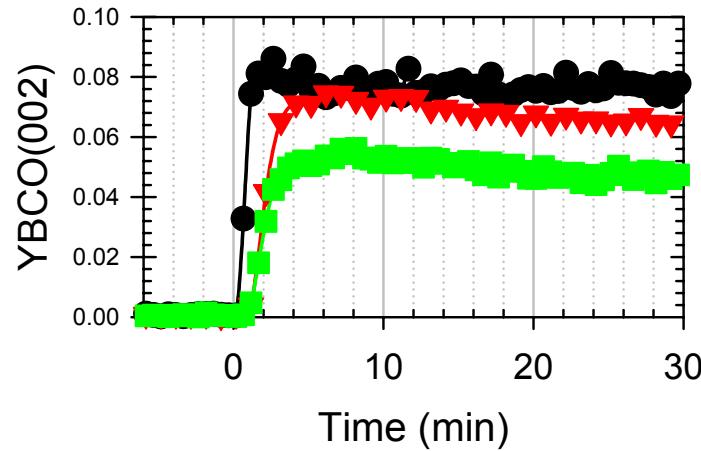
Shorter process times (~9x) are possible for TFA precursor using higher P_{H_2O} & ramp rate.



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TFA precursor reaction rates as high as 40 Å/sec have been observed for high P_{H_2O} .



