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Search for New Cuprate Compounds at Stanford University

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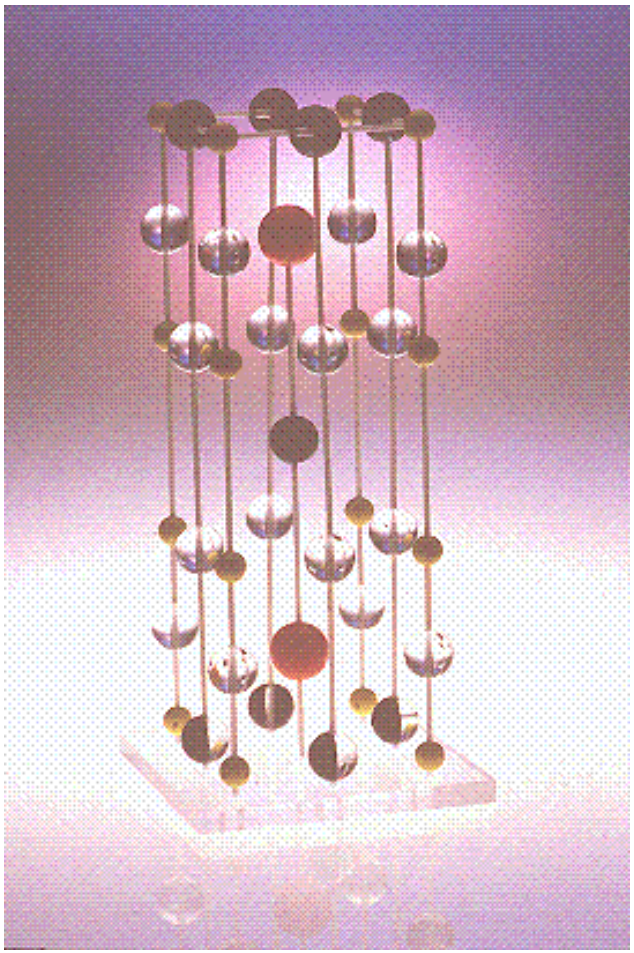
5th EPRI Superconductivity Conference & Task Force Meeting
20 - 21 September 2005, Albany, NY

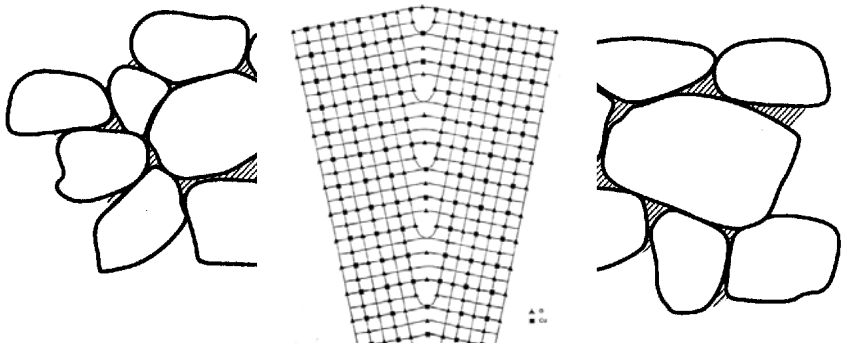
www.w2agz.com/epri-sctf5.htm

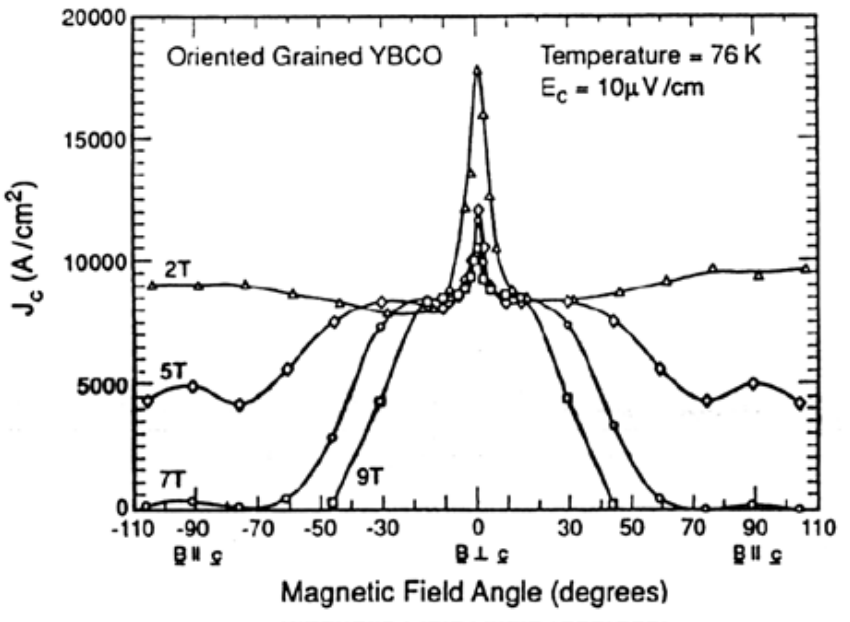
Stanford Applied Materials Team

- Ted Geballe, Emeritus Professor (discoverer of more than 100 superconductors)
- Mac Beasley, Professor of Applied Physics and former Dean of the Stanford School of Arts and Sciences (reported to Condi Rice)
- Bob Hammond, Research Professor (designed and built the GLAM MBS)
- Assisted by Gertjan Koster, Visiting Professor from the University of Twente, Hideki Yamamoto, Senior Scientist on sabbatical from the National Institute of Metals, Japan, and Wolter Siemons, PhD Candidate, Stanford and Twente Universities
- Paul Grant, Visiting Scholar in Applied Physics (Theory & Modeling)

