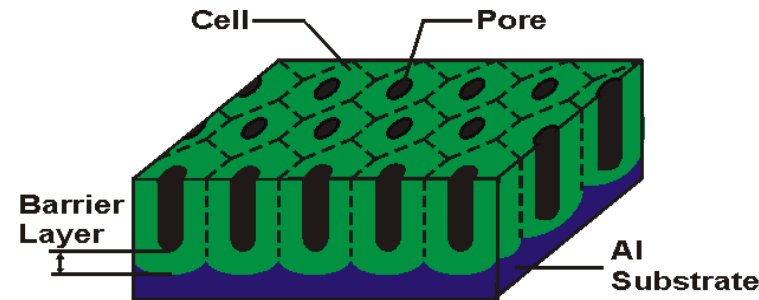


Session 10a

**Nano-Scale Structures Fabricated using Anodic
Aluminum Oxide Templates; Etching and
Thermal Evaportaion**

What is Anodic Porous Alumina?

- Aluminum oxide grown on an Al substrate in an electrolytic cell. The resulting structure consists of an array of **tunable** nanometer-sized pores surrounded by an alumina backbone.



Purpose:

- To understand the mechanisms involved in the growth and ordering of anodic porous alumina.

Motivation General

Motivation:

- Interest in using anodic porous alumina as a nano- template to fabricate nanometer-sized structures (e.g. nanofabrication of quantum dots).

Why do we want to fabricate nanostructures?

1. Fundamental physical interest in the nanometer size regime.
Properties of nano-sized structures are different from their bulk and molecular counterparts.
2. **Technological applications as electronic and optical devices.**

Motivation: Applications

1. Physics:

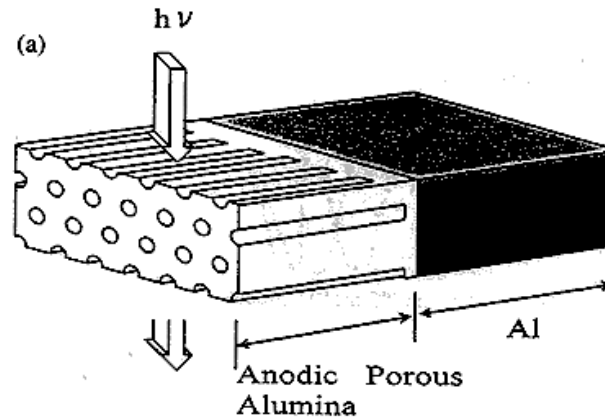
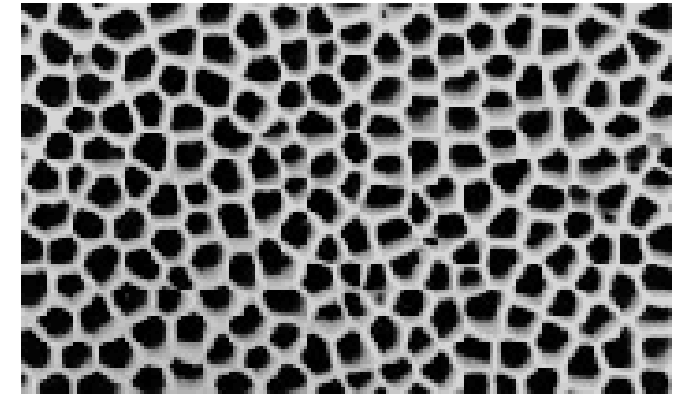
- Explore optical, electrical, and magnetic quantum confinement.

