Nanoscale Epitaxial Films of Cu_2O_{2-x}

An attempt to make cubic CuO

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MRS Spring meeting

HH4.9: Novel materials

Wednesday, April 19th 2006, 4:30pm

Nano scale epitaxial films of Cu_2O_{2-x}; a model system

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Here we present a detailed study on the growth of epitaxial CuO_x thin films on single crystal substrates 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 (X-ray Photo electron diffraction and RHEED) monitor the crystal structure and morphology 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 (O^*) and/or 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 possible in CuO_x system. In recent experiments we observe a new CuO phase (di-valent copper) for the first deposited unit cell layers which is found to be 45 degrees rotated with respect to the $SrTiO_3$ substrate lattice. Both RHEED as well as preliminary X-ray Photoelectron Diffraction confirm a four fault symmetric structure. In parallel we try to establish the relationship between (electronic) properties and crystal structure at different length scales. Although the copper system is the focus of this paper, we will also address whether such an approach is feasible for other oxide materials, for example dielectric materials.

People and funding

At Stanford University:

Wolter Siemons, Gertjan Koster, Hideki Yamamoto, Bob Hammond, Ted Geballe, Paul Grant, Malcolm Beasley

At University of Twente: Guus Rijnders and Dave Blank

This research is funded by EPRI, DoE, and NanoNed

Motivation

- Model system related to High-T_c cuprates
  - Expected to be 3D system, compared to the 2D planes
  - Increased superfluid density (raising T_c?)
  - Exploration of doping methods
  - More general: Exploration epitaxial stabilization