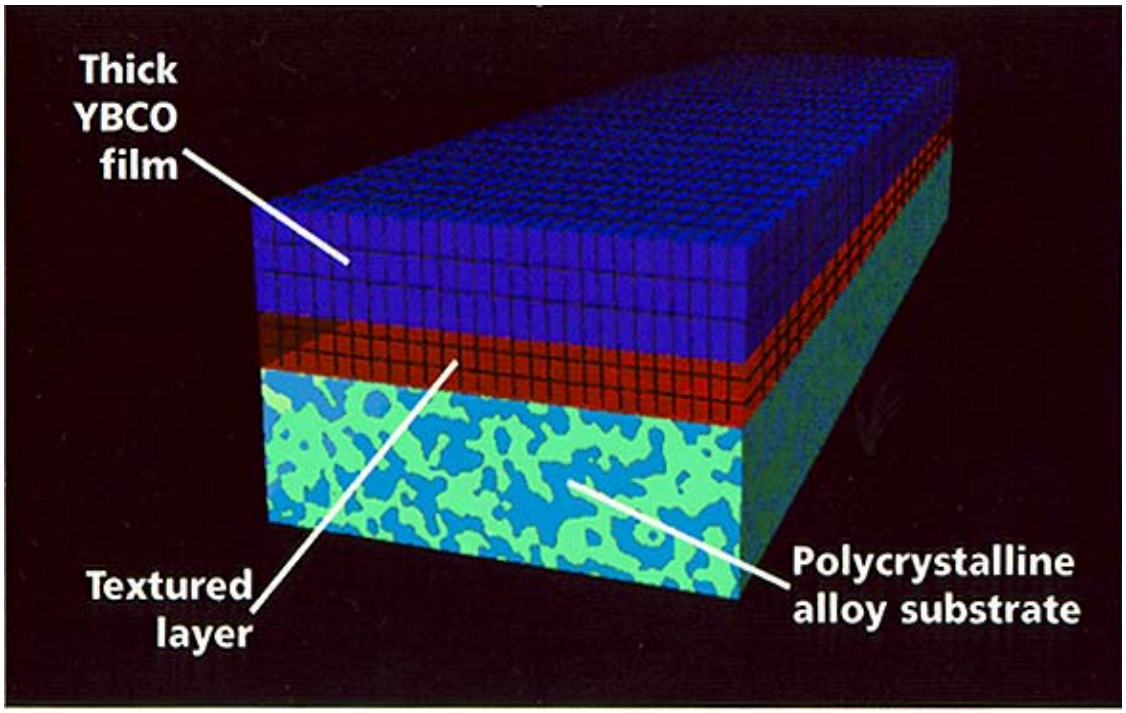
The Problem with Layered Perovskites





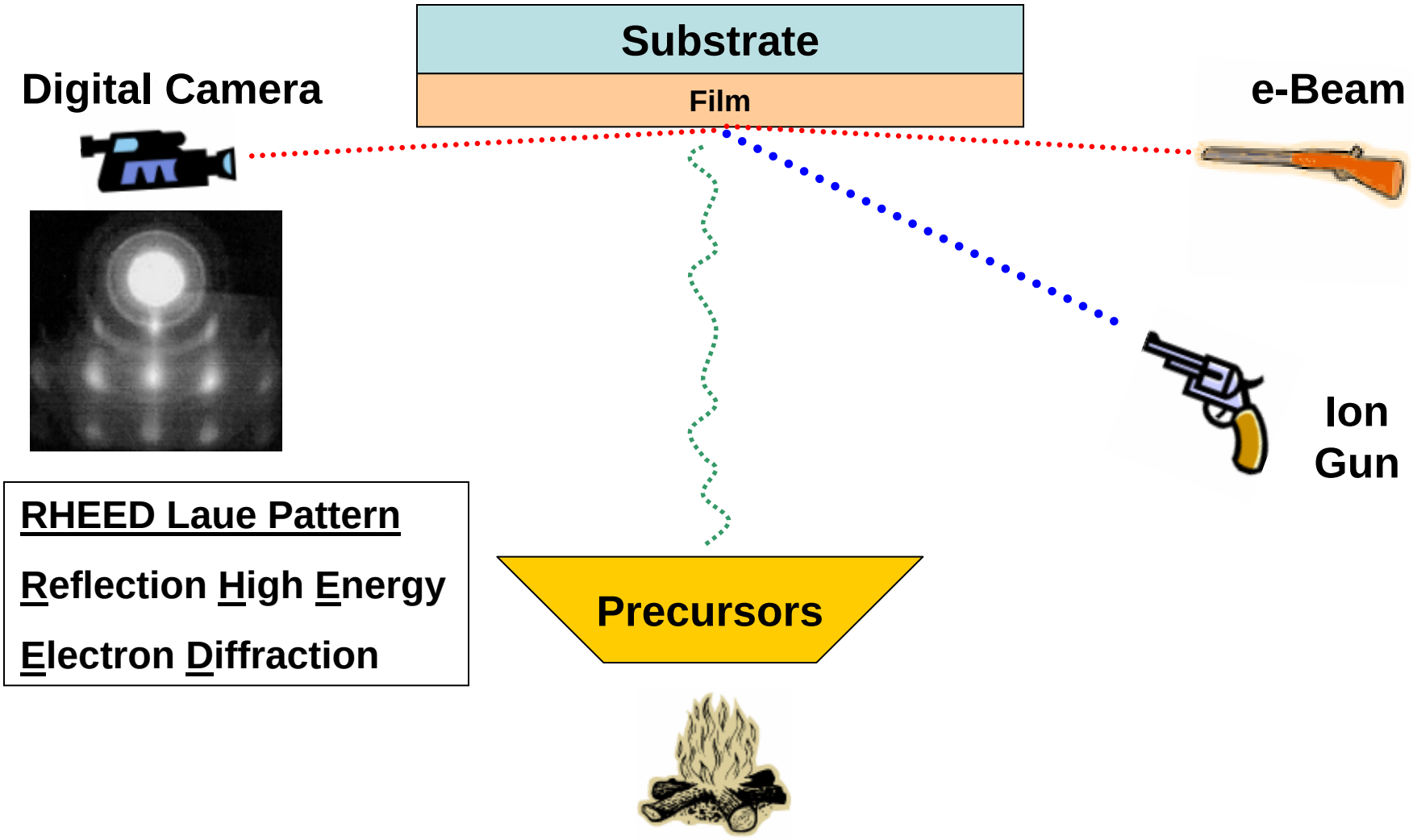


Multilayer HTSC Tape

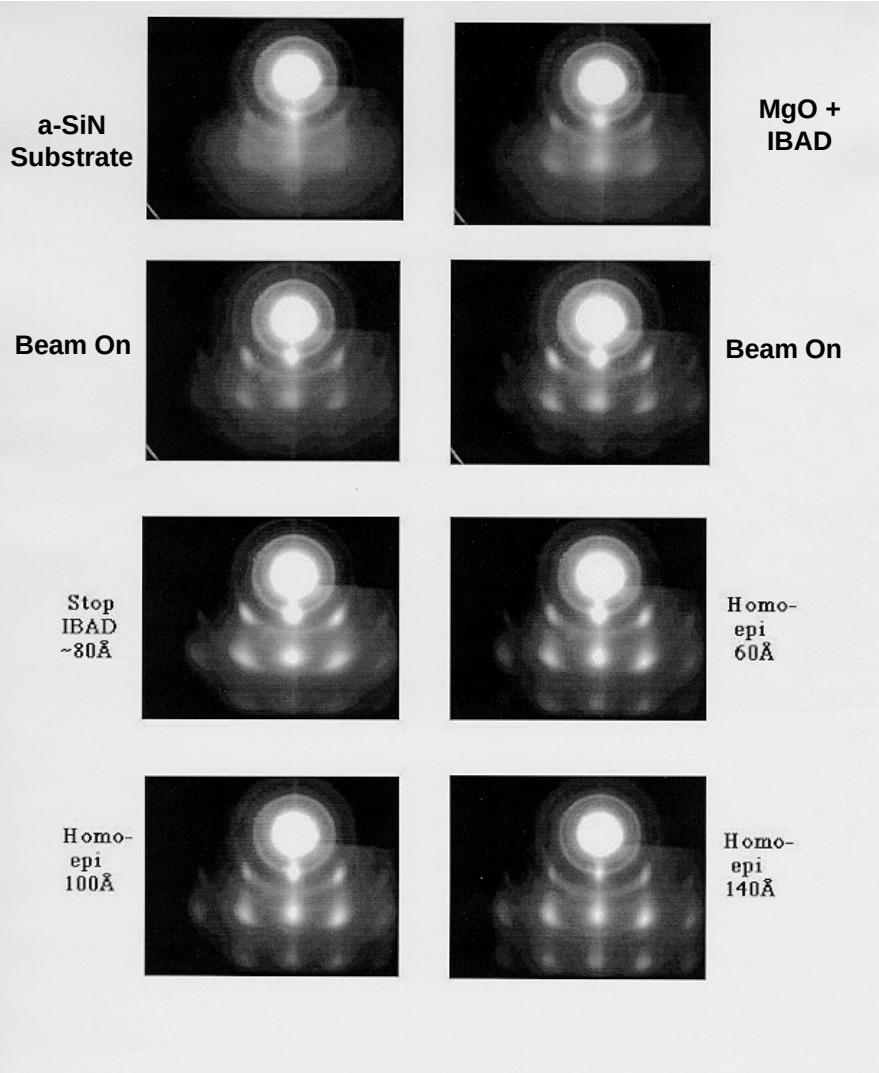


- Sumitomo Patent (filed 5/8/87 !)
- Fujikura IBAD (US Patent issued 1993)
- EPRI/Stanford IBAD – MgO (1994)
- LANL 1 MA/cm^2 (1995)

Ion-Beam Assisted Deposition (IBM, 1980)

