

3Q05 EPRI Project Report

“Consultant to EPRI Project Management on the
Fabrication of New Superconducting Materials”

EPRI Contract Agreement No. EP-
P18263/C9013

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EPRI Project Manager: Steven Eckroad

30 September 2005

Activities & Results

I. Experimental

II. Theory & Modeling

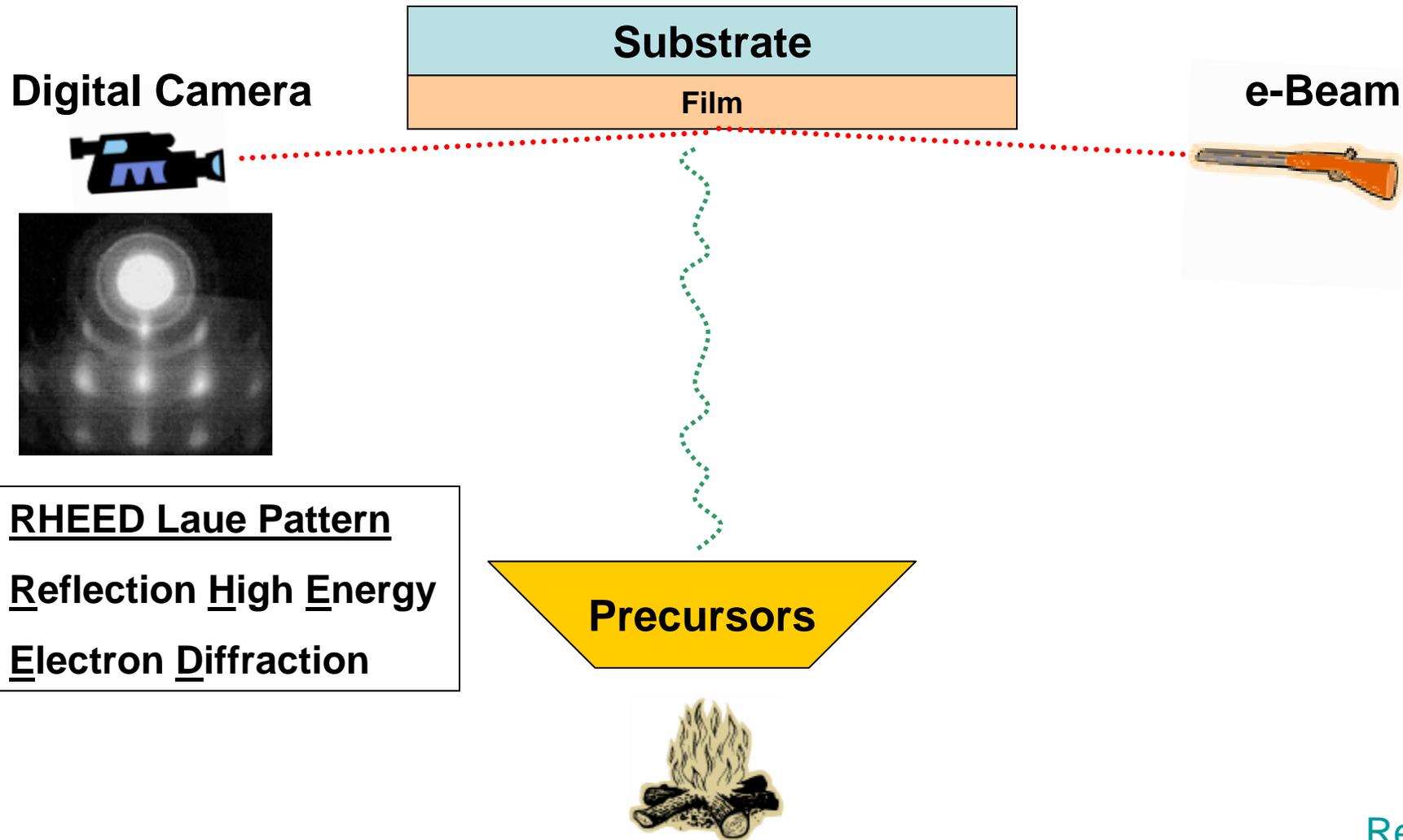
III. Poster Presented at the:

2005 Chatham Workshop on Oxide Electronics

I. Experimental

- Most experimental activity was suspended during 3Q05 due to retrofit of the MBG¹ to install new IBAD² ion gun.
- In the meantime, it was decided to try a few runs depositing CuO³ directly on STO⁴ single crystal substrates without an IBAD assist beam.
- Interestingly, it was found that CuO apparently grows epitaxially on the cubic face diagonal of STO for 3-6 unit cells of “cubic CuO.”
- These results are encouraging in that a very large distortion of the Cu-O bond can be sustained for at least up to a 25 Å thick film.
- It is hoped that when the redesigned IBAD assist gun is deployed in mid-October, much thicker films of “cubic CuO” can be grown.

