NNI- Synthesis and Characterization of Novel Nanocrystalline Oxide Film Structures

# Interface Controlled, Self Assembled Quantum Dots

## *Formation, Structures, Stability and Properties*

**Project Leaders**: D. R. Baer, S. A. Chambers

**Key Contributors:**

A. El-Azab, A. S. Lea, S. Thevuthasan, Z. Wang (FSD),

C. Windisch (ESTD)

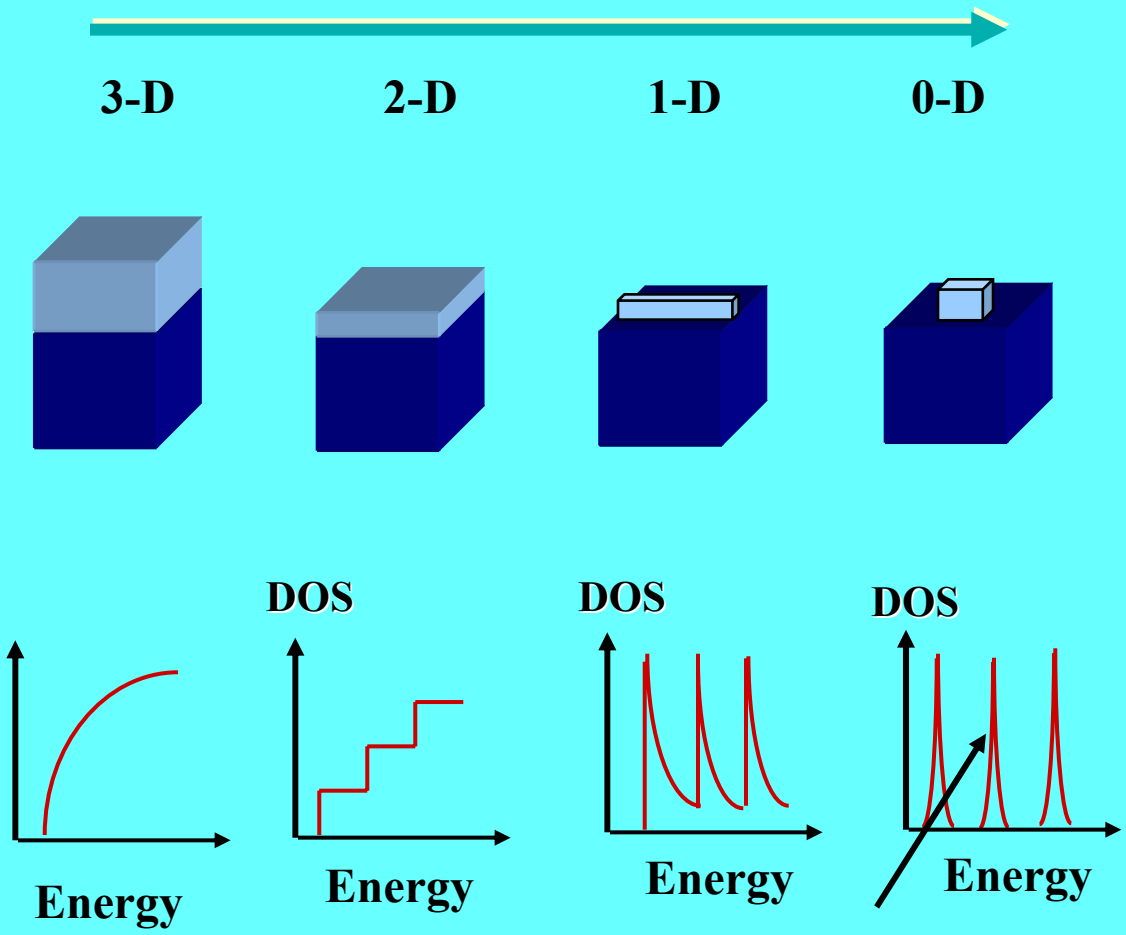
W. K. Pitts, M. Bliss (NSD)

- **Poster Topics:**
  - Quantum Dots(QDs), Oxide QDs and opportunities
  - Formation and Properties of Cu-Oxide Quantum Dots
  - Model of Cu-Oxide ring formation
  - Potential Applications

Battelle

U.S. Department of Energy
Pacific Northwest National Laboratory

# *Interface Controlled, Self-Assembled Oxide Quantum Dots and Quantum-Dot Molecules*




Atom-like behavior

**Quantum dots – Artificial Atoms**

*F. Julien et al, Science, 282 1429 (1998).*

**Our Focus**

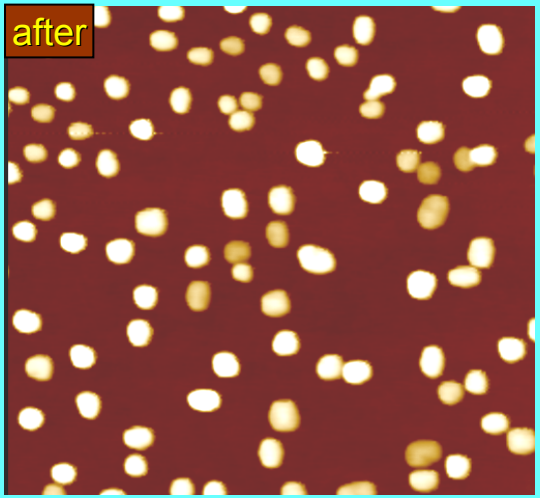
- **Interface control**
- **Self-assembly**
- **Oxides**

# Needs and Opportunities

- Quantum dots (QDs) have potential to impact several areas of importance to DOE:
  - Clean fuel production
  - Carbon management
  - Radiation detection
  - Fundamental properties
- Most QD work has focused on conventional semiconductor materials with a focus on optoelectronic (laser) and electronic properties
- Issues
  - Standard semiconductor materials need to be capped or stored in an inert environment and are not useful most “chemical” applications
  - Need for self ordering in 2d and 3d