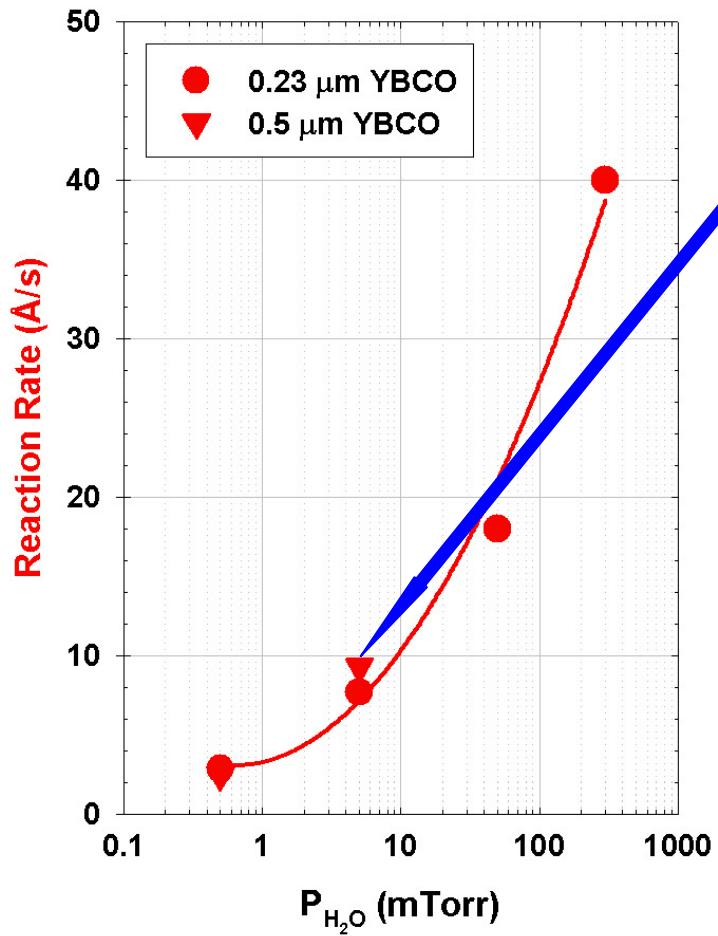
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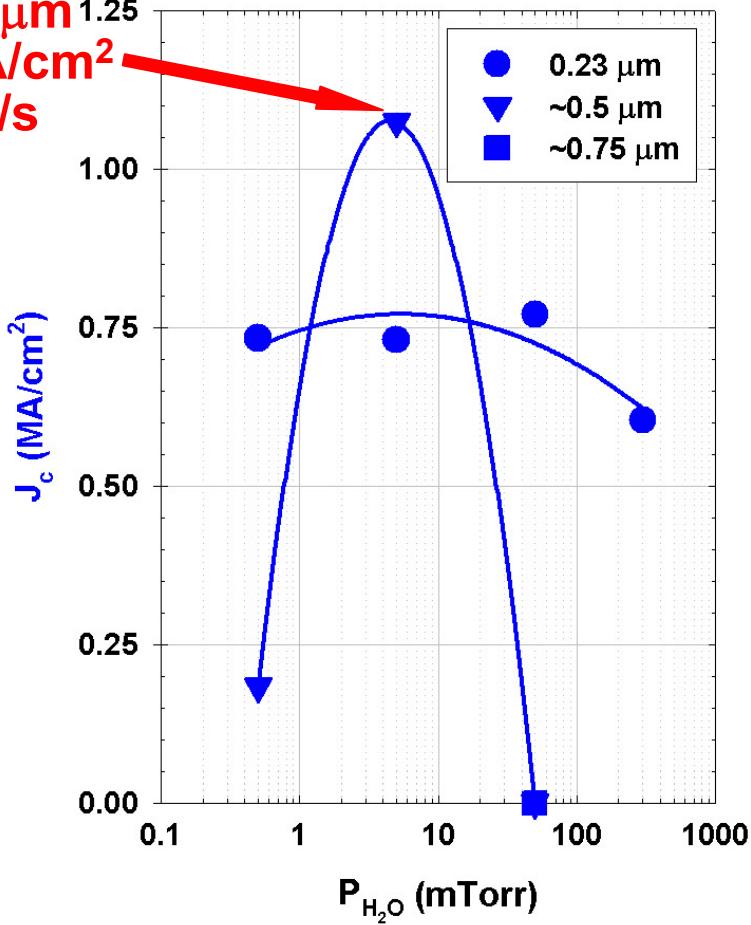
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Rapid conversion to high performance YBCO has been achieved for thicker TFA precursor.