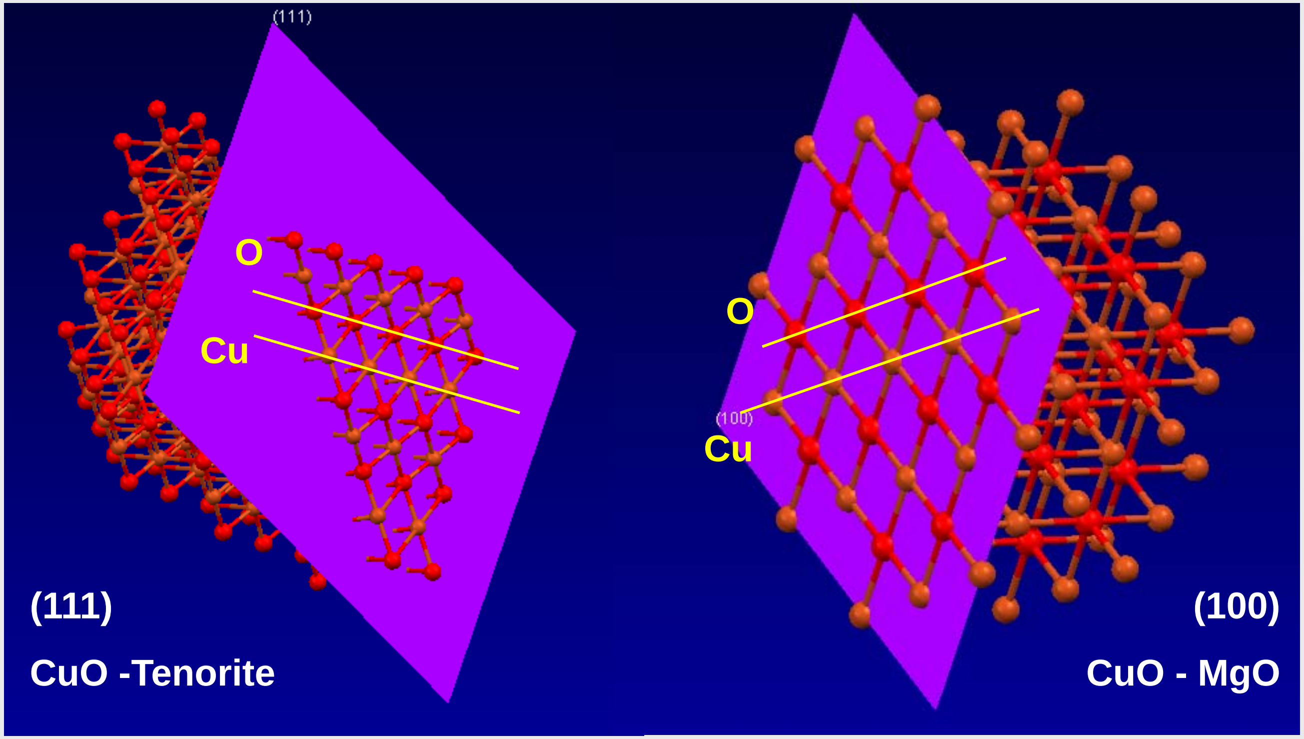
Material specifics

- CuO (tenorite) naturally has a monoclinic unit cell
- Charge transfer system (Mott-Hubbard), insulating in undoped form

Growth parameters:

- Grown in 10^{-5} Torr O_2 pressure with 600 W atomic oxygen source
- Various substrates at 500-600 ^{o}C
- Can be grown both with MBE and PLD

Proxy structure

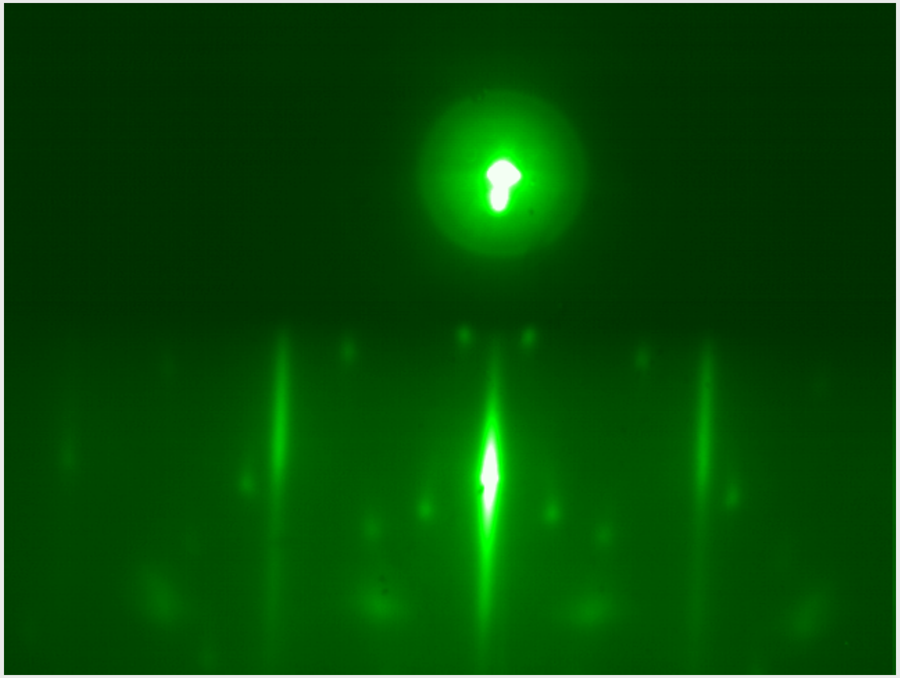


Average bond length:
1.92 A
(Shorter than cuprates)