# Robust Oxide Quantum Dots

- **New Class – Oxide Quantum Dots**
  - Can have high chemical and thermal stability
  - Wide range of material properties
  - Builds on our knowledge of growth of oxides and control of interfaces




**$Cu_2O$ quantum dots after exposure to water and intense light**

## Oxide Quantum Dots

# Technical Approach –Structure, Mobility and Lateral Ordering

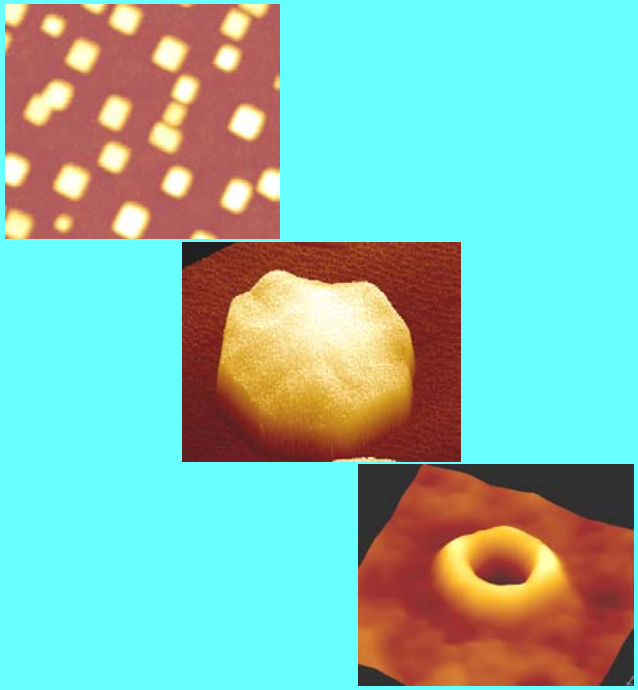
### Importance

- Artificial atoms combine to form artificial molecules
- Structure of QDs controlled by surface and interface energies and QD interactions
- Enhance/control functionality and stability

### Current Status

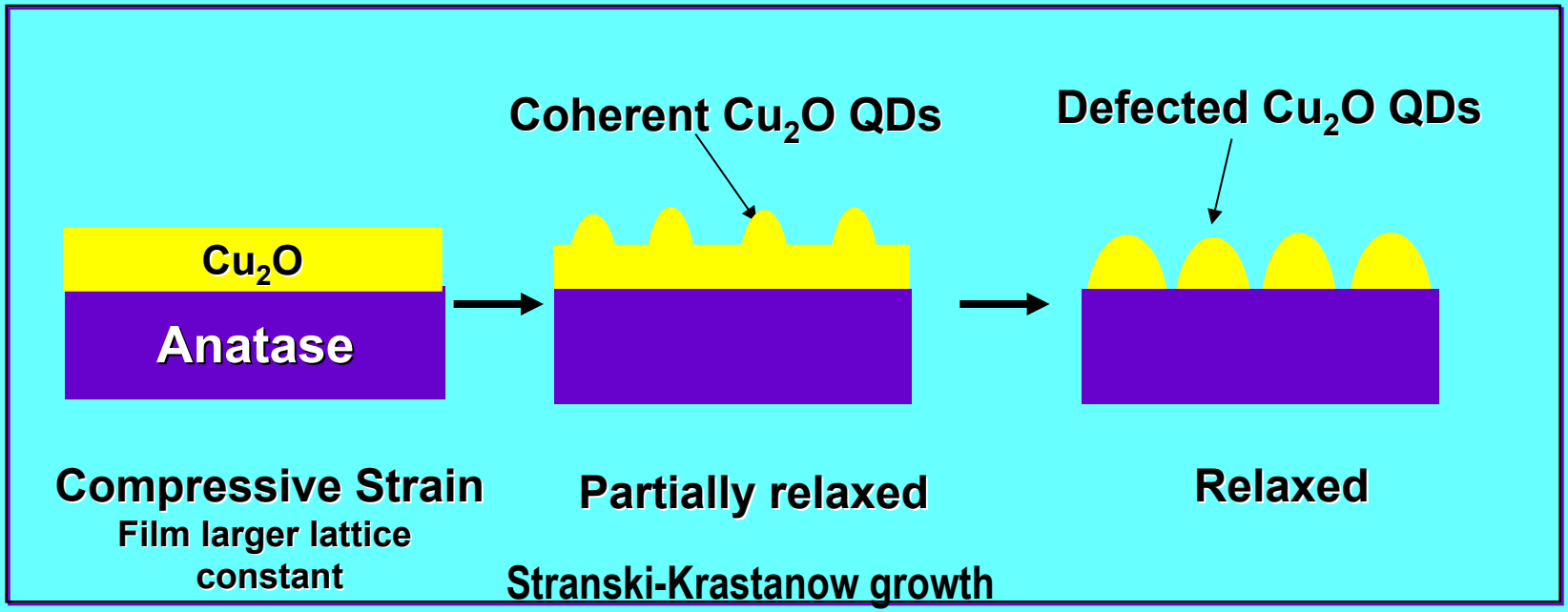
- We have observed the structure evolution and QD interactions observed for $Cu_2O/SrTiO_3$
- Controlled by synthesis and process conditions
- Theory of formation initiated for corrals and other structures
- Pt Diffusion on $TiO_2$ measured and examined by theory