~0.5 µm
1.1 MA/cm²
9 Å/s



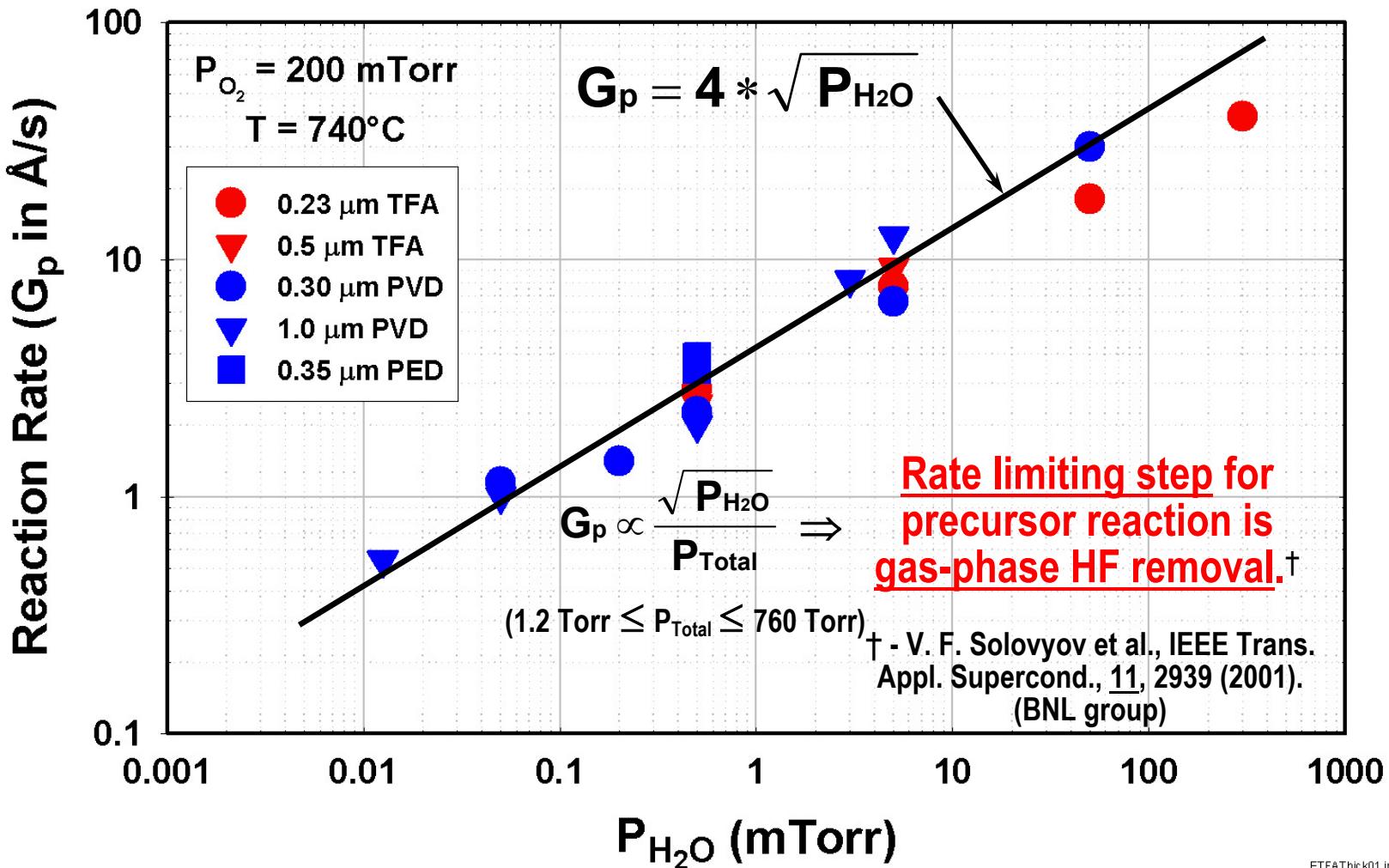
ETFA Thick01.jnb



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The rate at which precursor reacts is independent of both precursor type and precursor thickness .