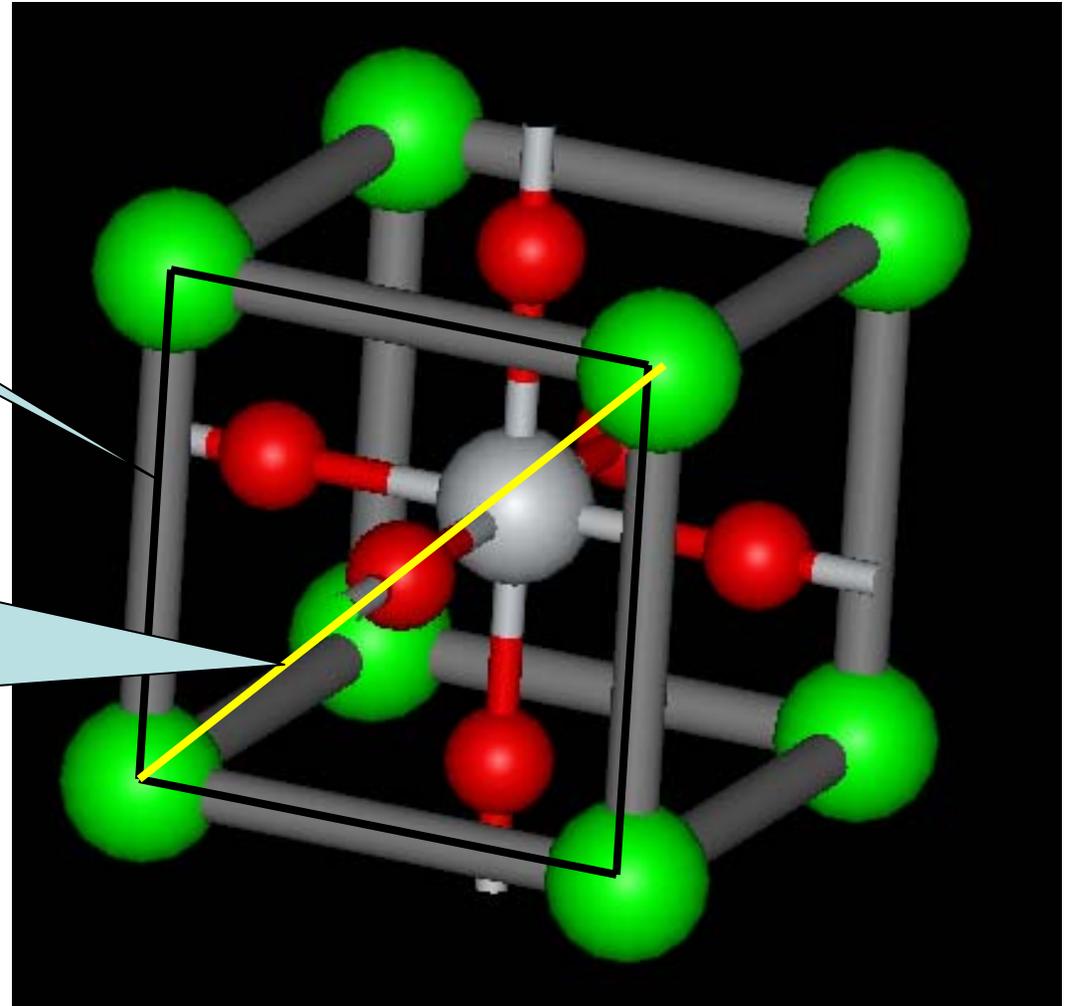
RHEED¹ Analysis During Film Growth



Possible CuO Growth on STO

The "100"
face of STO.