**$Cu_2O$ on $SrTiO_3$ - Self organization into a variety of structures**



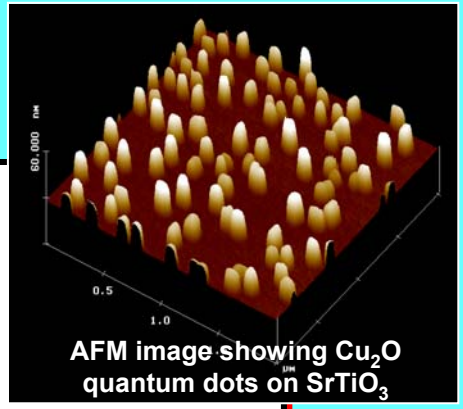
# Technical Approach

Grow in MBE System
Self Formation of Quantum Dots - $Cu_2O$ on $TiO_2$



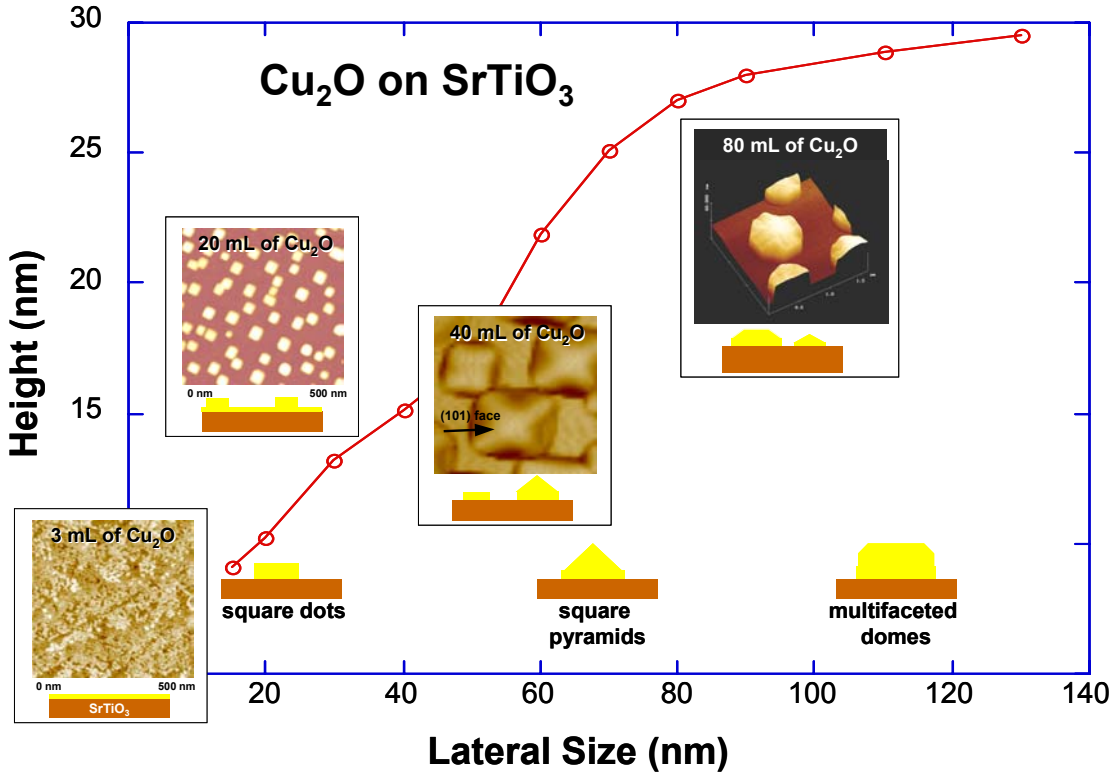
# Variety of QD Structures formed in Different Conditions

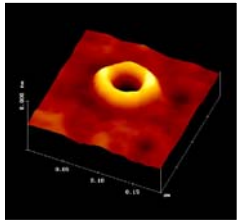
*Oxide QDs (nanoclusters with atomic-like properties) have potentially useful photochemical, ferroelectric, magnetic, and electronic properties that may not occur in conventional semiconductors.*




AFM image showing $Cu_2O$ quantum dots on $SrTiO_3$

## Self organization into a variety of structures

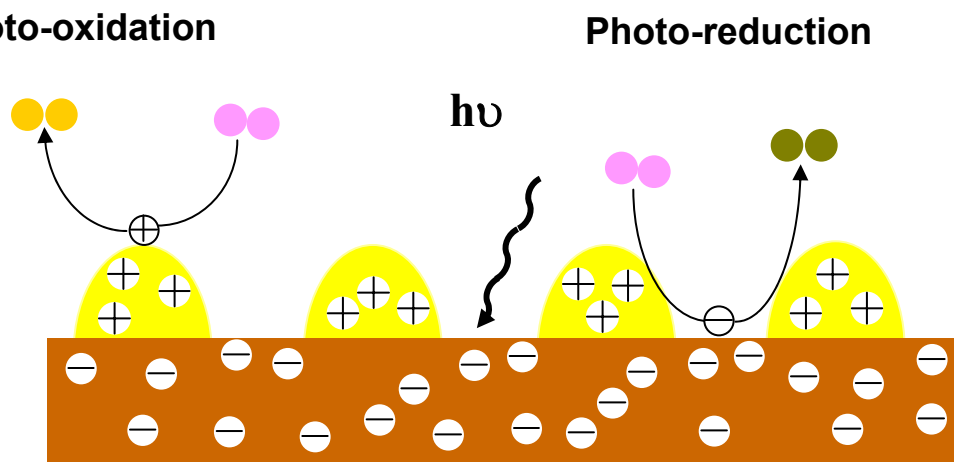


Ring structures form under different process conditions.

