Artificial Structures Through Layer-by-Layer Growth

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Materials 286G
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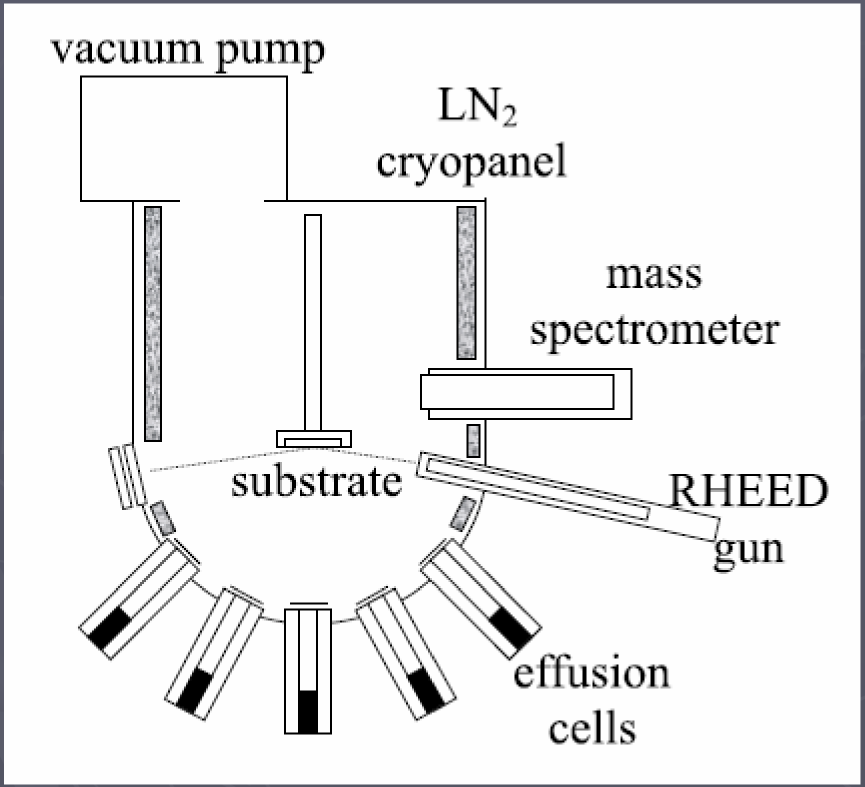
Overview

- Motivation
- Tools for Growth
- Factors Influencing Stabilization
- Representative Structures
- Surface Engineering

Motivation

- Structural Control
  - New and Metastable Phases
  - Surface Properties
- Magnetic Tunneling Junctions
- Wear and Oxidation Resistance
- Thin Film Transistors
- Improved Solar Cells