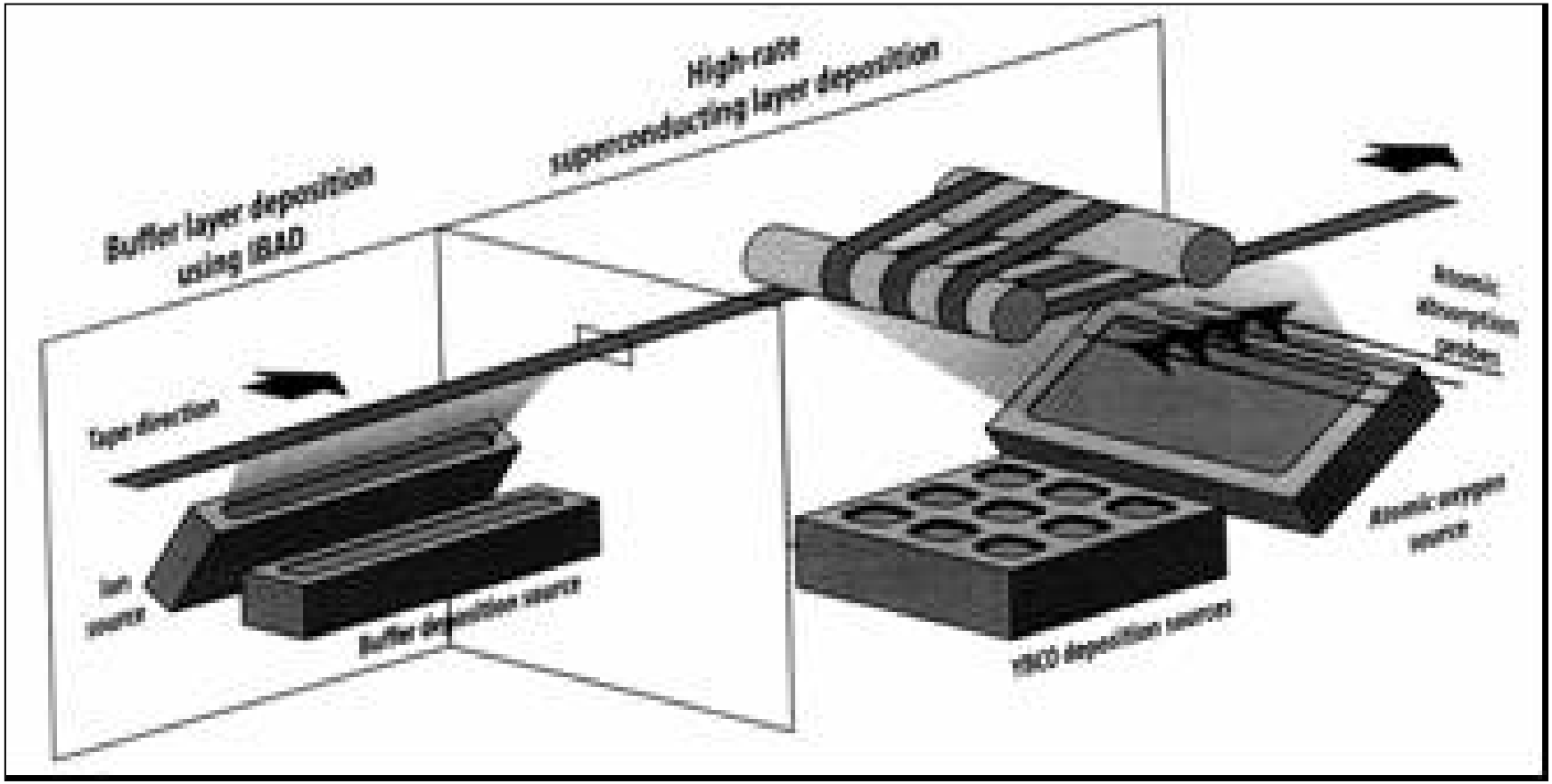


IBAD-MgO on a-SiN (EPRI/Stanford, 1994)



- IBAD is slow
- Epi is fast
- MgO (unlike other materials) only needs "assist" for a few monolayers
- Patent to Stanford (1998) (EPRI license, sub to AMSC)
- Method of choice at LANL & IGC-SP

Reel-to-Reel IBAD

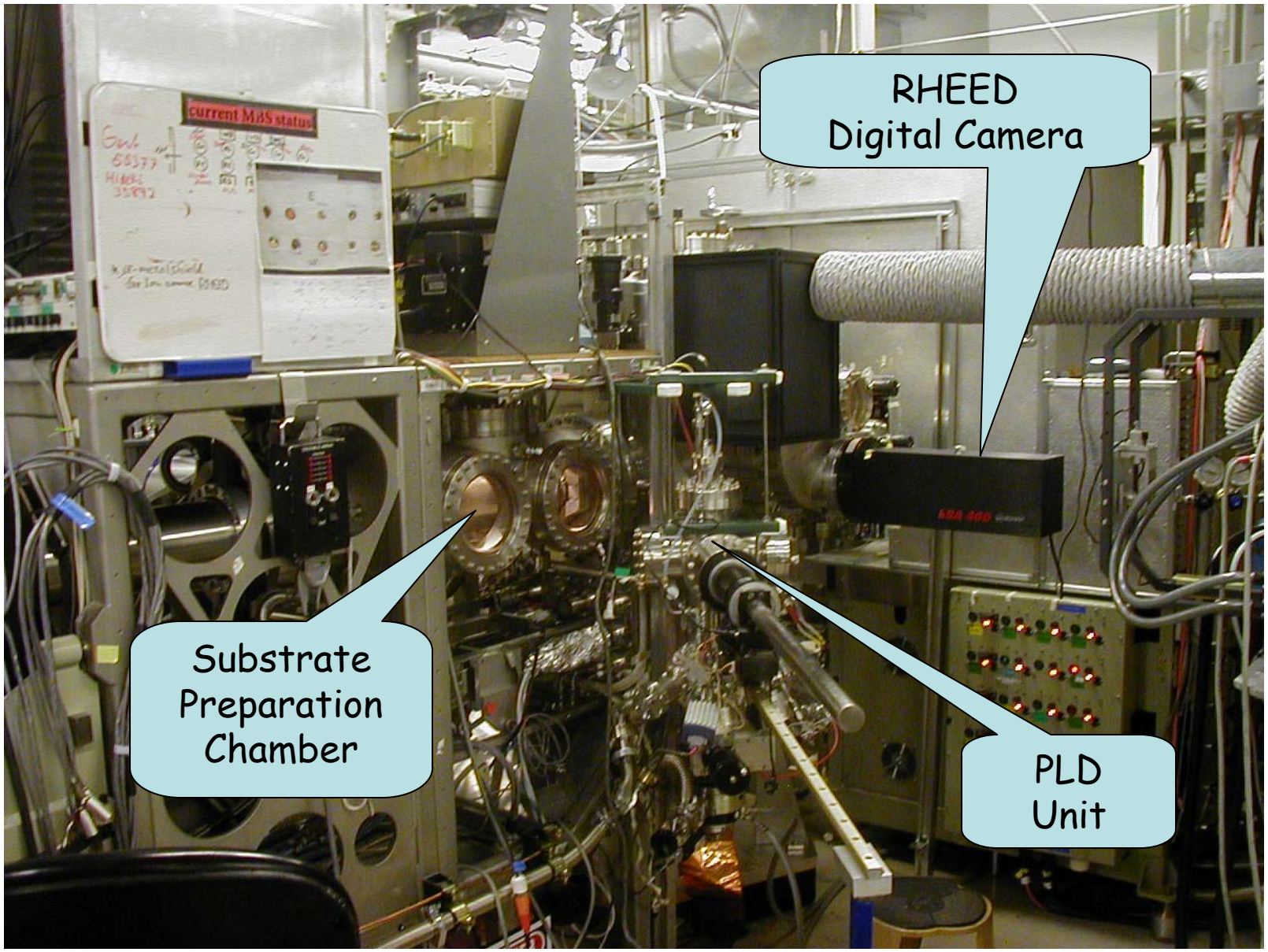


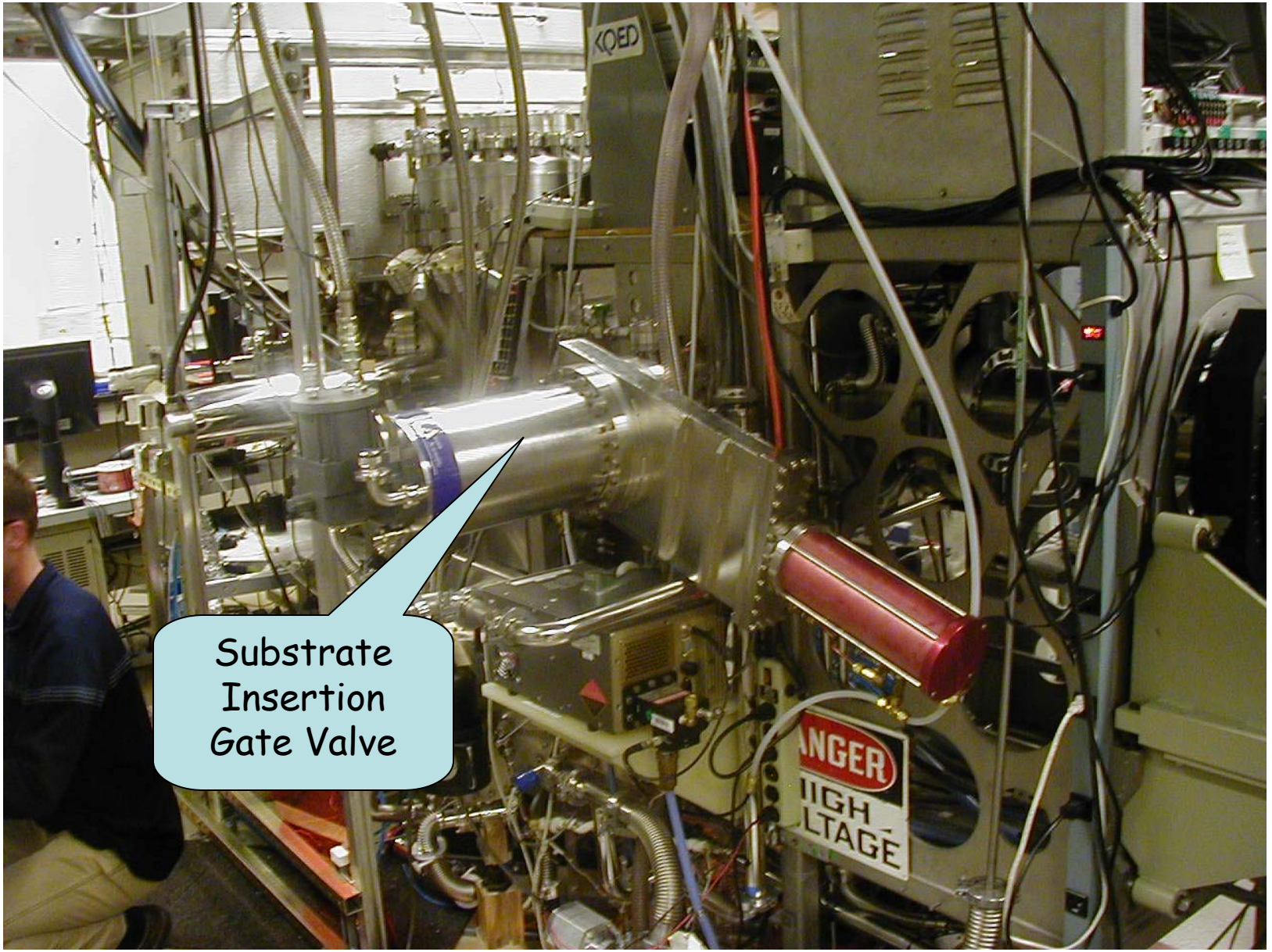
P. M. Grant, ASC'96 (Conception, R. H. Hammond, Stanford, 1994)