# Quantum Dots Created by Molecular Beam Epitaxy (cont)

**Potential for enhanced photocatalysis: water splitting and organic destruction**

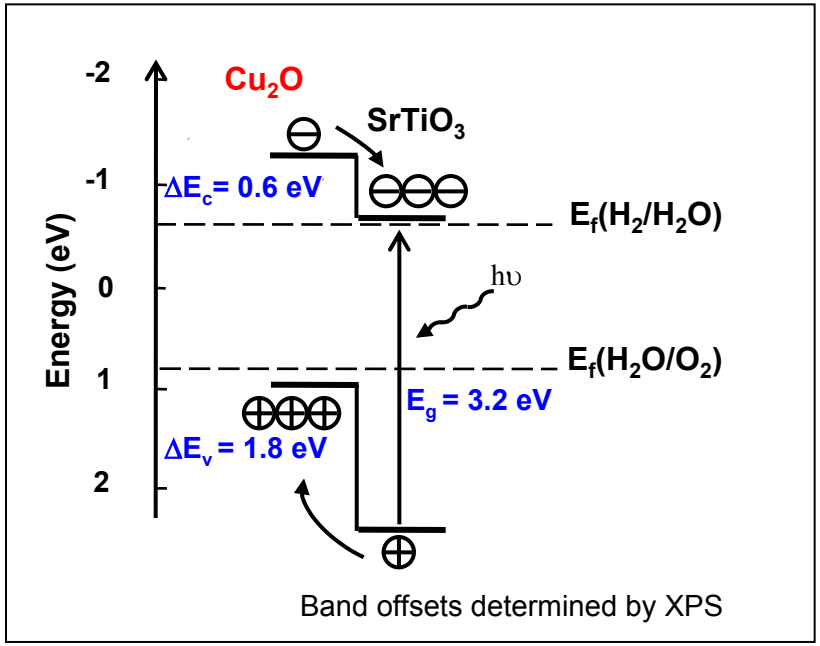



$$2H_2O \xrightarrow{h\upsilon} 2H_2 + O_2$$

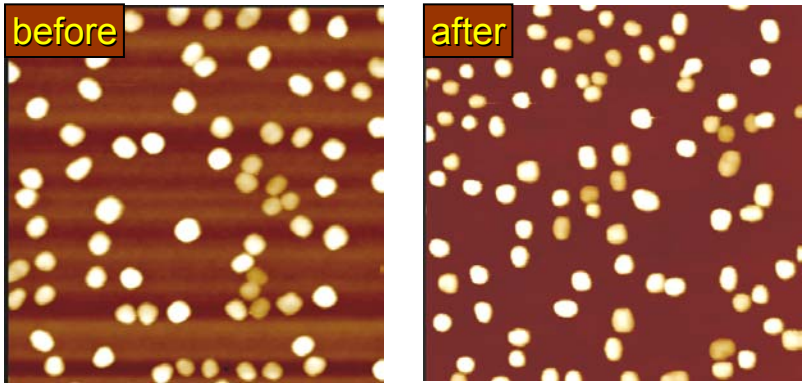
- Need to pick energy levels and band alignment to
  - separate charge
  - increase adsorption of solar spectrum
  - split water.
- Must form system that is stable in water.

# Quantum Dots Created by Molecular Beam Epitaxy (cont)

## Proper energy levels for separating charges and splitting water



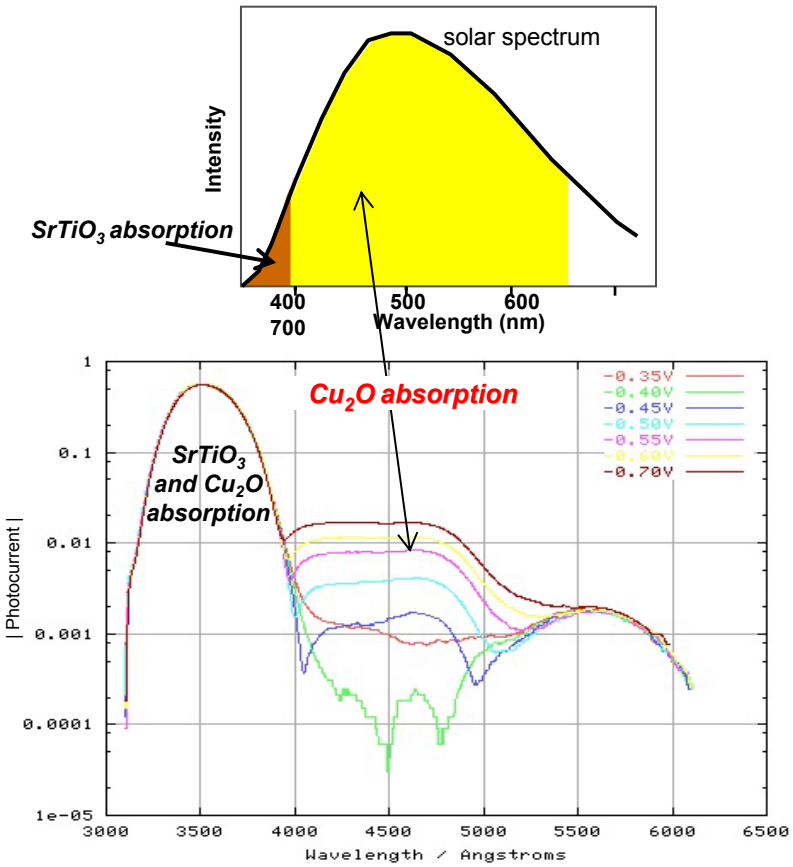

## Stable in water




$Cu_2O$ quantum dots remain stable in water under intense light irradiation.

# Quantum Dots Created by Molecular Beam Epitaxy (cont)

## Better match to solar spectrum




Because the $Cu_2O$ band gap is less than that for $SrTiO_3$, light is absorbed at lower energies (longer wavelengths). This means that the $Cu_2O$ absorbs a larger portion of the solar spectrum.

During AC photocurrent measurements in a 0.1M $Na_2SO_4$ solution, it was possible to selectively measure the photochemical signals from $Cu_2O$ by using wavelengths above 400 nm.

