Self-assembly and Guided self-organization of oxide nanostructures from chemical solutions

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**MOTIVATION AND AIM OF THE WORK**

- **Nanotechnology** aims the low-cost and mass fabrication of increasingly small devices required for present and future applications.

**APPROACHES**

**Top-down**
- e-beam lithography
- X-ray/UV lithography
- μC-printing
- Focused Ion Beam
- Nanoimprint Lithography (NIL)
- SPM...

**Bottom-Up**

Self-assembly and Self-organized growth at surfaces
- supramolecular engineering
- metallic, semiconductor and oxide nanostructures...

Our interest: self-assembling of oxide nanostructures with substrate modification through **NANOINDENTATION**, Focused Ion beam, …

**Single crystal oxide nanostructures**
SELF-ASSEMBLY OF NANOISLANDS

Working Framework: THERMODYNAMICS

Liquid nucleus in equilibrium model

γsv = γfs + γfv \cos θ

Young's equation

γsv = γfs + γfv \cos θ

Heteroepitaxy

\{ Surface Free Energy (∼γ) \\
Elastic Relaxation Energy (∼ε²; \ ε = (a_s - a_f)/a_f) \}

ΔE \sim ΔE_{surf.} + ΔE_{elast. relax.}

3 Growth Modes

• 3D growth (Volmer-Weber)
  γsv < γfs + γfv

• 2D (Frank van der Merwe) growth
  γsv > γfs + γfv

• Layer + Island growth (Stranski-Krastanov)
  (ex; when strain energy due to lattice mismatch is present)

BUT...

B. Voigtländer/Surface Science Reports 43 (2001)
Working Framework: KINETICS

Real growth phenomena are non-equilibrium

Barth et al. NATURE 2005 Vol 437 I 29

D → Diffusivity
F → Deposition rate

Chemical Solution Deposition (CSD)

CSD Vs Vacuum Techniques:

- Low Cost
- Scalable
- Rapid

Different initial conditions!
CHEMICAL SOLUTION DEPOSITION (CSD)

1 Precursor solution synthesis (of a given concentration)

   e.g. Ce$_{1-x}$Gd$_x$O$_{2-y}$ metallorganic precursor solution preparation (MOD-CSD)

2 Solution Deposition by Spin Coating onto the substrate

3 Heat treatment

PYROLISIS of the organic species (~300ºC/400ºC)

High temperature treatment for the amorphous layer crystallization

• X (III) 2,4-pentanedionato

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O}^{-} \quad \text{O}^{-} \\
& \quad \text{CH}_3 \quad \text{X}^{3+}
\end{align*}
\]

X = Ce, Gd

• Isopropanol

• Propionic acid

Growth Atmosphere: O$_2$, Ar-H$_2$

Islands’ characteristics (size, morphology,...) can be tuned through the kinetic parameters (temperature, atmosphere, dwell time,...)
CSD: A general tool for nanostructured template fabrication

Fluorite: Ce$_{1-x}$Gd$_x$O$_{2-y}$

YSZ$_{fluorite}$

LaAlO$_3$_perovskite

Cubic: Re$_2$O$_3$

Perovskite: BaZrO$_3$

AIR

NdGaO$_3$_perovskite

SrTiO$_3$_perovskite

0.5 μm

Strain induced interfacial self-assembled nanostructures

Ce$_{1-x}$Gd$_x$O$_{2-y}$ (CGO)/LaAlO$_3$: a system of interest

- **Wide range of applications:**
  - Catalysis, optical properties, ionic conductivity, dielectric properties, buffer layer, nanostructured templates for high T$_c$ superconductors...

- **Oxide Heteroepitaxy:** fluorite (Ce$_{0.9}$Gd$_{0.1}$O$_{2-y}$) over perovskite (LaAlO$_3$) structure

  Ce$_{0.9}$Gd$_{0.1}$O$_{2-y}$ (CGO)
  
  a$_{CGO}$$\approx$ 5.41 Å

  LaAlO$_3$ (LAO)
  
  a$_{LAO}$ = 3.79 Å

Thermally treated perovskite single crystal substrates show atomically flat terraces

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A.Benedetti, F.Sandiumenge
ICMAB-CSIC
NANOINDENTATION: A tool for nanopatterning

- A sharp diamond tip is driven into and withdrawn from the material
- Ultra low loads are used (< 10mN) and small deformations induced (<100nm)

The equipment

- Force actuator
- Force, $P$
- Machine compliance, $C_m$
- Displacement sensor
- Displacement, $h$
- Indenter
- Specimen

The tip

- Top-down and lateral views of a Berkovich tip

The Indentation

- The Scratch
Nanoindentation on perovskite type substrates: tuning of the parameters