2. Engineering:

- Microfiltration.
- Optical waveguides and photonic crystals for optical circuits.
- Template for carbon nanotube growth for electronic, mechanical applications.
- Ordered arrays of quantum dots for lasers, photodetectors.
- Ultra Large Scale Integraton (ULSI) memory devices and Integrated Circuits (ICs)

Commercially available
Anopore filter.

http://www.2spi.com/catalog/spec_prep/filter2.html

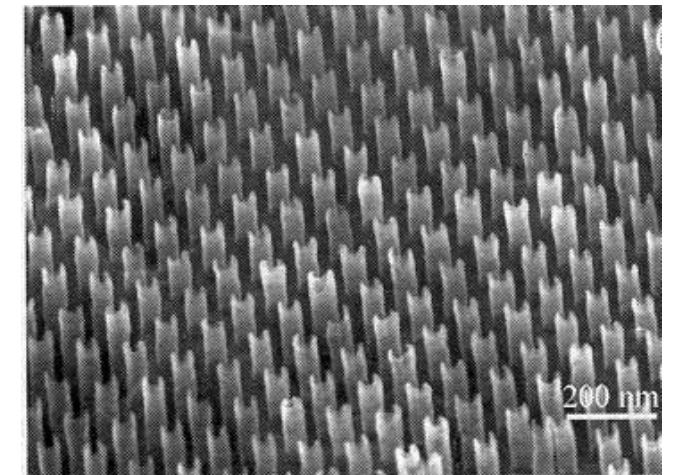


Porous Alumina used as optical
waveguide.

H. Masuda, et. al., *Jpn. J. Appl. Phys.*
38, L1403 (1999).

Ordered arrays of carbon
nanotubes fabricated using a
porous alumina template.

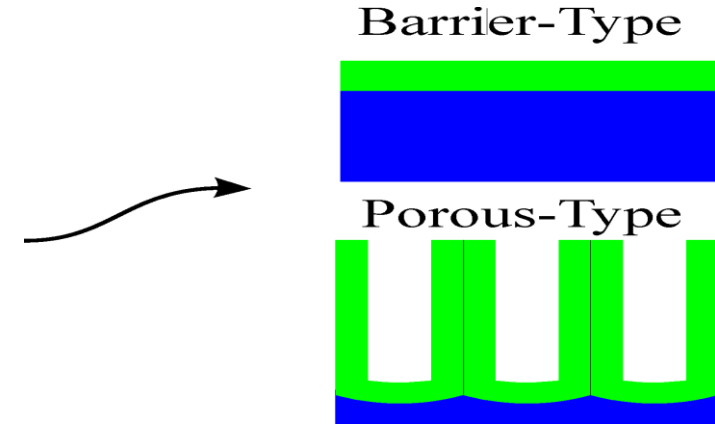
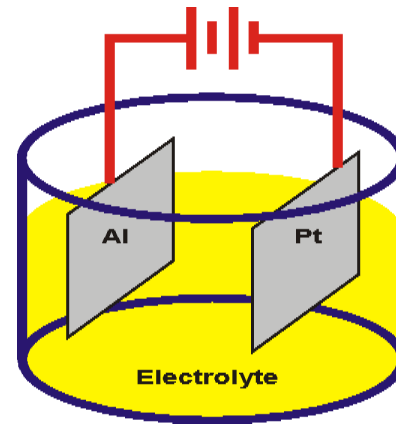
J. Li, et al., *Appl. Phys. Lett.*
75(3), 367 (1999).



Overview of Anodic Oxide Films

Fabrication

- Anodize aluminum in electrolyte
(*e.g.* Oxalic Acid)



Two main types of anodic oxide films can be grown depending on the nature of the electrolyte:

1. Barrier-Type Films:

- Grown Oxide Insoluble in Electrolyte
- Nearly Neutral Electrolytes (pH 5-7)

2. Porous-Type Films:

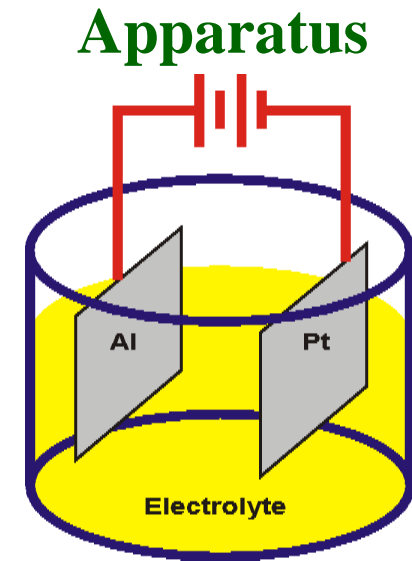
- Grown Oxide Slightly Soluble in Electrolyte
- Aqueous Sulfuric, Oxalic, and Phosphoric Acid Electrolytes