Molecular Beam Epitaxy

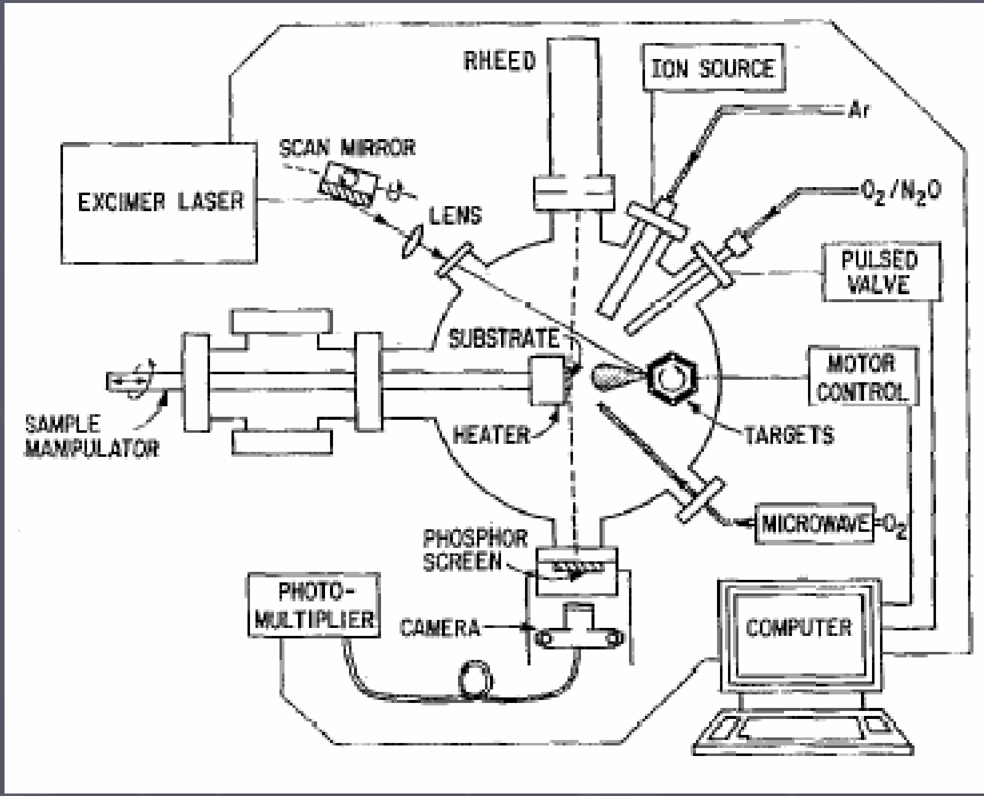


F. Rinaldi. Annual Report 2002, Optoelectronics Department, University of Ulm

- Growth occurs through slow evaporation of components
- Composition controlled through opening and closing of mechanical shutters
  - Allows control to the monolayer level

Pulsed Laser Deposition

- Target consists of stoichiometric pellets of starting materials
- Laser superheats target resulting in a plasma plume that coats the substrate
- Plume has same stoichiometry as pellet



M. Y. Chern, A. Gupta and B. W. Hussey, Appl. Phys. Lett. 60, 3045 (1992)

Thermodynamic Stabilization

- Stabilization Increases with
  - Decrease of film thickness
  - Increasing coherency between substrate and growing crystal
  - Decrease of shear and elastic moduli of growing crystal
  - Ability to form periodic multiple-domain structures

Gorbenko, O.Y.; Samoilenkov, S.V.; Graboy I.E.; Kaul, A.R.; Chem. Mater. 2002, 14, 4026-4043

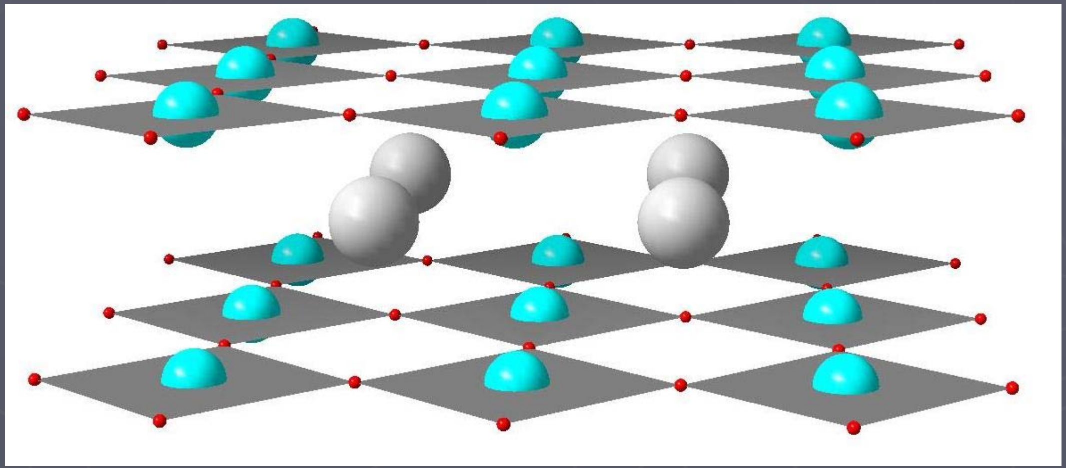
Kinetic Stabilization

- Determined by growth conditions
  - Substrate temperature, annealing etc
    - Pt will only wet $SrTiO_3$ surfaces at low temperatures
- High surface diffusion
  - Enables growth of oriented crystal phases
- Low bulk diffusion
  - Prevents phase transformations

