Artificial Structures
Through Layer-by-Layer Growth

Brent Melot
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Ram Seshadri
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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

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

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

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

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

(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-$\text{Zr}_3\text{N}_4$

- 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
- 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)

Surface Properties

- Surfaces are not typically smooth
- Formation of island structures is common during epitaxial growth
  - Form with increasing film thickness
- Smooth surfaces are desirable for most applications

AFM Image of La$_{0.67}$Ca$_{0.33}$MnO$_3$ grown on SrTiO$_3$ (001)

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.

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.

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.