Historical Time Line

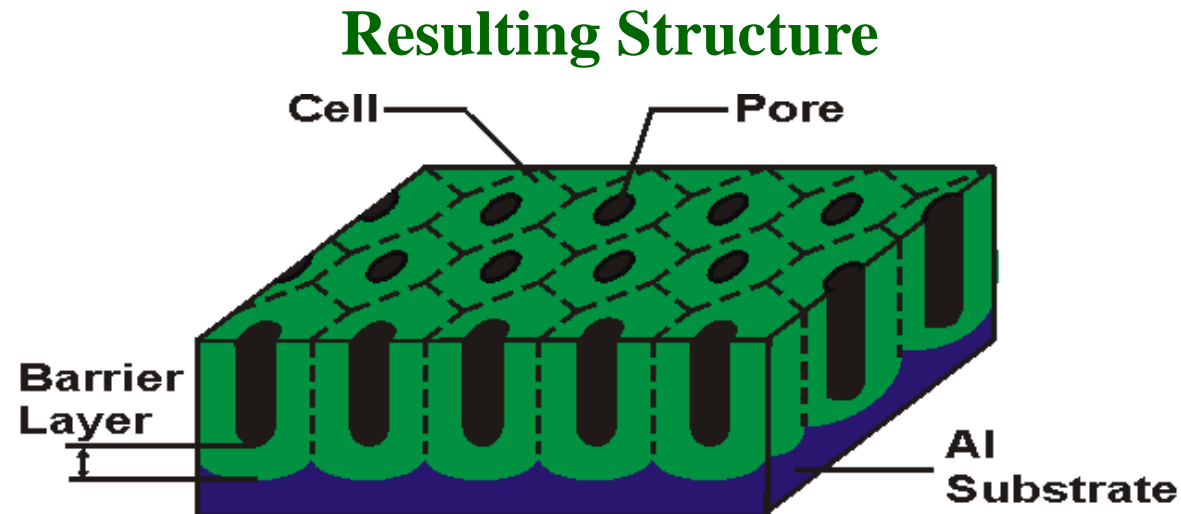
- **1920' s** Porous alumina starts to be used commercially to protect and finish bulk Al surfaces.
- **1940' s-1960' s** With advent of electron microscopes, first characterization of structure of porous alumina, but growth theories are experimentally unsubstantiated.
- **1970** Manchester group does first real experimental work showing pore radius dependence on applied voltage, etc.
- **1992** First “quantitative” theoretical attempt to explain pore growth from first principles by Belorus group.
- **1995** Japanese group discovers pores will self-order into close packed array under the right anodization conditions.
- **1996-Present** Use of porous alumina for nano-applications abound.
- **1998** Although mechanism for ordering still not clear, German group proposes one **possible** mechanism.

Historical Time Line

- Anodize aluminum in electrolyte (e.g. Oxalic Acid).
- Oxide grows at the metal/oxide and oxide/electrolyte interfaces, pores initiate at random positions by field-assisted dissolution at the oxide/electrolyte interface.
- Ordering requires appropriate potentials and long anodization times.
- Ordering results from repulsion between neighboring pores due to mechanical stress at the metal/oxide interface.