Gorbenko, O.Y.; Samoilenkov, S.V.; Graboy I.E.; Kaul, A.R.; Chem. Mater. 2002, 14, 4026-4043

$(Ca,Sr)CuO_2$

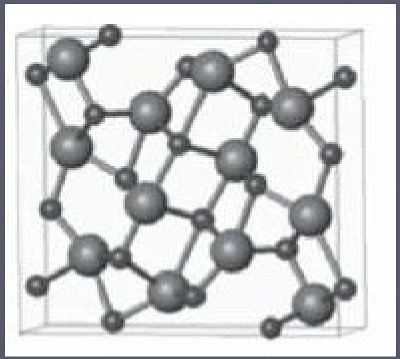
- $CaCuO_2$ is highly metastable and difficult to grow except in layer-by-layer deposition



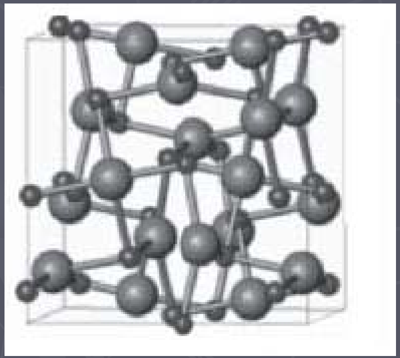
- Terminating CuO_2 from $SrCuO_2$ layer acts as a template that stabilizes and promotes nucleating of $CaCuO_2$ layers
- Creation of $(Ca,Sr)CuO_2$ layers is fundamental in the creation of superconducting thin films

Cubic-Zr_3N_4

- Grown with a modified filtered cathodic arc (FCA)
  - Metal vapour generated by an arc discharge on pure zirconium cathode reacted with fully ionized atomic nitrogen



orthorombic-Zr_3N_4



cubic-Zr_3N_4

- Bulk growth requires pressures up to 18 GPa and temperatures on the order of 2500-3000K
- Cubic form is significantly harder (~36 GPa) than orthorhombic (~27 GPa)

Chhowalla, M.; Unalan, H. E.; Nature Materials 4, 317-322

Surface Properties

- Surfaces are not typically smooth

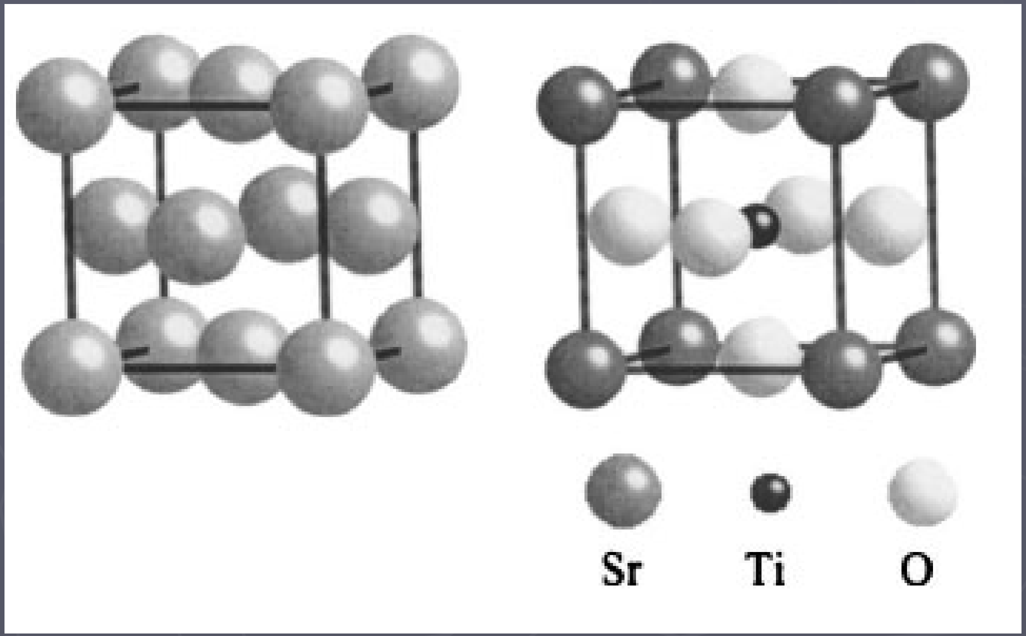
AFM Image of $La_{0.67}Ca_{0.33}MnO_3$ grown on $SrTiO_3$ (001)