# Summary of Results

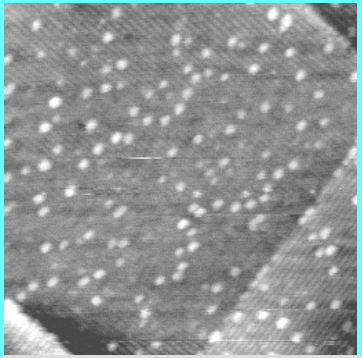
## Structure and Properties of $Cu_2O$ QDs formed on $SrTiO_3$

- Formed OQDs of various shapes and configurations
- Measured photo-electrochemical behavior of OQD
- Developed Model of nano-ring formation
- Presented Invited Paper on Synthesis and Characterization of Self-Assembled $Cu_2O$ Nano-Dots, at Electrochemical "Synthesis and Characterization of Self-Assembled $Cu_2O$ Nano-Dots," in *State-of-the-Art Application of Surface and Interface Analysis Methods to Environmental Material Interactions: In Honor of James E. Castle's 65th Year* , edited by D.R. Baer, C. R. Clayton, G. P. Halada, G. D. Davis, PV 2001-5, (2001 The Electrochemical Society, Washington, DC) page 125.

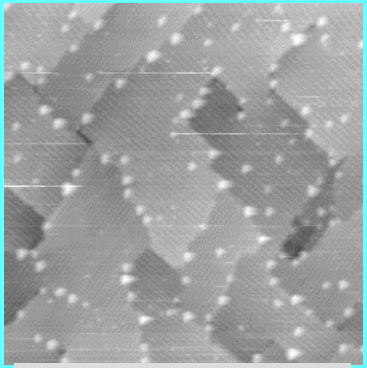
## Influence of Oxide Surface Structure on Nanoparticle Stability

**Pt cluster formation and movement on $TiO_2$**

- Formation and Diffusion of Pt nanoclusters on highly corrugated anatase $TiO_2$ (001)-(1x4) surface, Surface Science Letters 479 (2001) L369-L374),
- Effects of titania surface structure on the nucleation and growth of Pt nanoclusters on rutile $TiO_2$(110) Surface Science 475:159-170)
- Diffusion of Pt Nanoclusters on Anatase $TiO_2$(001)-(1x4) Surface accepted Surface Science