Porous Alumina

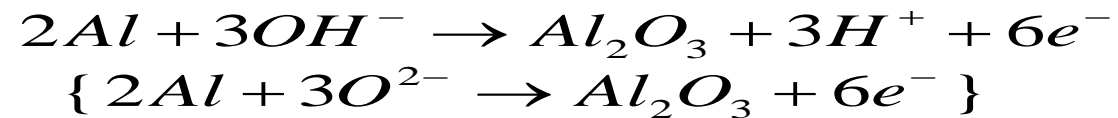


Barrier-Type Anodic Oxide Films

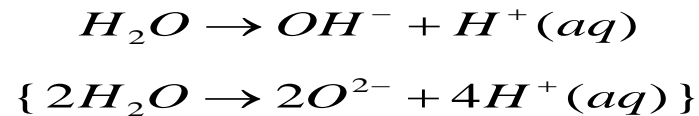
Growth Mechanism

- Oxide growth proceeds at the Aluminum anode (+).
- Hydrogen gas is evolved at the Platinum cathode (-).
- The current between the cathode and anode is carried by the electrolyte.

- Oxidation reactions at the Al anode



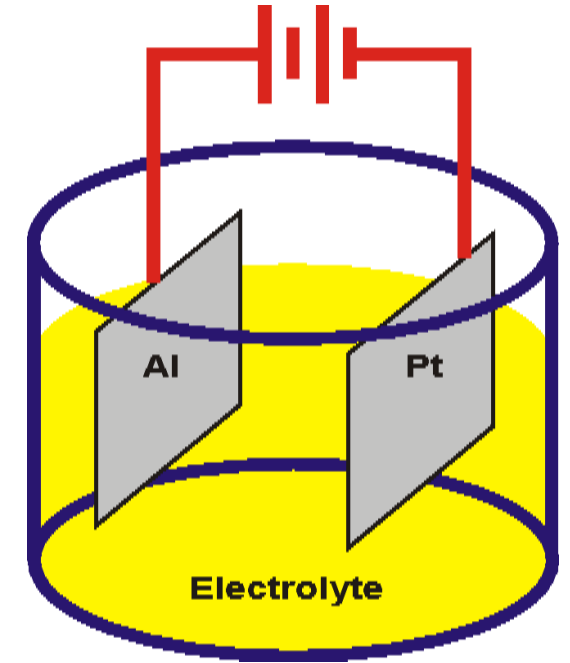
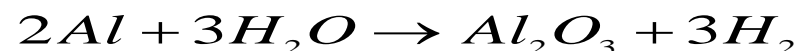
- Electrolysis of water at aluminum oxide/ electrolyte interface



- Reduction reaction at the cathode:



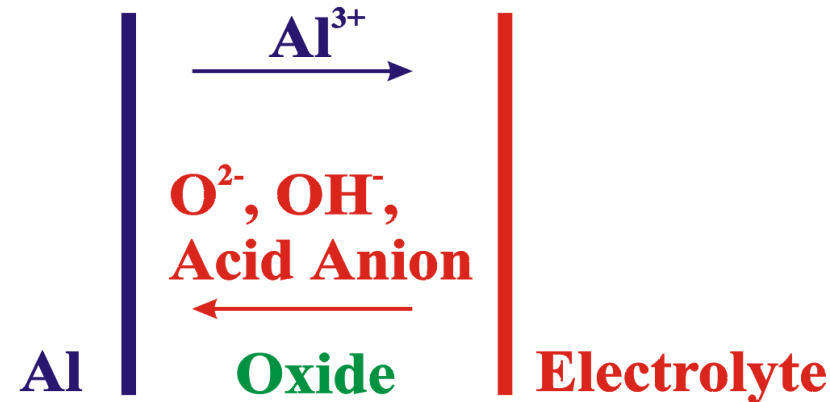
- The overall electrochemical reaction occurring is:



Barrier-Type Anodic Oxide Films

Growth Mechanism

- Oxide growth proceeds at the metal/oxide *and* the oxide/electrolyte interface.
- Growth proceeds due to the motion of ions under the applied field.