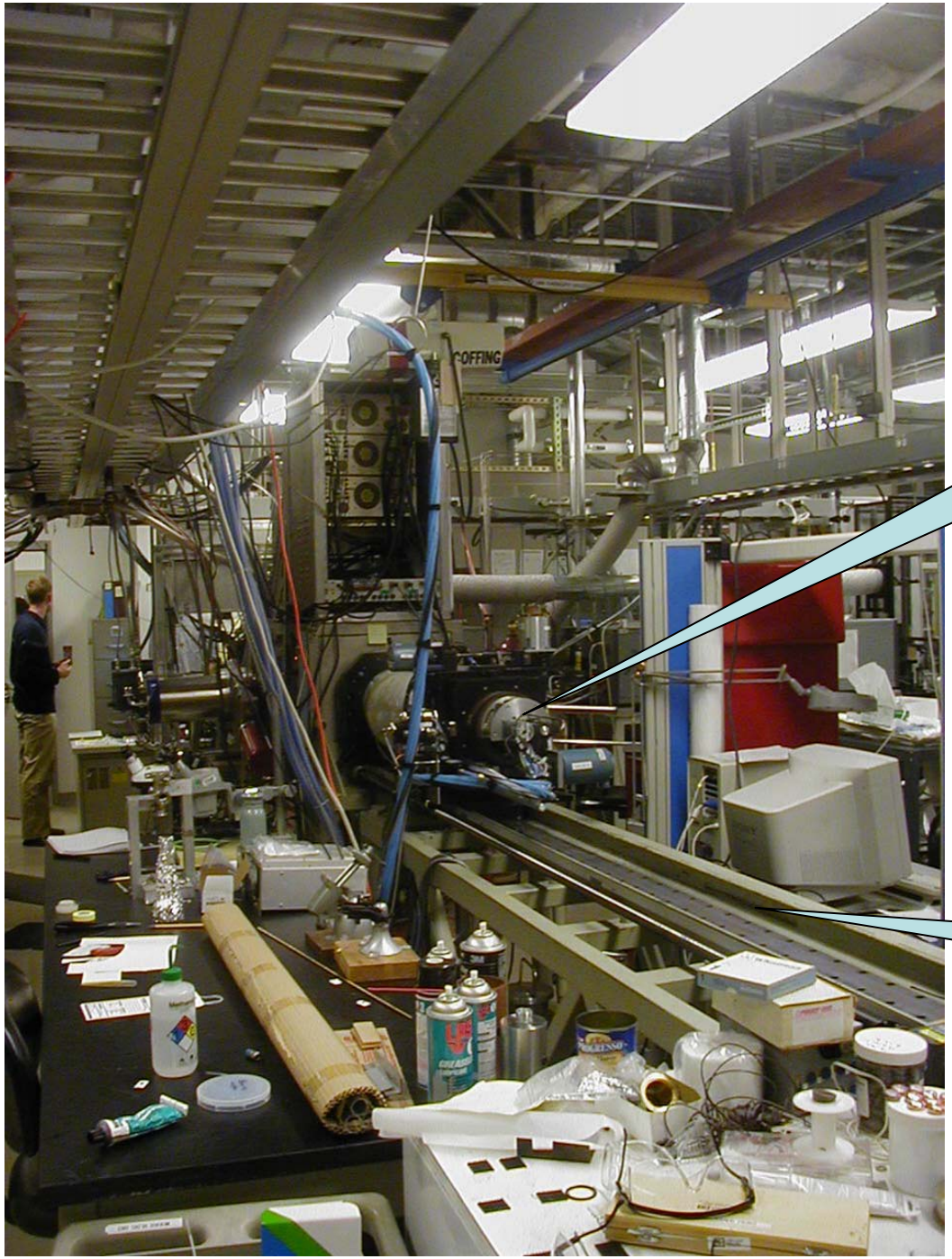
EPRI-AMSC CC Alliance (1996 - 2000)

- $10 M, 4 Years
  - AMSC $6 M (included work in place)
  - EPRI $4 M (included ongoing contracts, e.g., Stanford and EPRI exclusive license)
- EPRI received AMSC warrants @ $14
  - In January, 2001, first batch vested, AMSC @ $18
- When shares were sold, AMSC @ $61 !

The Machine That Made EPRI $2.5 M

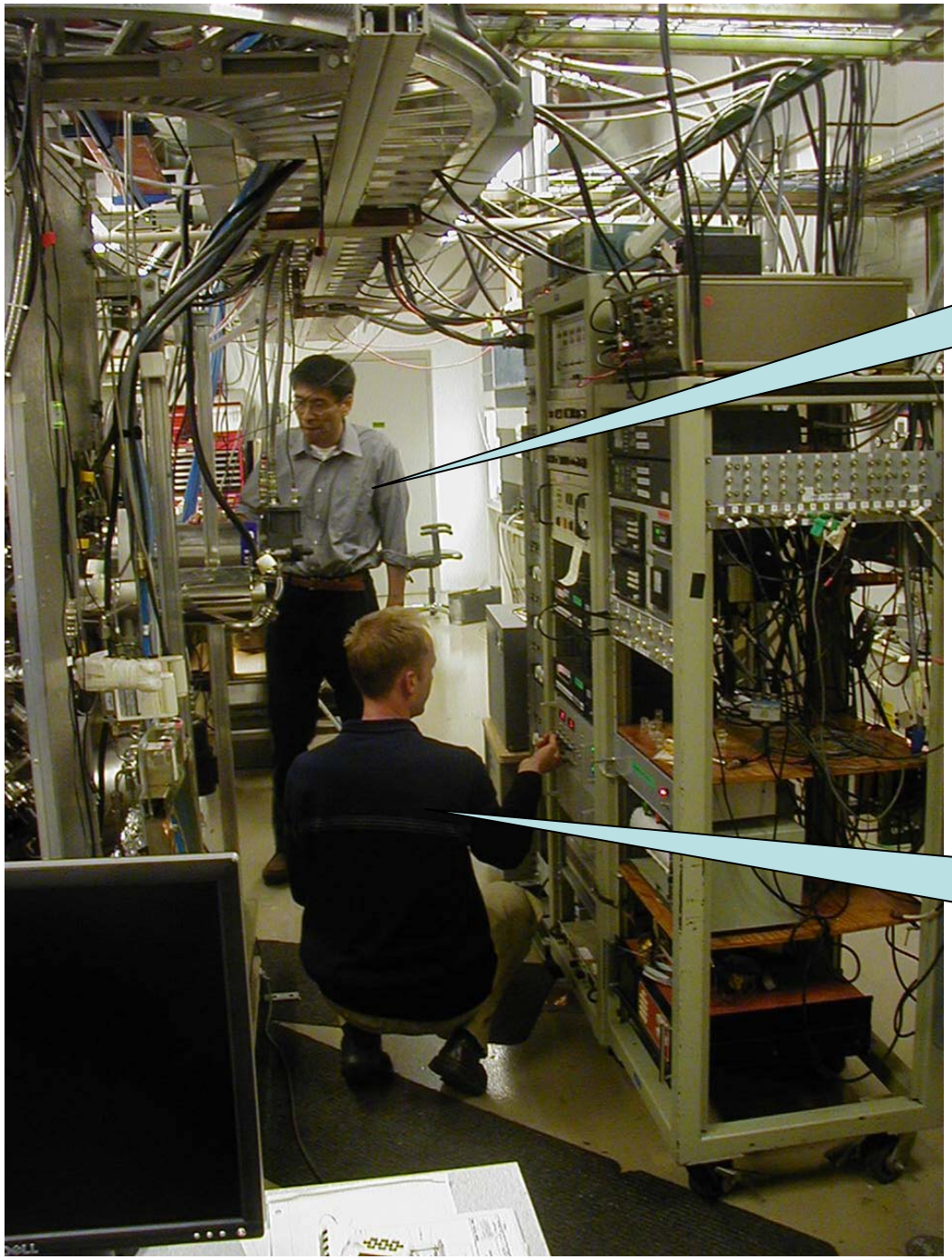



KQED
Substrate
Insertion
Gate Valve
NGER
IIGH
LTAGE



5 – meter
Substrate/Sample
Carriage (inserted)