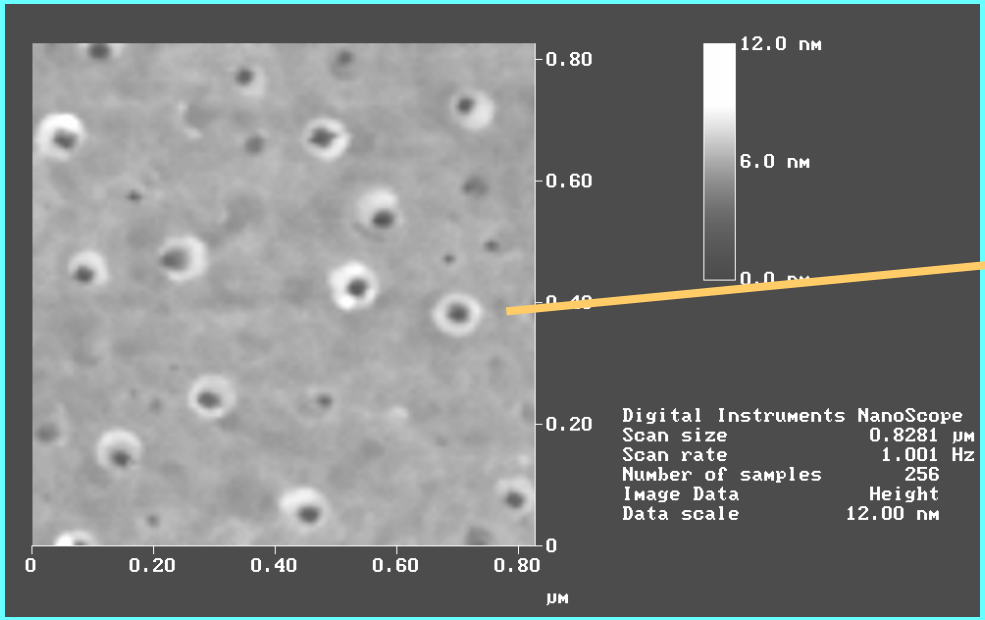
Prior to annealing

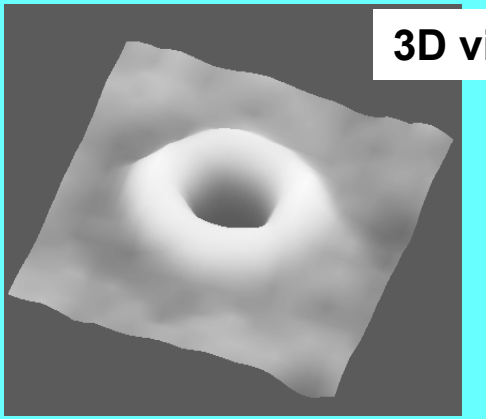


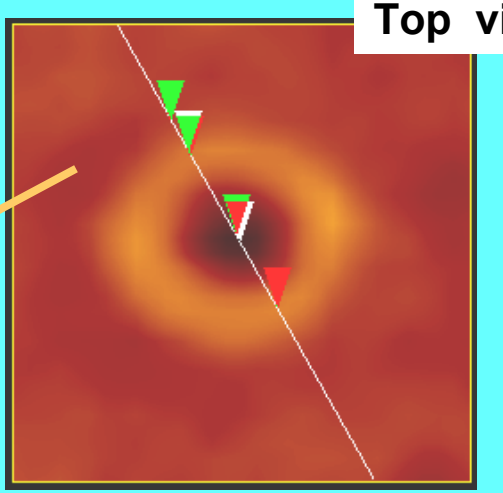
After annealing

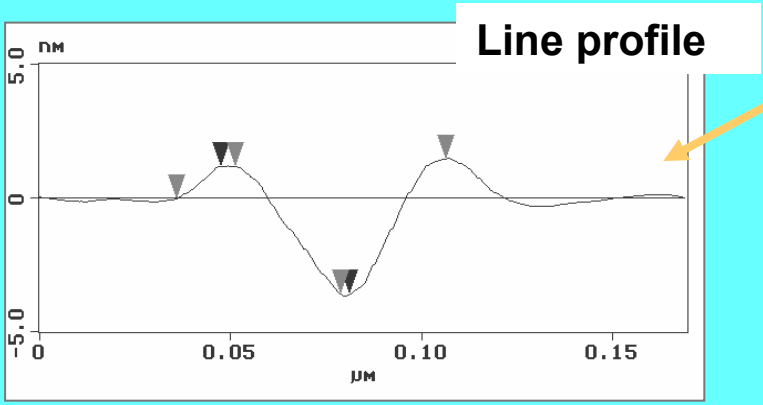
# Self-Assembled Nano Ring Structure

**Self-assembled $Cu_2O_x$ quantum rings obtained by O-plasma processing of pre-deposited Cu film on $SrTiO_3$**



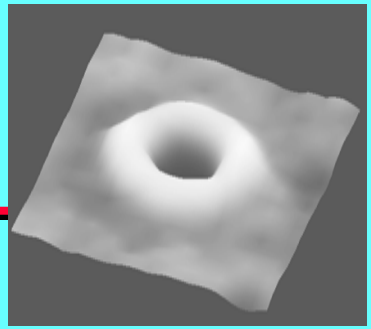




Battelle

U.S. Department of Energy
Pacific Northwest National Laboratory

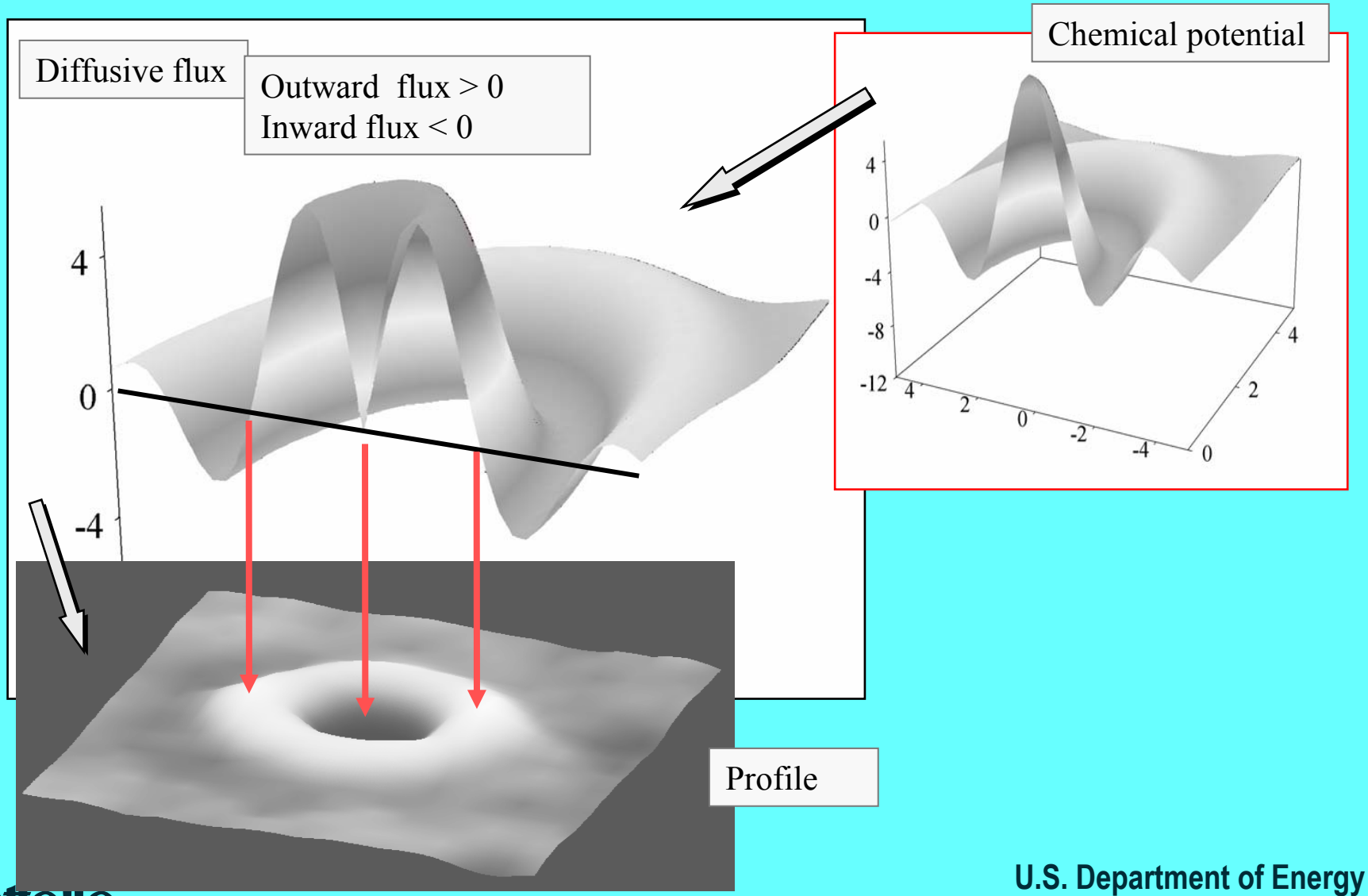
# Model: Phenomenology and Assumptions



- Initial film non-epitaxial
- Raise temp for processing—thermal strain in film
- Nucleation of small surface defects—due to interaction with plasma
- This induces chemical potential gradient on surface and drives surface diffusion
- Copper evaporation from the surface due to interaction with plasma