Most likely alignment (11) direction for the growth of a linear Cu-O-Cu bond. The Sr-O distance is 2.8 Å, almost 70% larger than the average Cu-O bond!



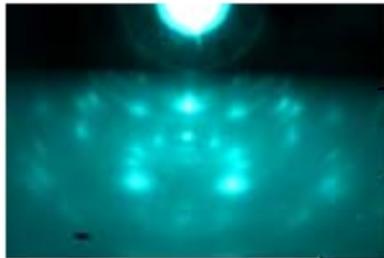
RHEED Patterns: CuO growth on (100) STO

"Bare" (100) STO substrate before start of Cu-O deposition. This pattern is typical of cubic symmetry.



(10) SrTiO₃

~35Å CuO on STO
(500°C, 0.23 Å/s)



Indication of completed "crossover" to tenorite at thickness of 35 Å.

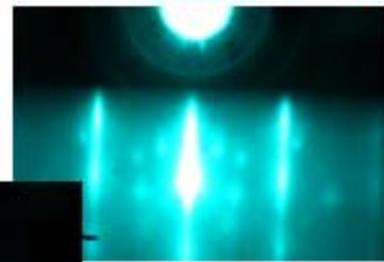
~24Å CuO on STO
(600°C, 0.14 Å/s)



(10)STO

(11)STO

~16Å CuO on STO
(500°C, 0.08 Å/s)



RHEED pattern after a few seconds of deposition. Indicates some kind of "cubic" orientation of CuO

~10Å CuO on STO
(500°C, 0.08 Å/s)



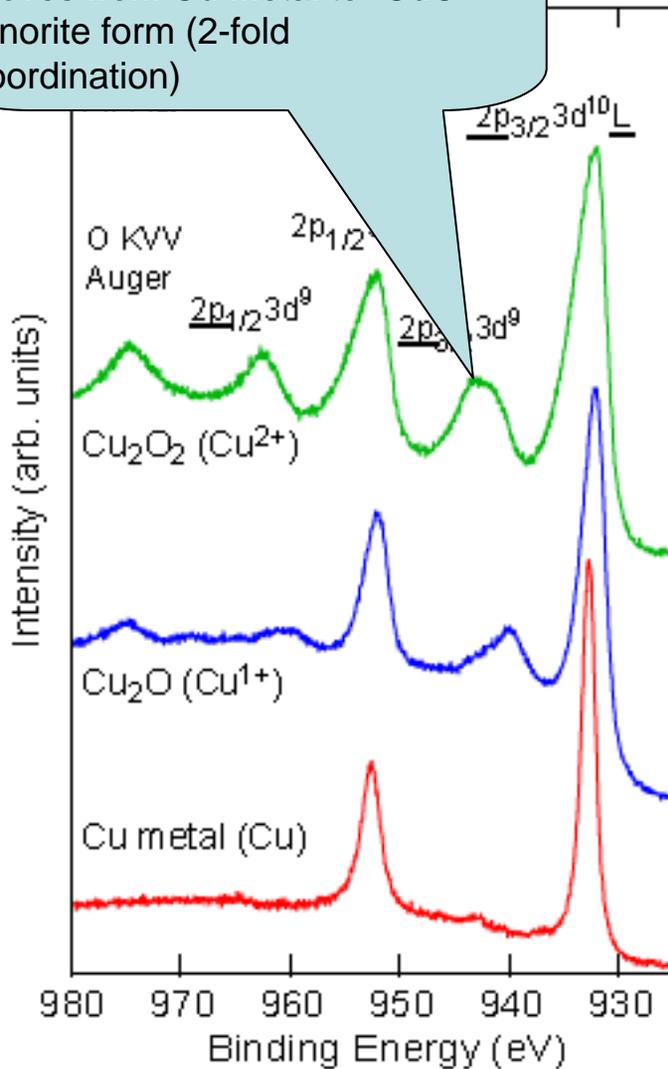
Beginning of "crossover" from cubic to monoclinic form of CuO. Note clean pattern along (11) direction.