Carriage
Arm Rail

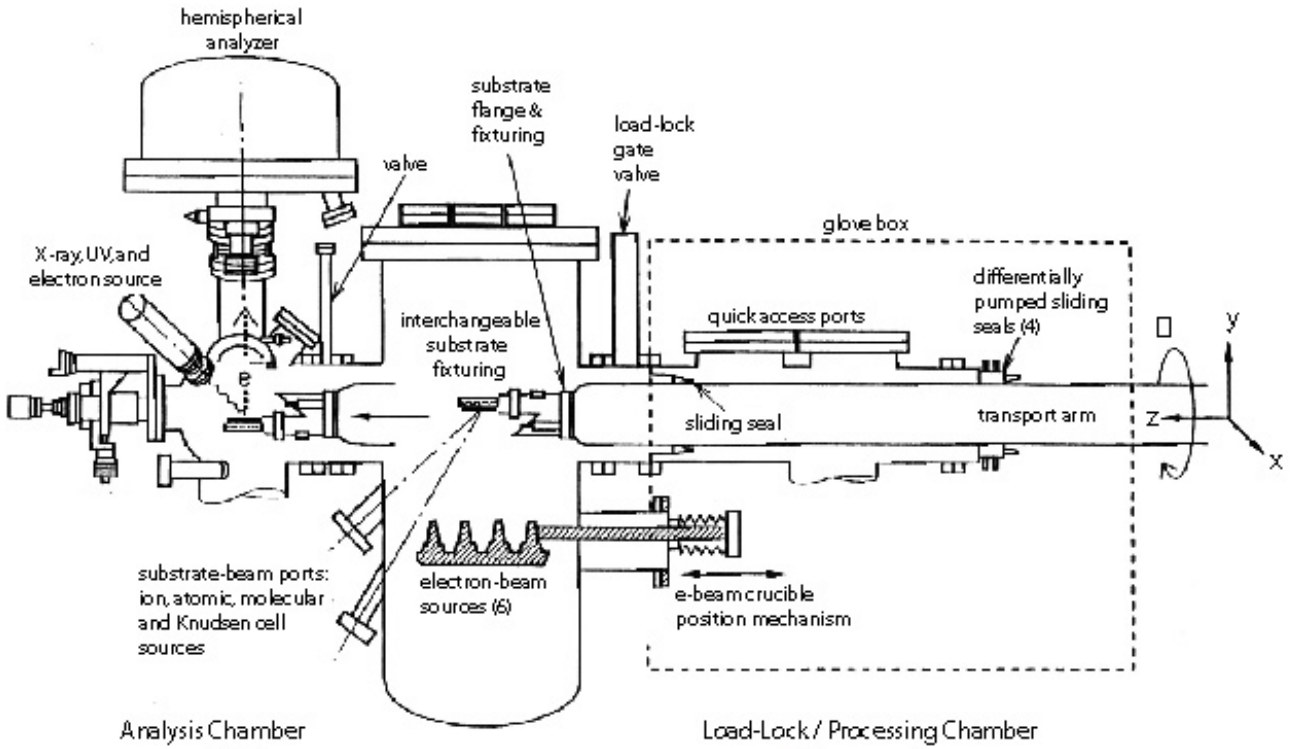


Dr. Hideki Yamamoto
Visiting Scientist from
NRIM, Japan

Dr. Gertjan Koster
Visiting Scientist from
U. Twente, Netherlands

MBS Machine

MOLECULAR BEAM SYNTHESIS SYSTEM (MBS)



Analysis Chamber

- LEED
- XPS
- UPS

UHV Deposition Chamber

- Electon beam sources (6 emitters, 10 crucibles)
- Atomic Absorption rate control
- Atomic Oxygen Sources (2)
- Ion beam processing
- RHEED
- 4000 L/sec cryopump

Load-Lock / Processing Chamber

- Gas annealing

In 2004, There was a Problem…

- Stanford wanted its fair share of the stock sale windfall
  - The Stanford license to EPRI called for royalties…but there were no royalties!
  - It was mutually agreed that a 10% cash payment ($250 K) would settle matters
  - But there was no assurance that the money would go to GLAM
  - Both parties agreed that EPRI would fund a $250 K, 3-year, research effort on a "mutually interesting project."
- EPRI's CEO and CFO signed such an agreement with Stanford in 3Q04.

"Possible High T_c Superconductivity in the Ba-La-Cu-O System," Georg Bednorz and K. Alex Mueller, IBM, 17th April 1986

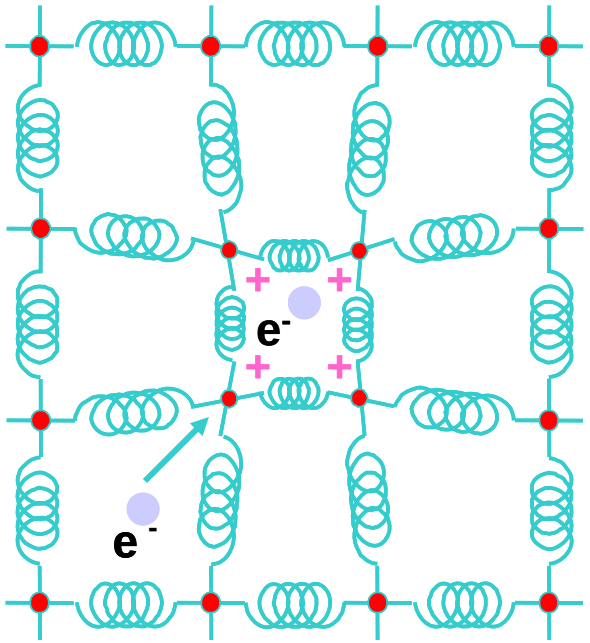
"At the extreme forefront of research in superconductivity is the empirical search for new materials"

M. R. Beasley, 1985

Superconductivity 101

Characteristic Boson Temperatures

- **300 K for phonons (LTSC)**
- **500 K for magnons (HTSC ??)**
- **11,000 K for excitons (RTSC ??)**
- **10^9 K for gluons (quarks in neutron stars)**



pairs

Fermion-Boson Coupling Constant

- **Want this as big as possible**
- **Be near a critical point in LRO**
- **Look for materials with this property**
- **e.g., with metastable LRO**