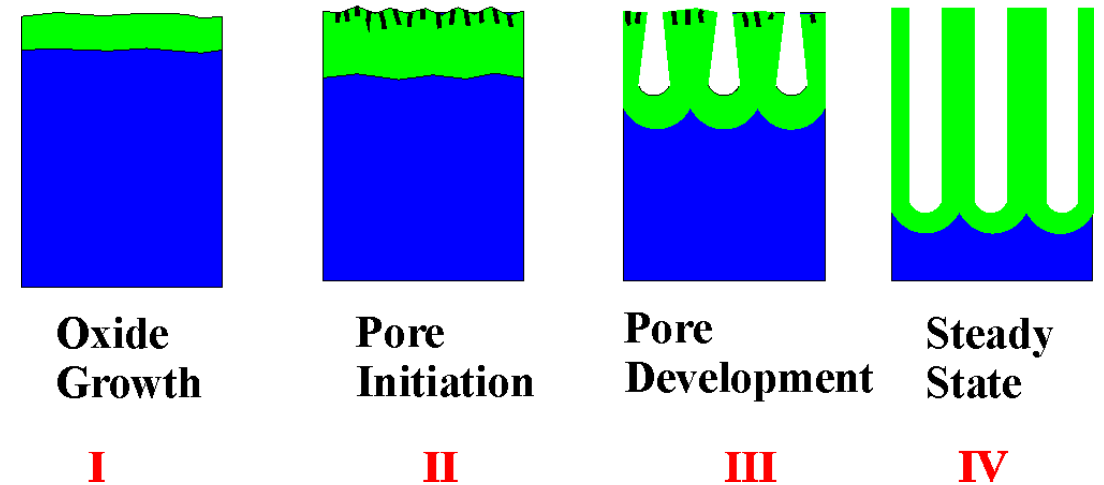
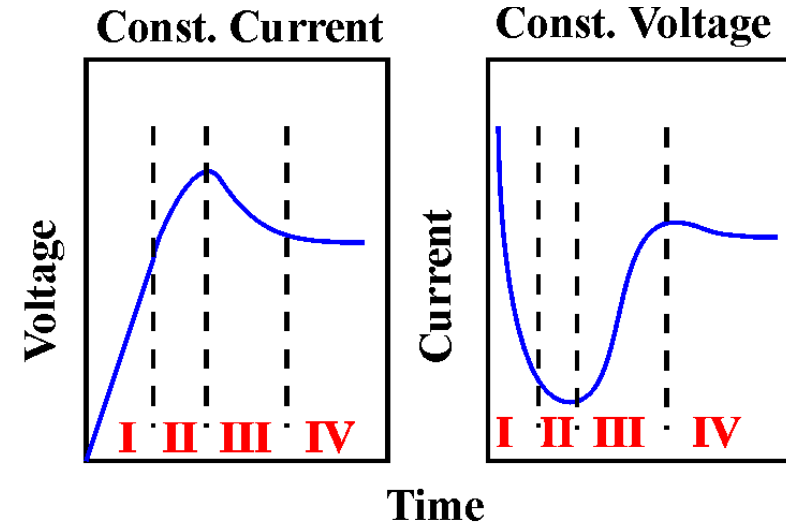


- Growth at the metal/oxide interface is due to oxygen containing anions (mainly OH^- and O^{2-}) moving through interstitial/vacancy sites.
- Growth at the oxide/electrolyte interface is due to Al^{3+} cations moving through interstitial/place exchange mechanisms.

Overview of Film Anodization

- Oxide growth proceeds via ionic conduction and reaction of Al cations and oxygen containing anions under the influence of an applied field.
(*e.g.* $2\text{Al}^+ + 3\text{OH}^- \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}^+ + 6\text{e}^-$)
- Pores initiate at random positions through field-assisted dissolution of the oxide at the oxide/electrolyte interface.