Average bond length:
2.10 A

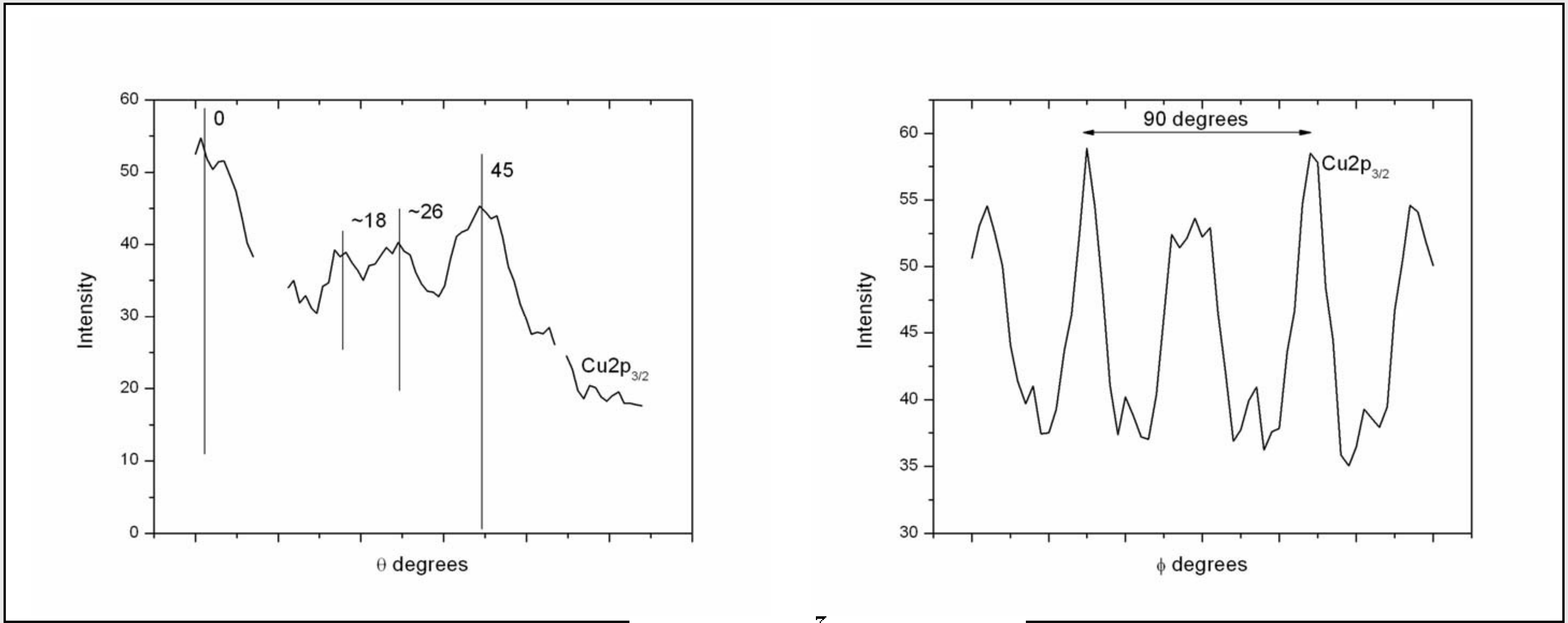
- Stabilized Cu_2O_2 by epitaxy on TiO_2 terminated $SrTiO_3$ substrates

RHEED

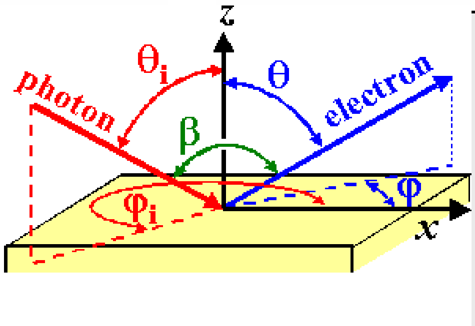


- CuO, like MgO and NiO, grows epitaxially on $SrTiO_3$
- Grows 45 degrees rotated with respect to substrate
- After critical thickness (~25-30A) structure changes to tenorite
- Critical thickness depends on temperature, substrate, and oxidation conditions