$\exp(-1/\lambda)$

75 K ,

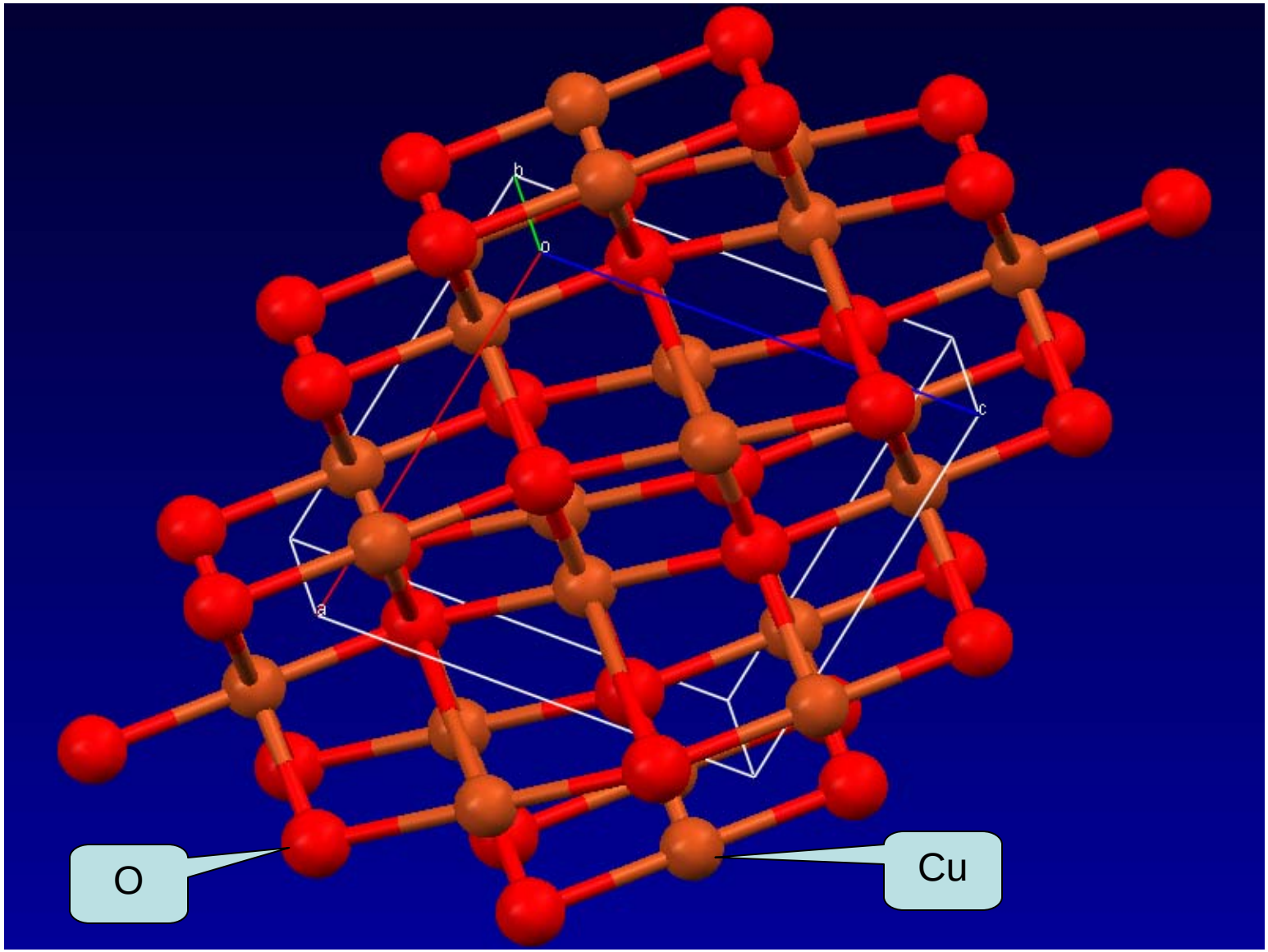
28 ,

9.5 K (Niobium)

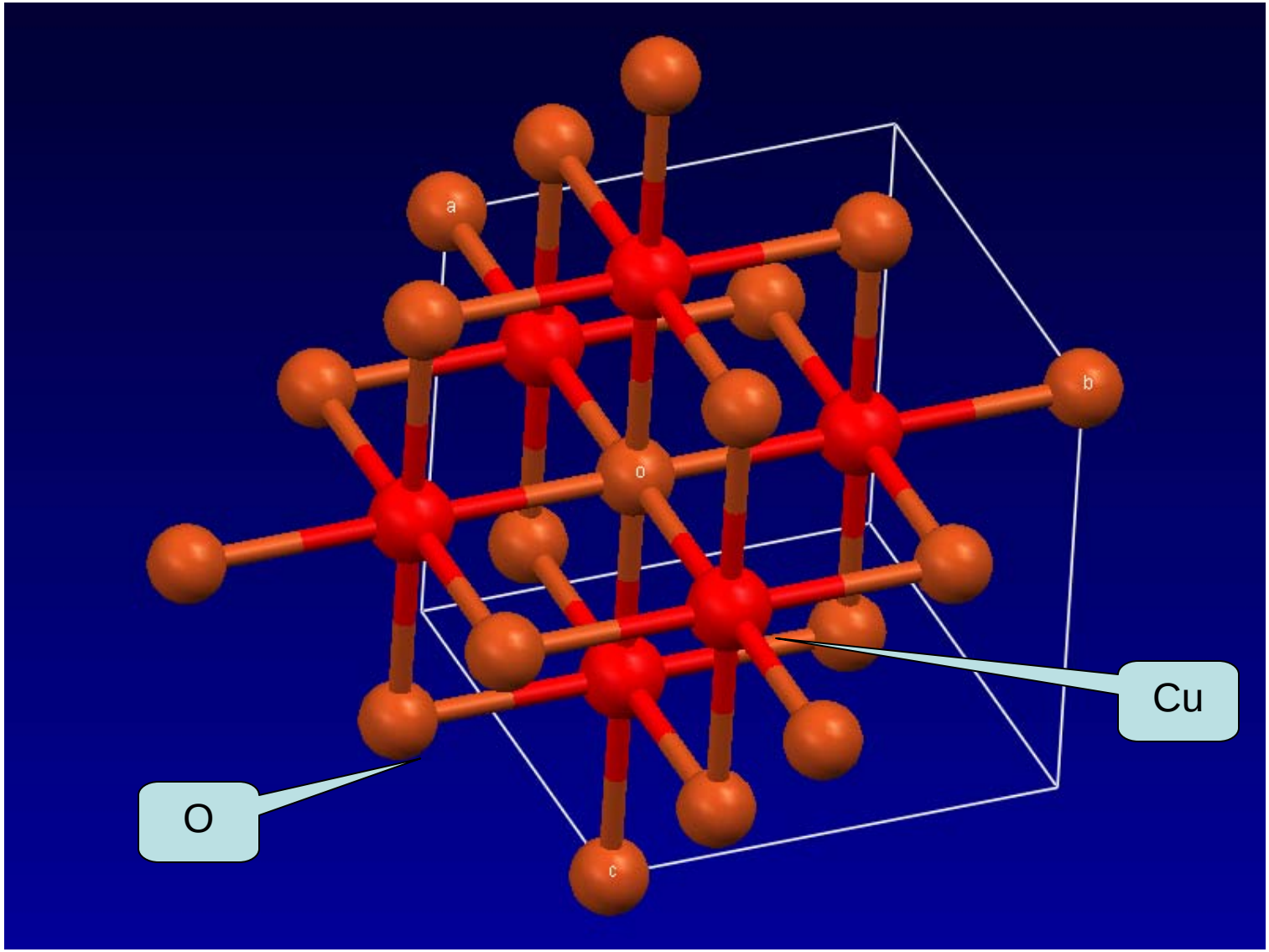
What to Do?

- The "mother liquor" of HTSC is in the doped copper – oxygen bond
  - The most basic form of copper oxide is the mineral tenorite, monoclinic in structure
  - Yet repeated attempts over the years to "dope it" resulted in nothing "interesting."
- Ted Geballe had had a long-standing idea
  - Try to use IBAD to force CuO into a metastable cubic phase (near an LRO critical point)
  - Then dope it and something "interesting" might show up!

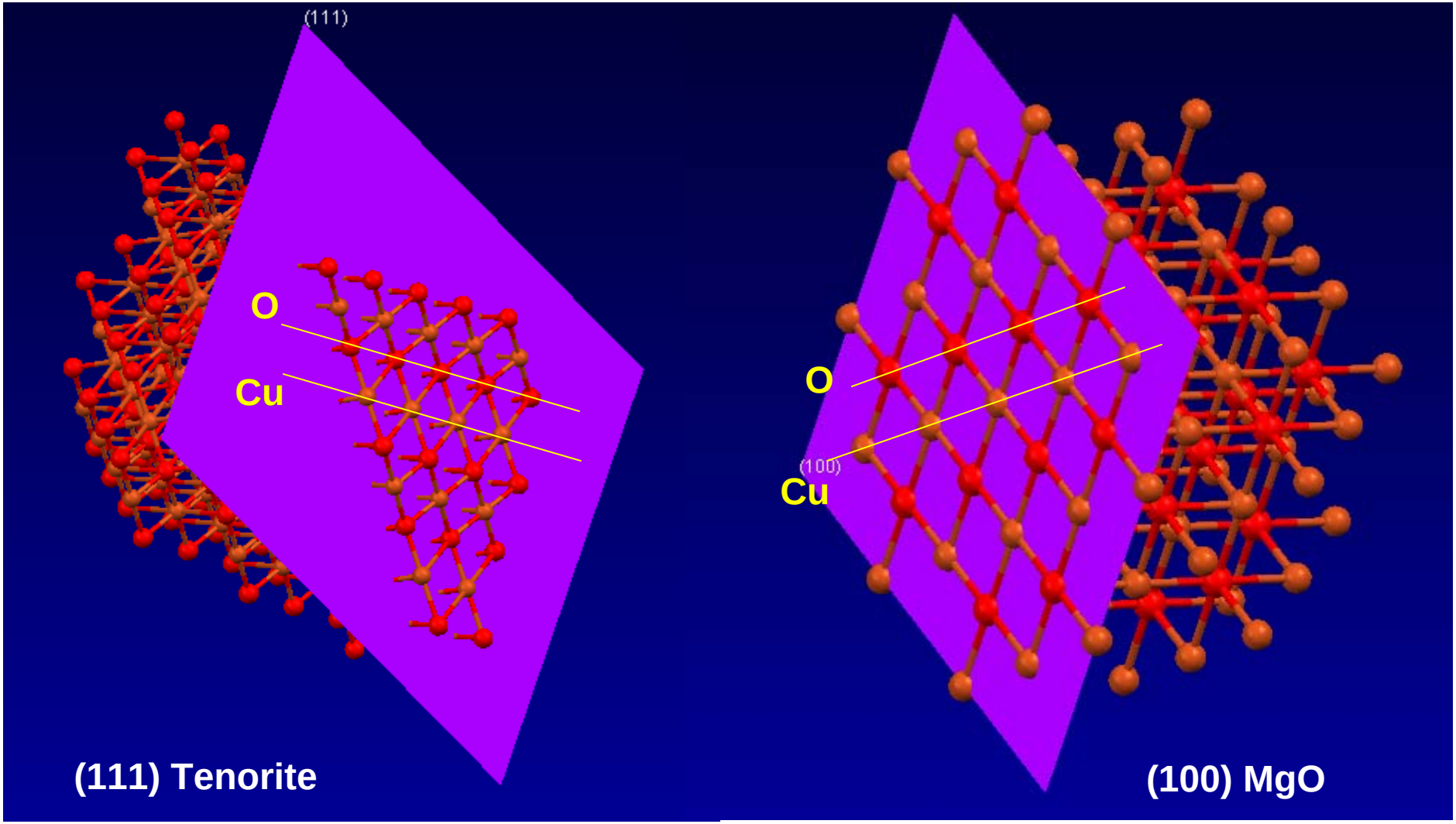
Tenorite (Monoclinic CuO)