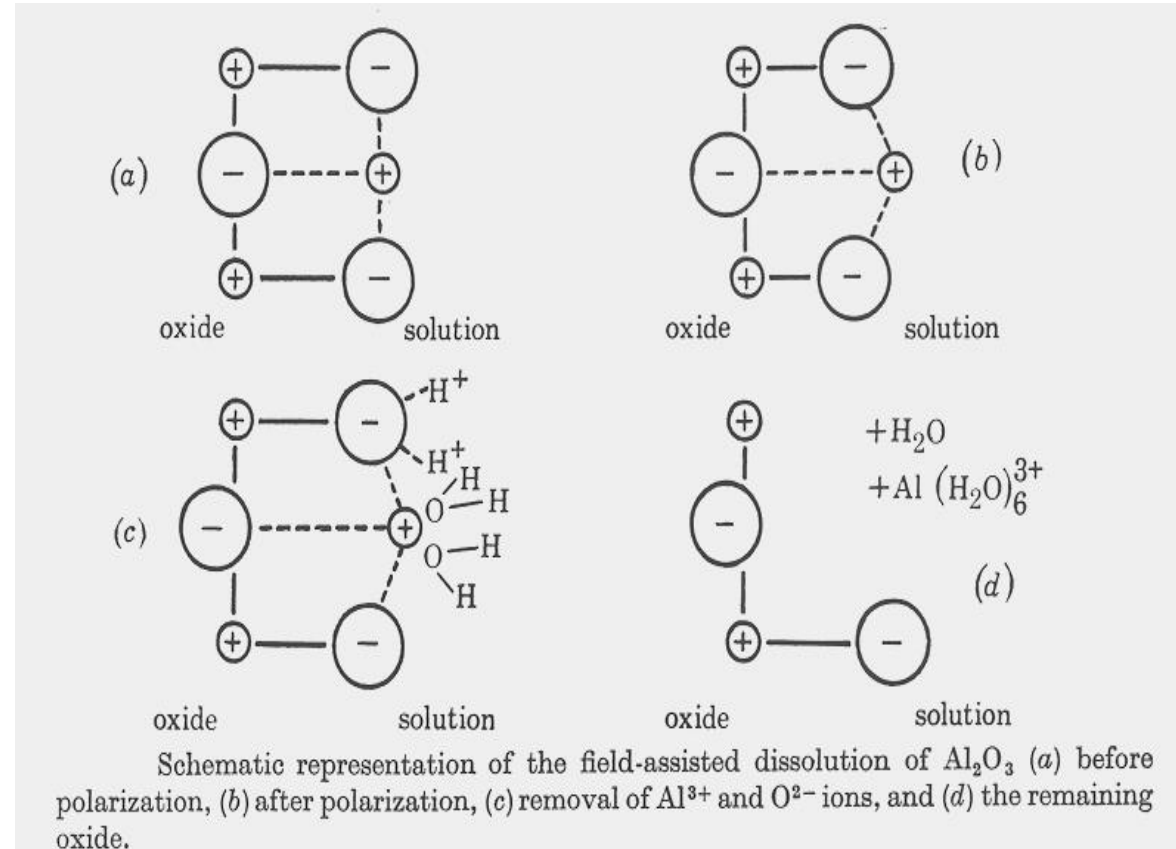
- Initially oxide growth dominates. (I)
- Dissolution becomes competitive, barrier layer thins, and pores initiate. (II)
- Approaches steady state where both mechanisms occur at roughly the same rate. (III and IV)