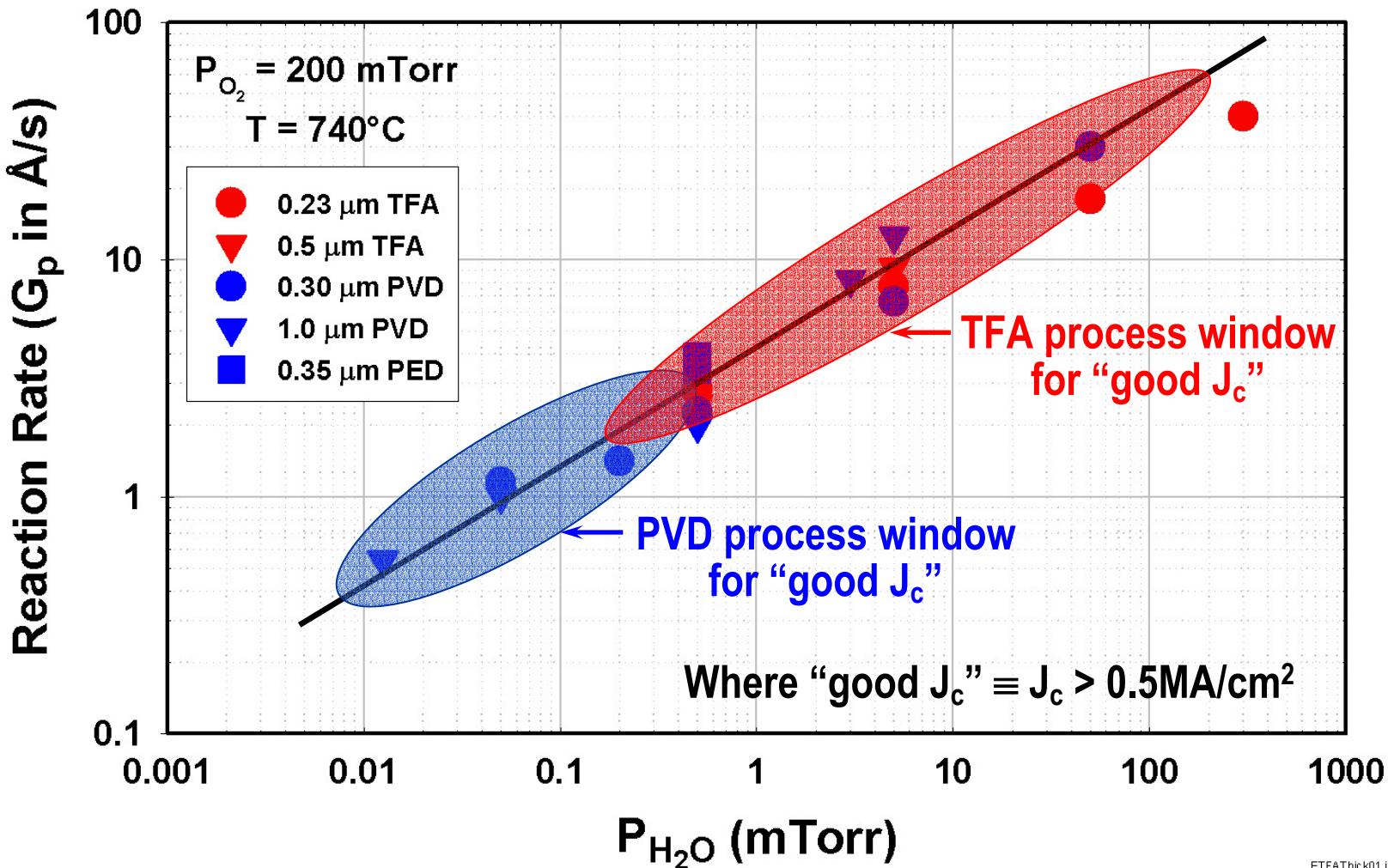
ETFAThick01.jnb



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However, the critical current is dependent on both the precursor type and precursor thickness.