NB: No IBAD assist was employed in this run

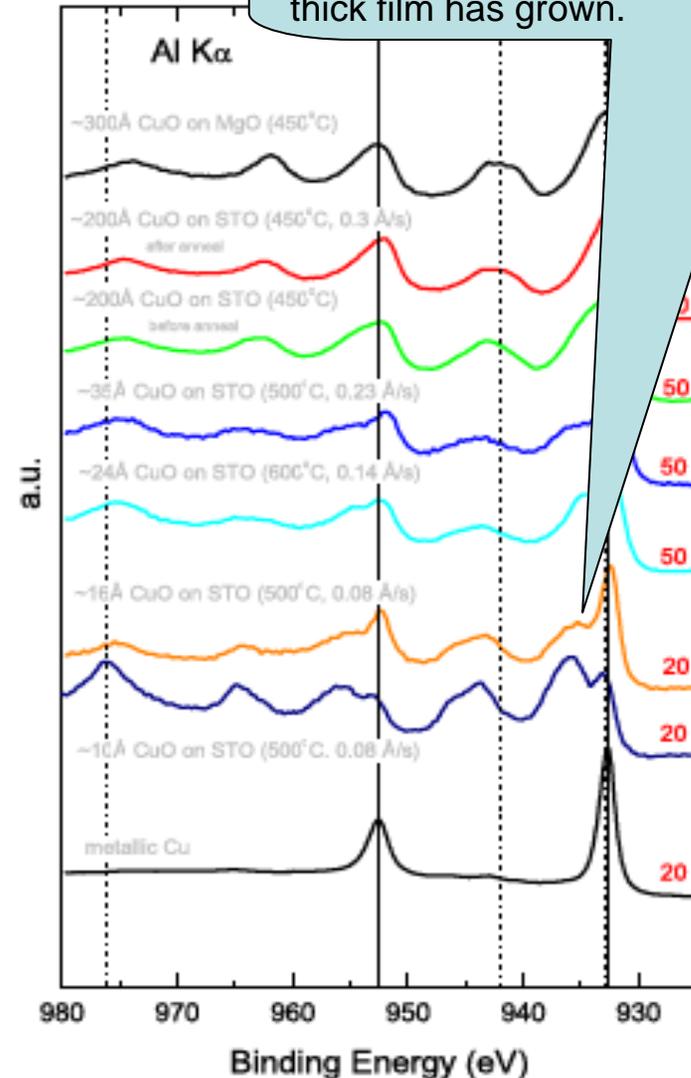
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XPS¹ of Cu 2p Shell² in Copper Compounds

Observe the “emergence” of the 3d⁹ peak at 940 eV as one moves from Cu metal to “CuO” tenorite form (2-fold coordination)



Note the “absence” of the 3d⁹ side-structure until a sufficiently thick film has grown.



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II Theory & Modeling

- Modeling efforts this quarter focused on testing whether the CASTEP density functional tool could optimize the values of the internal atomic coordinates in highly correlated¹ electronic structures such as tenorite (CuO) and NiO.
- Using the experimental values of the atomic positions as input, CASTEP varied these values to “juggle the atoms around” in a search for lower energy coordinates while retaining the overall crystal symmetry.
- Results showed the program found new “optimal” coordinates displaced by only a few percent from the experimental values, suggesting that despite the neglect of coulomb correlation, density functional methods can be trusted as a means to test relative equilibrium energies for differing crystalline symmetry arrangements of a given set of atoms, e.g., copper and oxygen.
- Therefore, the comparison of various CuO proxy cubic structures with monoclinic CuO performed last quarter appear reliable.

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

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Here we present a detailed study on the growth of epitaxial CuO_x thin films on single crystal substrates (MgO and SrTiO₃) 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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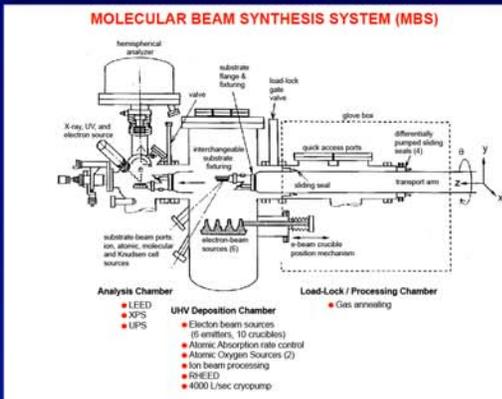
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Introduction

● Vapor phase deposited copper oxide has shown a rich variety of epitaxial relationships as a function of the flux ratios of three species on the substrate surface (i.e., Cu, O* and Ar*) (Kita et al. APL 60 (1992) 2684, Catana et al. PRB 46 (1992) 15477). This will be used to explore the possibility of the highest crystal symmetry possible in Cu(II)O_x system, which is an ongoing effort.