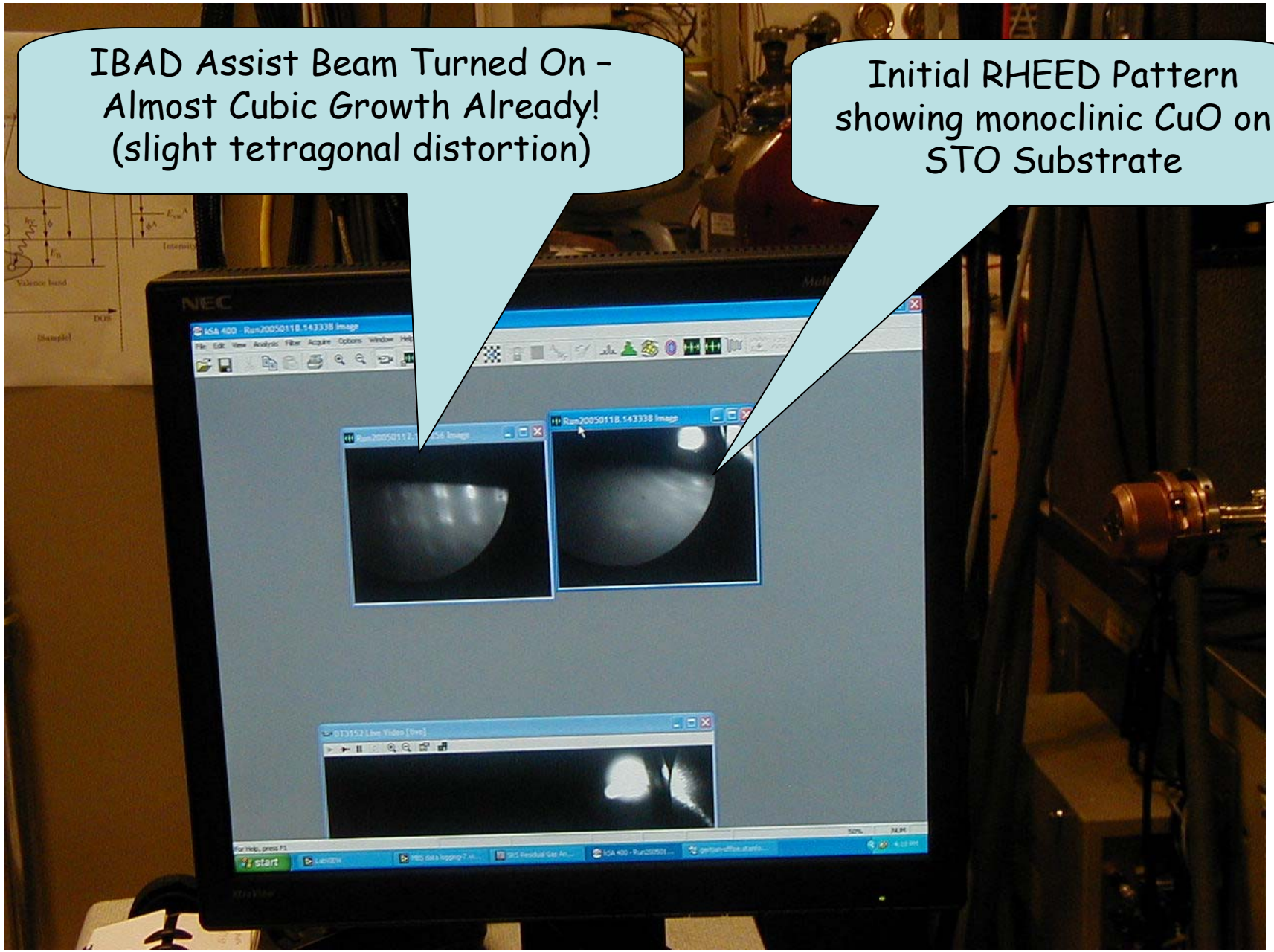
CuO as Cubic MgO



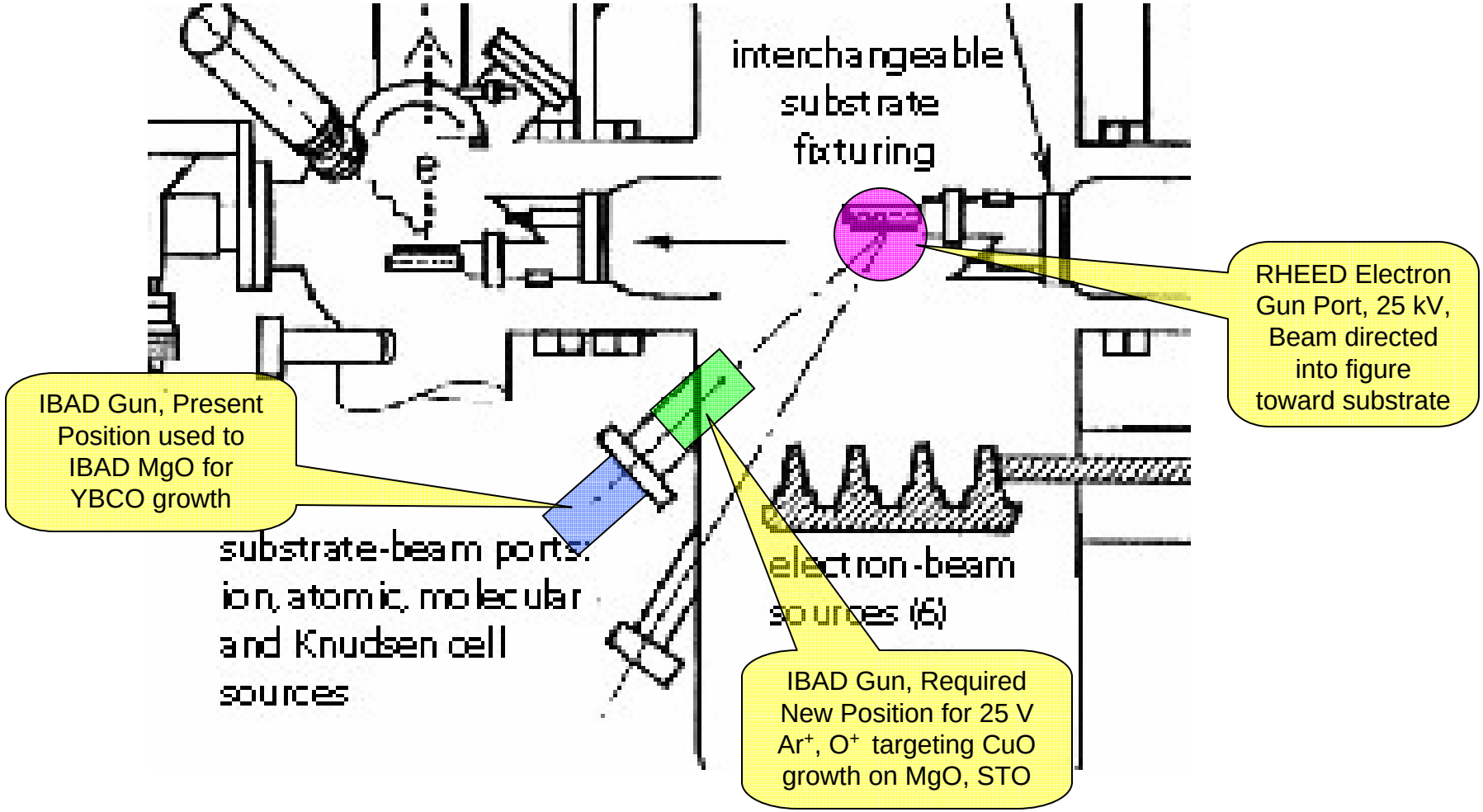
Comparison of Tenorite (111) to CuO – MgO Proxy (100)