- Formation of island structures is common during epitaxial growth
  - Form with increasing film thickness
- Smooth surfaces are desirable for most applications

Sanchez, F.; Infante, I.C., Abad, Ll.;Luders, U.; Martinez, B.; Fontcuberta, J.; Thin Solid Films. 495 (2006) 154-158

Surface Properties

- Platinum crystallizes in an FCC structure with a very similar shape to that of the perovskite



Unit cell representations of (a) Pt and (b) SrTiO3. Atoms for (b) are indicated.

AJ Francis, PA Salvador, J. App. Phys. **96**, 5, pp. 2482-2493

Surface Properties

- Pt deposited on $SrTiO_3$ (6 2 1) exhibits chiral centers at kink points
- Shows great potential for application in catalysis and enantiomeric selection

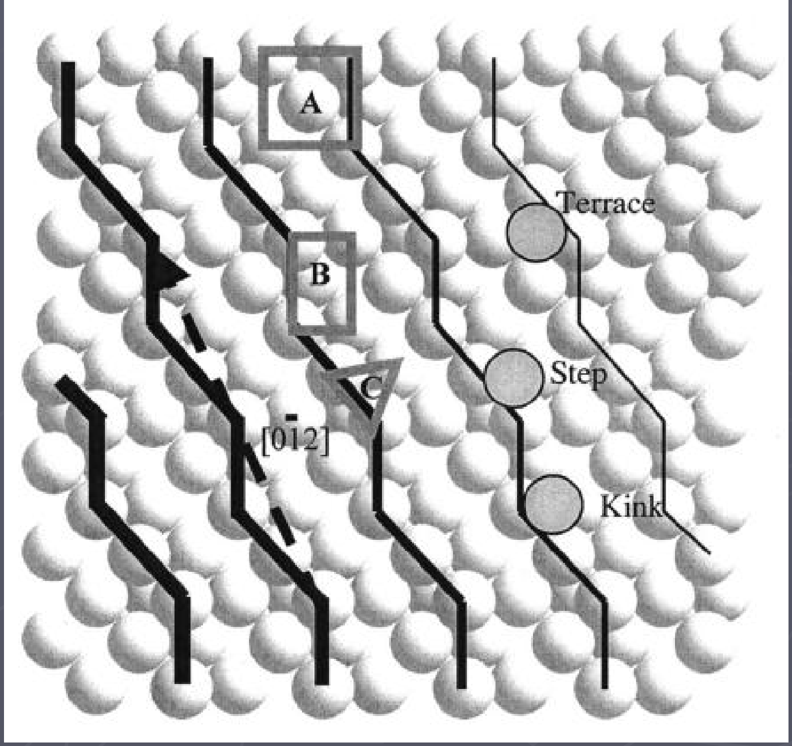


Illustration of surface structure of Pt grown on (6 2 1) $SrTiO_3$ Bolder lines indicate planes coming out of the board at the viewer

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Conclusions

- Thin film growth present the opportunity to stabilize phases normally not stable in the bulk
- PLD and MBE allow for robust growth techniques
- Surface structures can be tailored by manipulating the crystallographic angles of the substrate.