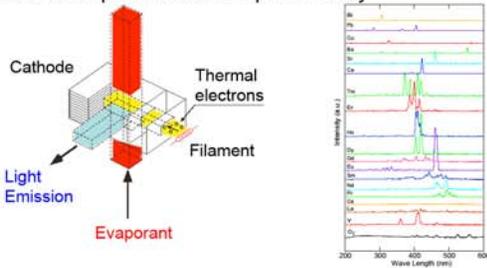
● Here we present a detailed study on the initial growth of thin epitaxial CuO_x films on single crystal substrates by MBE. *In situ* photo electron spectroscopy (X-ray PES and UV-PES) is used to establish the degree of oxidation of Cu while *in situ* electron diffraction (RHEED) monitor the crystal 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 activated oxygen and a flux of low energy Ar⁺ ions.

System

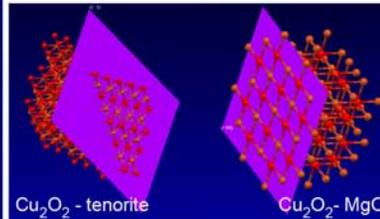


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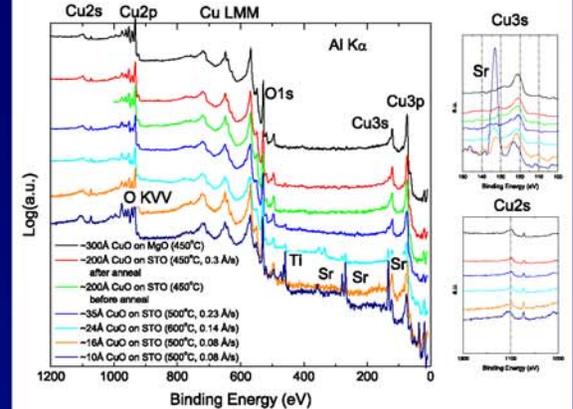
Electron Impact Emission Spectrometry



CuO_x structures - Cu-O bond length 10% difference



In situ XPS Cu₂O₂



Acknowledgements

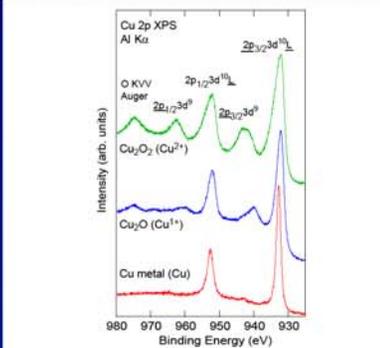
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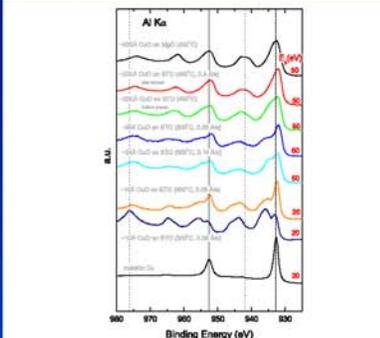
Affiliations

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- γ) NTT Basic Research Laboratories, Kanagawa, Japan
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In situ XPS - Cu 2p



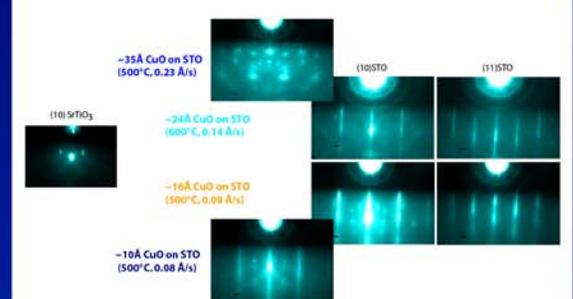
In situ XPS - Cu 2p



Conclusions

- RHEED: Epitaxy is observed for films thinner than roughly 20Å
- XPS: A large chemical shift is observed for the Cu 2p peaks
- Note: This shift is usually only seen for copper compounds with a high cation coordination number
- MBE: Chemical- and Field Effect doping will be part of future experiments

RHEED initial growth



RHEED thick films