ETFAThick01.jnb



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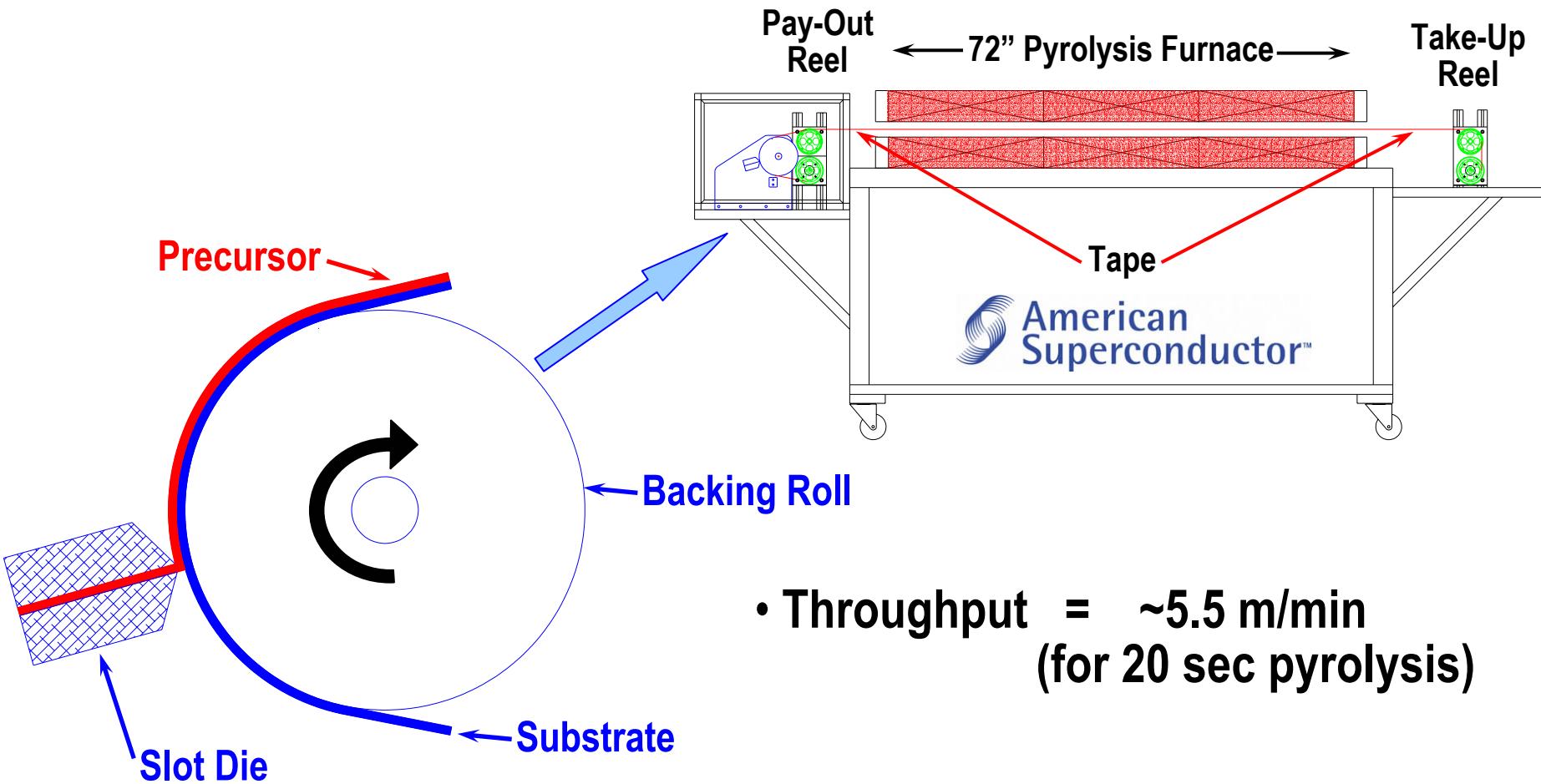
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TFA precursor conversion results[†] in reduced and atmospheric pressure systems are promising.

Thickness	Coats	P _{total}	P _{O₂}	P _{H₂O}	T _{max}	Rate	Time	I _c (A)	J _c (MA/cm ²)
0.23 μm	1	0.1 atm	150 mTorr	7 Torr	730°C	25°C/m	30 m	24.18	1.05
0.69 μm	3	1.5 atm	135 mTorr	3-35 Torr	740°C	25°C/m	180 m	27.23	0.57
0.7 μm	1	1.5 atm	135 mTorr	3-35 Torr	740°C	25°C/m	180 m	18.73	0.58
1.4 μm	2	1.35 atm	200 mTorr	3-35 Torr	740-765°C	13°C/m	300 m	12.27	0.13
1.4 μm	2	1.35 atm	200 mTorr	3-35 Torr	740-765°C	25°C/m	300 m	12.27	0.17
2.1 μm	3	1.5 atm	135 mTorr	3-35 Torr	740°C	25°C/m	315 m	N/D	N/D