Initial Experimental Results



IBAD – RHEED Port Positions



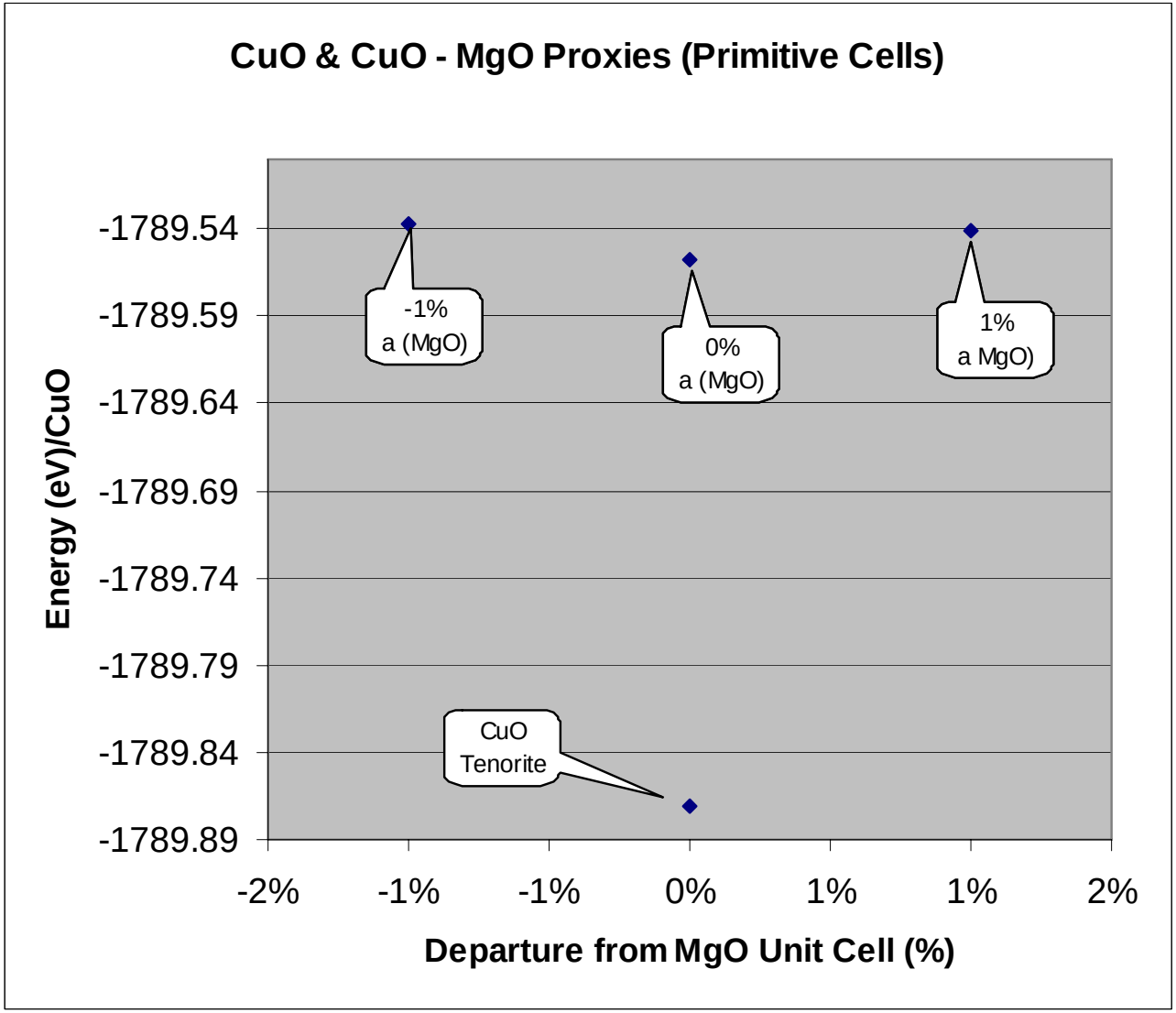
Results & Future Plans

- Initial results encouraging…CuO grows epi on STO and MgO for several monolayers with no assist
- Then switches to tenorite phase with thickness
- IBAD seems to give tetragonally distorted cubic structure
- Resume experimental runs when new ion gun shield in place
- Undertake doping (probably Ca) at an appropriate stage

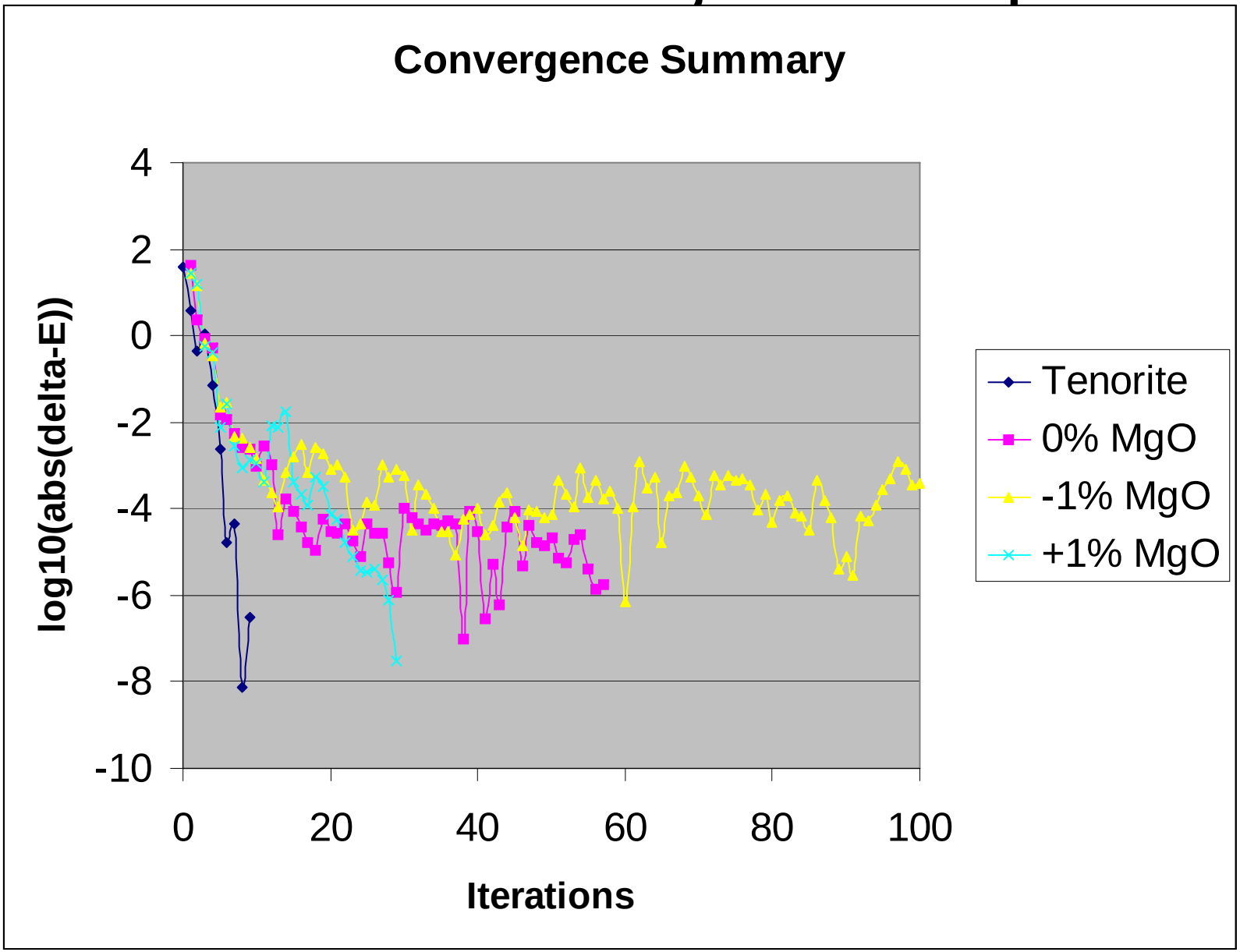
Theory & Modeling

- Apply Density Functional Theory to search for possible "quasi-stable" CuO structures
  - 1998 Nobel Prize in Chemistry
  - Essentially an exact calculation of the physical and chemical properties of s-p electron molecules, solids and liquids (don't need to go to the lab anymore!)
  - Extensively used by the pharmaceutical industry to search for new drugs
- Concentrate on cubic "proxy structures," e.g., MgO, STO, NiO, ZrO…
  - Employ commercial CASTEP software under license to Stanford

"CuO – MgO Proxy" Converged Energies



Trial Runs Convergence Properties



III. Paper Submitted to:

The 12th International Workshop on Oxide Electronics

Chatham, Cape Cod, Massachusetts, USA

October 2-5, 2005

The effect of low energy Ar^+ ion bombardment on epitaxy and oxidation of thin films of CuO_x

Gertjan Koster[1], Hideki Yamamoto[1,2], Wolter Siemons[1,3], Arturas Vailionis[1], R.H. Hammond[1], P.M. Grant[4], T.H. Geballe[1] and M. Beasley[1]

[1]Geballe Laboratory for Advanced Materials, Stanford University, Stanford, CA

[2]NTT Basic Research Laboratories, Kanagawa, Japan

[3]Inorganic Materials Science, Faculty of Science and Technology, Twente University, The Netherlands

[4]W2AGZ Technologies, Palo Alto, CA

Here we present a detailed study on the growth of epitaxial CuOx thin films on single crystal substrates (MgO and $SrTiO_3$) by MBE. *In situ* photo electron spectroscopy (XPS and UPS) is used to establish the degree of oxidation of Cu, while *in situ* electron diffraction (LEED and RHEED) monitor the crystal structure of the growing thin film. We particularly pay attention to the valence state of Cu and the crystal symmetry as influenced by a combination of the substrate, activated oxygen and a flux of low energy Ar^+ ions. We observe a rich variety of epitaxial relationships as a function of the flux ratios of three species on the substrate surface (ie, Cu, O^* and Ar^+) which will be used to explore the possibility of the highest crystal symmetry achievable in CuO_x system. The relationship between (electronic) properties and crystal structure is being investigated at different lengths using scanning probes. Although the copper system is the focus of this paper, we will also address whether such an approach is feasible for other oxide materials

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This work is supported by DOE, EPRI and Netherlands Organization for Scientific Research (VENI).

Stay Tuned

For copies of this talk and more in-depth technical background, please visit

http://www.w2agz.com/epri-sctf5.htm