SCRATCH

INDENTATION

Extremely low-loads in the 0.05mN-0.6mN range are of interest

\[ Y(\text{nm}) = 19.86 \times X(\text{mN}) \]

\[ Y(\text{nm}) = 27.15 \times X(\text{mN}) \]

\[ d \sim 6 \pm 1 \text{ nm} \quad \text{and} \quad \text{w} \sim 140 \pm 20 \text{ nm} \]

\[ \text{Load Applied (mN)} \]

\[ \text{Penetration depth (nm)} \]

\[ \text{nm} \]

\[ \mu \text{m} \]

\[ 0,25 \text{ mN} \]

\[ 0,0 \ 0,1 \ 0,2 \ 0,3 \ 0,4 \ 0,5 \ 0,6 \]

\[ 0 \ 0.5 \ 1 \ 1.5 \ 2 \ 2.5 \ 3 \ 3.5 \ 4 \ 4.5 \ 5 \]

\[ 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \]

\[ 0 \ 0.2 \ 0.4 \ 0.6 \ 0.8 \ 1 \ 1.2 \ 1.4 \ 1.6 \ 1.8 \ 2 \ 2.2 \ 2.4 \ 2.6 \]

\[ 0 \ 0.5 \ 1 \ 1.5 \ 2 \ 2.5 \ 3 \ 3.5 \ 4 \ 4.5 \ 5 \]

\[ 0 \ 0.2 \ 0.4 \ 0.6 \ 0.8 \ 1 \ 1.2 \ 1.4 \ 1.6 \ 1.8 \ 2 \ 2.2 \ 2.4 \ 2.6 \ 2.8 \ 3 \ 3.2 \ 3.4 \ 3.6 \ 3.8 \ 4 \]

\[ 0 \ 1 \ 2 \ 3 \ 4 \ 5 \ 6 \ 7 \ 8 \]

\[ \text{nm} \]

\[ \mu \text{m} \]

\[ 0 \ 0.5 \ 1 \ 1.5 \ 2 \ 2.5 \ 3 \ 3.5 \ 4 \ 4.5 \ 5 \]

\[ 0 \ 0.2 \ 0.4 \ 0.6 \ 0.8 \ 1 \ 1.2 \ 1.4 \ 1.6 \ 1.8 \ 2 \ 2.2 \ 2.4 \ 2.6 \]

\[ 0 \ 0.5 \ 1 \ 1.5 \ 2 \ 2.5 \ 3 \ 3.5 \ 4 \ 4.5 \ 5 \ 6 \ 7 \ 8 \]

\[ 0 \ 2 \ 4 \ 6 \ 8 \]

\[ \text{Load Applied (mN)} \]

\[ \text{Penetration Depth (nm)} \]
Towards guided self-organization through Nanoindentation

CGO on SrTiO$_3$ (STO)

CGO on LaAlO$_3$ (LAO)
CGO nanowalls on LAO: the influence of scratches

<table>
<thead>
<tr>
<th>0.1 mN Scratches</th>
<th>POPULATION DISTRIBUTION</th>
<th>ISLAND-OCCUPIED AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>At Indentations</td>
<td>CGO [0-11] //LAO [010] ~ 99%</td>
<td>~40%</td>
</tr>
<tr>
<td>In between indentation lines</td>
<td>CGO [0-11] //LAO [010] ~ 60%</td>
<td>~5%</td>
</tr>
</tbody>
</table>
**DISCUSSION**

**Curvature (κ) dependent energy balance**

\[ E_{\text{island}} \sim E_{\text{surface}} + E_{\text{interface}} + E_{\text{elastic relax}} + \ldots \]

- **\( E_{\text{int}} \)**: related to chemical bonding among the interface atoms

\[ E_{\text{int}} \]

- **\( \kappa < 0 \)** concave

- **\( \kappa > 0 \)** convex

**\( E_{\text{elast relax}} \)**: related to the lattice mismatch between the solid crystalline materials

- **compressive (\( a_f > a_s \))**

- **tensile (\( a_f < a_s \))**

**CGO/LAO** grows under compressive strain

**Concave and convex surfaces** compete in lowering the local energy with respect to the flat substrate system’s energy.
Competition between the surface-energy and strain-energy terms leads to multiple local minima.

SUBSTRATE MORPHOLOGY INDUCED DIRECTED ORDERING

Nanowall LOCATION

Flat surface

Scratch

~2 nm

~60 nm

~10 nm
Why do nanowalls align their long axis with the Scratch direction?

The orientation in which the nanowall maximizes its location at an energy minimum will be favoured.
CONCLUSIONS

✓ CSD has been shown a general method for generation of self assembled oxide nanoislands

✓ Nanoindentation has successfully been used as a nanopatterning technique

✓ Guided Self-Organized $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-y}$ nanoisland growth has been evidenced

✓ The substrate curvature effect on the different energy contributions has been proposed to be responsible for the results observed in the CGO/LAO system
  - nanowall location at scratch edges is evidenced
  - pre-existing nanowall orientation balance is broken

The nanoislands’ kinetic evolution, under study, seems to give very rich phenomena suggesting further influence of the nanoindentation parameters

THANK YOU!