[†] - for conversion conditions optimized to PVD precursors

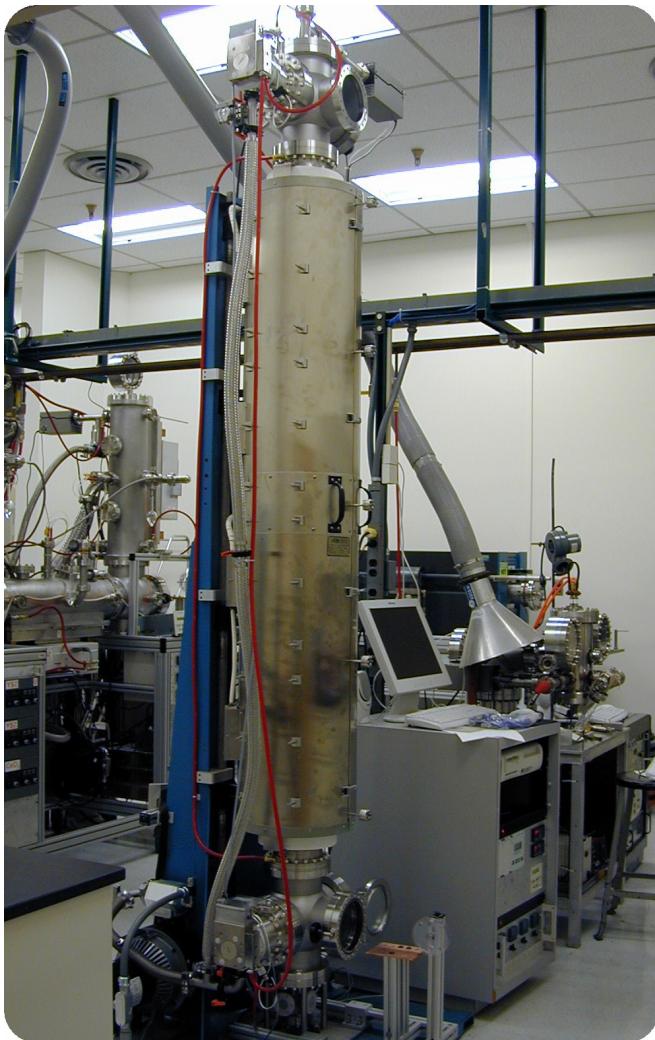
A slot die coater has been jointly designed and is being constructed at ORNL for continuous deposition of solution precursors.



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A vertical reel-to-reel vacuum furnace is being tested at ORNL for continuous conversion of precursor.



- 4-zone, 2-meter furnace
- $P_{\text{base}} \approx 1 \times 10^{-6}$ Torr
- $P_{\text{total}} \leq 1$ Torr
- Capacity ≈ 40 meters
- Throughput :
 - ~ 10 m/hr (0.5 μ m TFA)
 - ~ 2 m hr (0.5 μ m PVD)



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FY2003 Performance Summary

- ✓ Develop rapid solvent pyrolysis for the TFA-YBCO dip-coating process (**successful 20-second pyrolysis on LAO & RABiTS**)
- ✓ Demonstrate continuous dip coating and solvent pyrolysis for meter length tapes (**3-m length at 90 m/h, 1 MA/cm² demonstrated**)
- ✓ Investigate the conversion of precursor films for a wide range of pressure (**200 mTorr to 1.5 atm**)
- ✓ Attempt to increase YBCO film thickness on RABiTS substrates toward 2 μ m (**54 A/cm-width, 2-coat, ~0.5 μ m thick, 1.1 MA/cm²**)
- ✓ 1.4 μ m and 2.1 μ m YBCO deposition/rapid pyrolysis processes developed; conversion process under investigation.

FY2004 Plans

- Continue development of instant pyrolysis toward 2 μm films with emphasis on Y:Ba:Cu stoichiometry control
- Develop high performance (100-300 Å) conductor using thicker single layer ($\sim 1 \mu\text{m}$) and multilayer (1-3 μm) approaches
- Identify characteristics of the TFA precursor that enable rapid low-pressure conversion
- Use slot die coating system and reel-to-reel vacuum furnace to continuously deposit and convert precursor
- Collaborate to improve tape coating, continuous pyrolysis furnace design, and processing conditions

Research Integration

- SNL ⇒ experience with rapidly pyrolyzed TFA precursors.
- ORNL ⇒ experience continuous processing, thick precursor processing, and vacuum processing on RABiTS.
- AmSC ⇒ advice on design of slot die coater system.
- Buffered tapes, TFA solutions, and pyrolyzed precursor films have been routinely exchanged.
- Results and advice have been freely shared via telephone, e-mail, and personnel exchange.
- Key processing issues have been identified and addressed more rapidly at both labs as a result of this collaboration.