- **MODEL**: Stress-driven surface morphological instability leading to ring formation

# Chemical Potential and Diffusive Flux



# Surface Profile

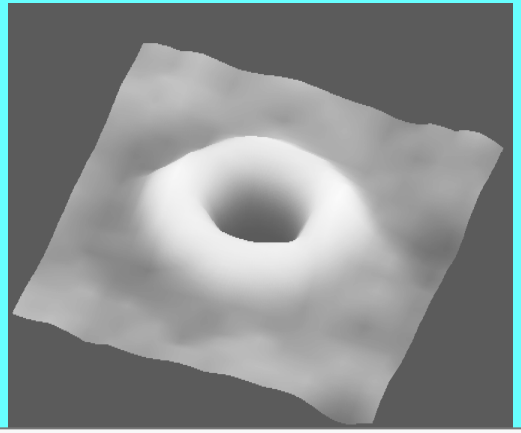
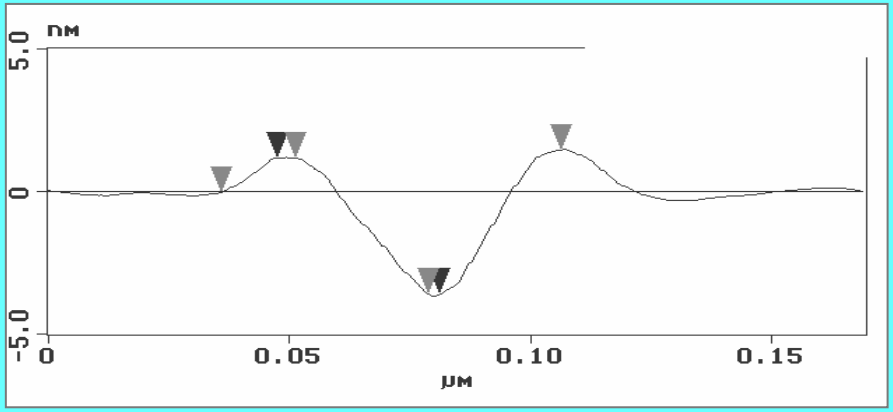
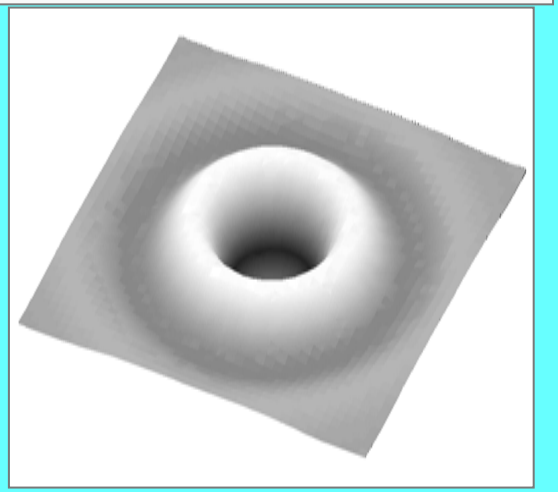
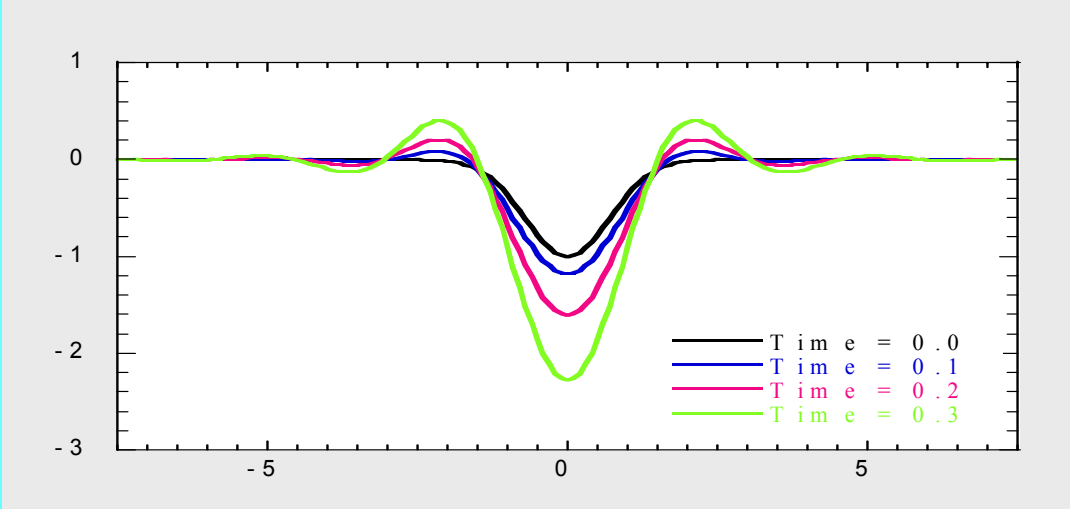