Porous-Type Anodic Oxide Films

Field-Assisted Dissolution

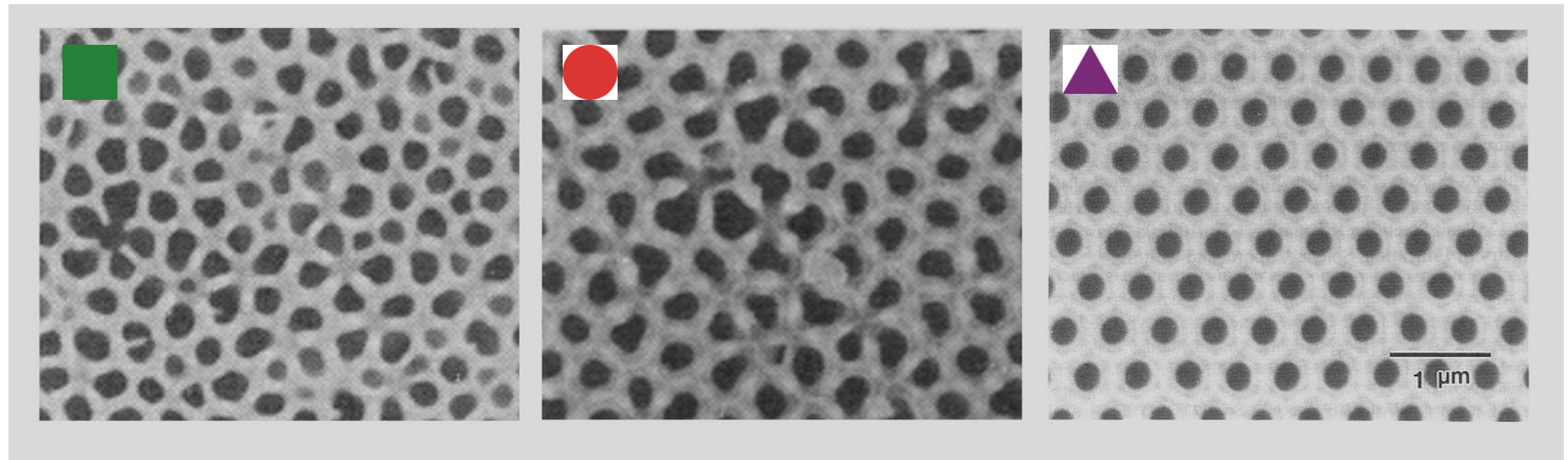
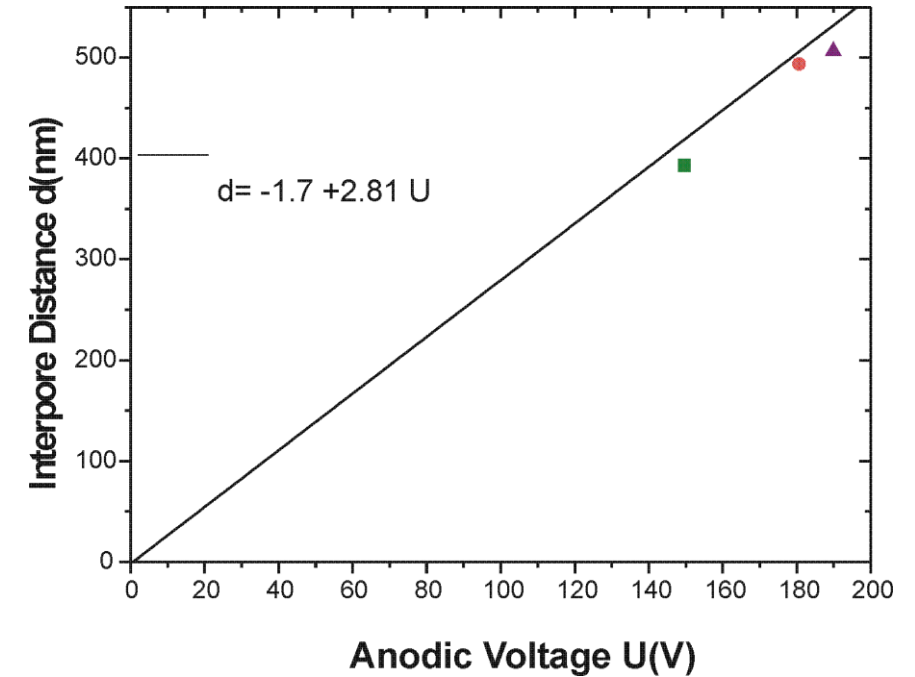
- Application of a field across the oxide polarizes the oxide bonds.