X-ray Photoelectron Diffraction



Along $SrTiO_3$ 110



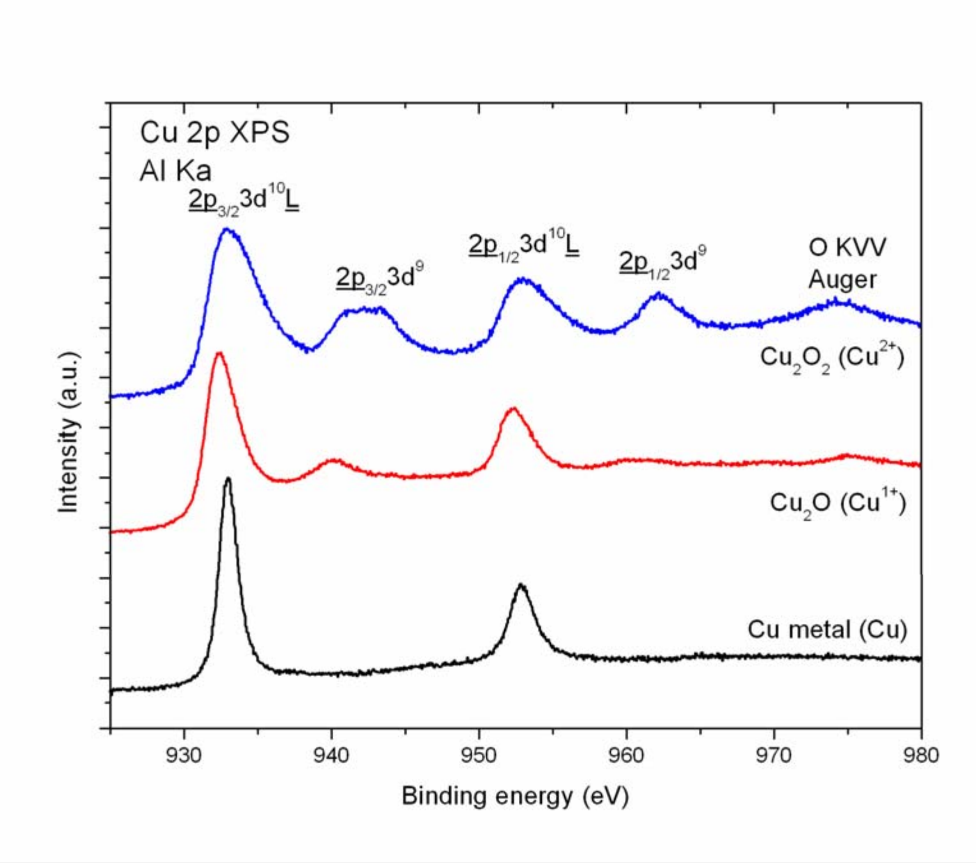
Instability

- Structure wants to change to tenorite structure
- Taking sample out of vacuum might have this effect, and certainly does this going beyond the critical thickness