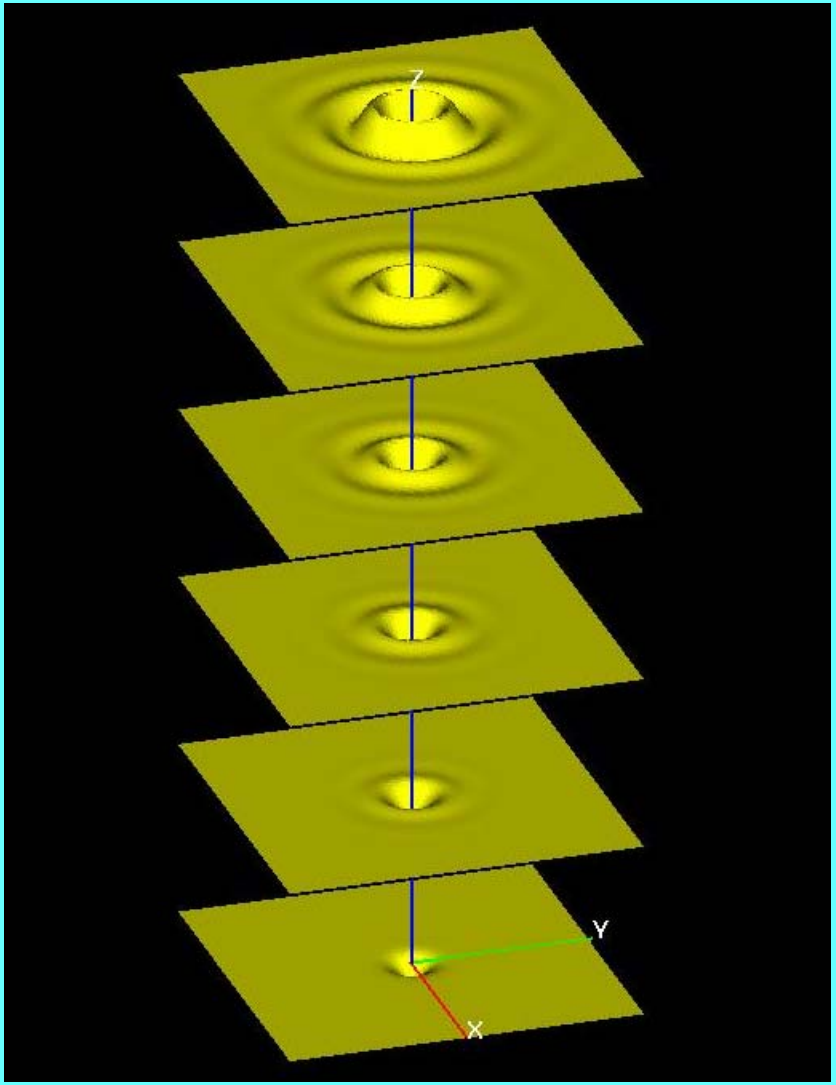
Image size 150 nm x 150 nm (simulation versus exp.)



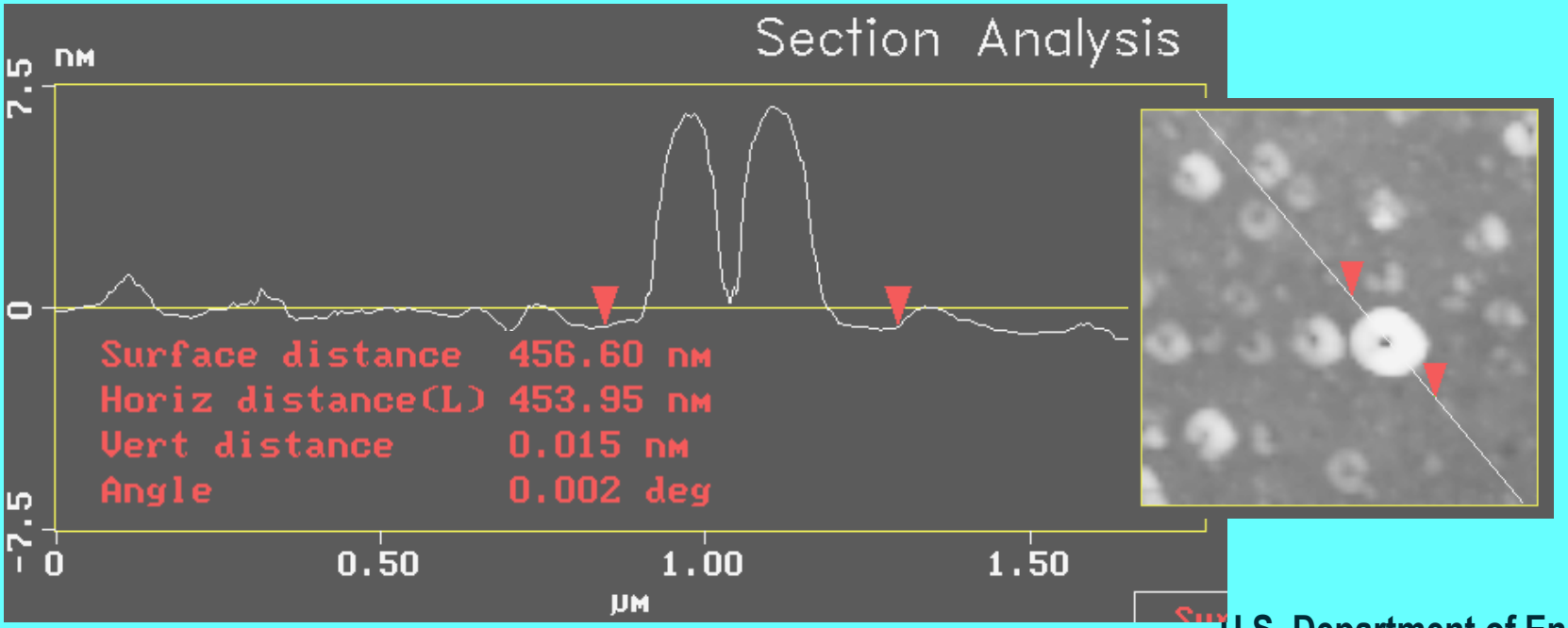





# Initial Growth of a Single Ring




time

# Final Growth Regime

- Film thinning due to evaporation
- Eventual STO terrace exposure
- Film becomes epitaxial as it becomes thinner
- Oxide phase--epitaxial