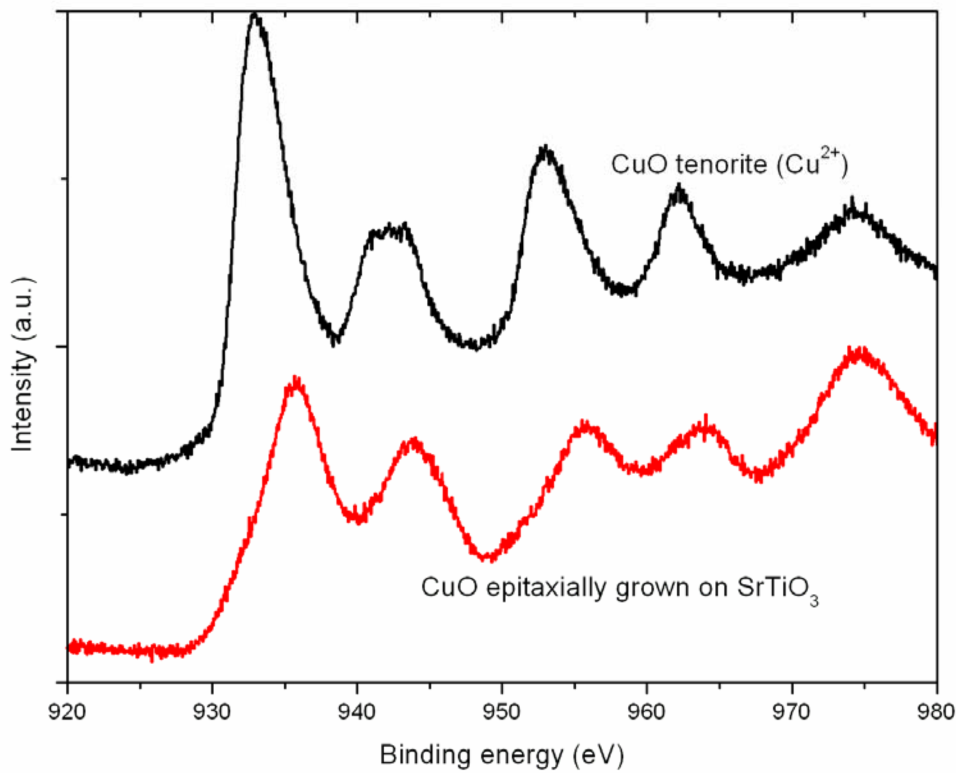
In situ XPS from Cu to CuO

In situ technique to avoid degradation of the material

Detailed studies of the XPS Cu 2p multiplet structure have been used to estimate the charge transfer energy (Δ)



XPS shifts



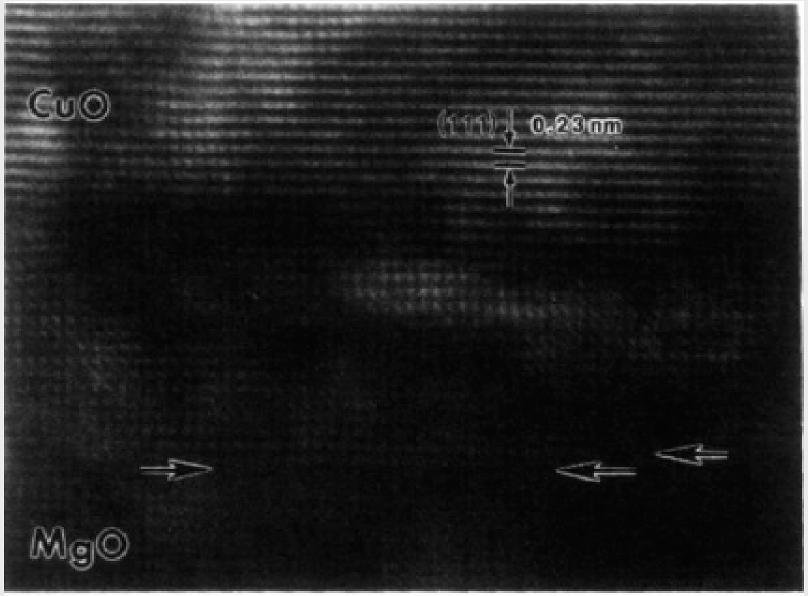
Different chemical environment

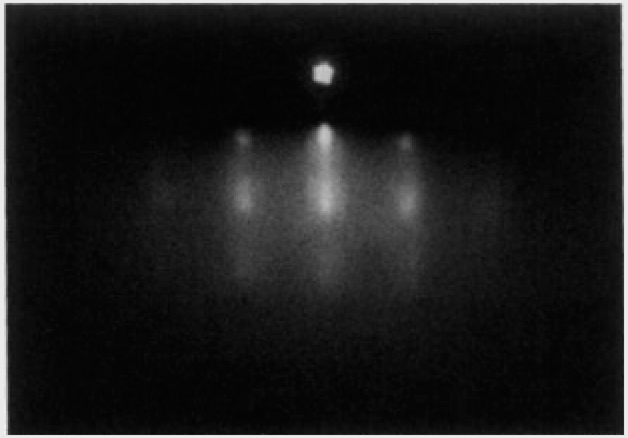
Future experiments

- Determine the out of plane lattice constant (through simulation of XPD)
- Doping of CuO: chemical, charge transfer overlayers and field effect
- Determination (with Kapitulnik and Xia) of the magnetic properties, with the help of a sagnac interferometer, by measuring Kerr rotation (could be done *in situ*)

Work by other groups

Critical thickness and instability make it very hard to analyze the material. XRD, TEM, etc. almost impossible.





Catana, Locquet, Paik, and Schuller, PRB 46, 15477 (1992)