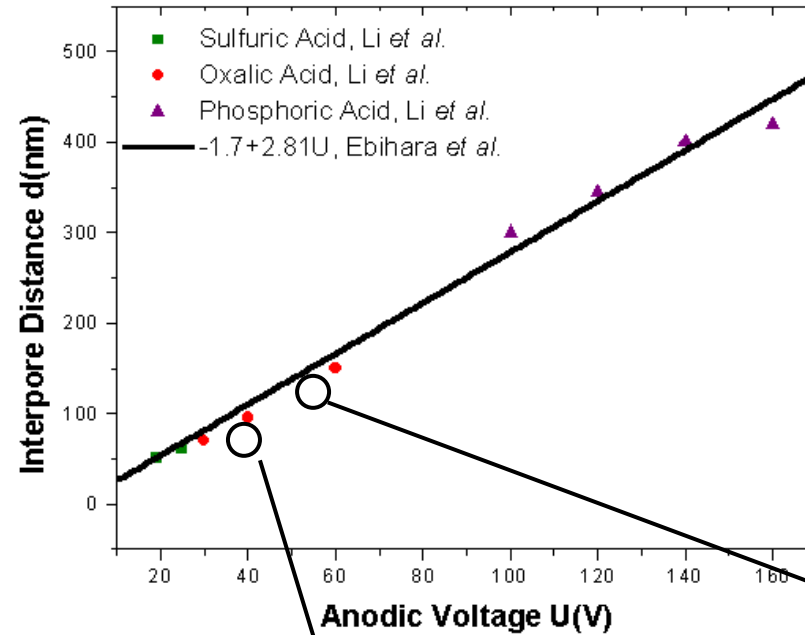
- This polarization effectively lowers the activation energy for dissolution of the oxide.
- This promotes solvation of Al^{3+} ions by water molecules and the removal of O^{2-} ions by H^+ ions.
- This processes is strongly dependent on the E-field strength.

Ordered Growth of Porous Alumina

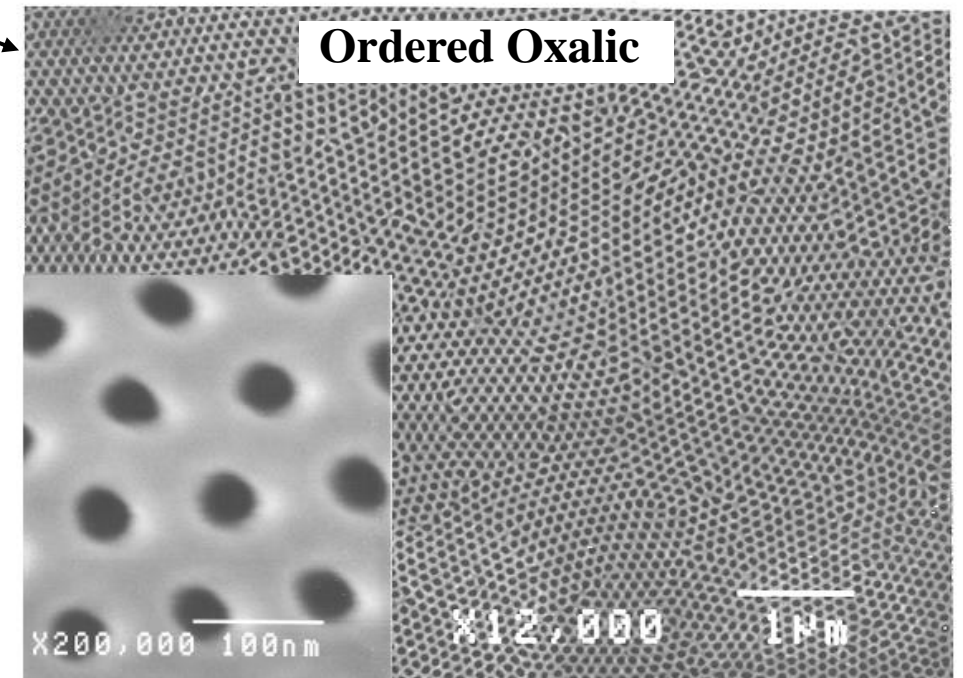
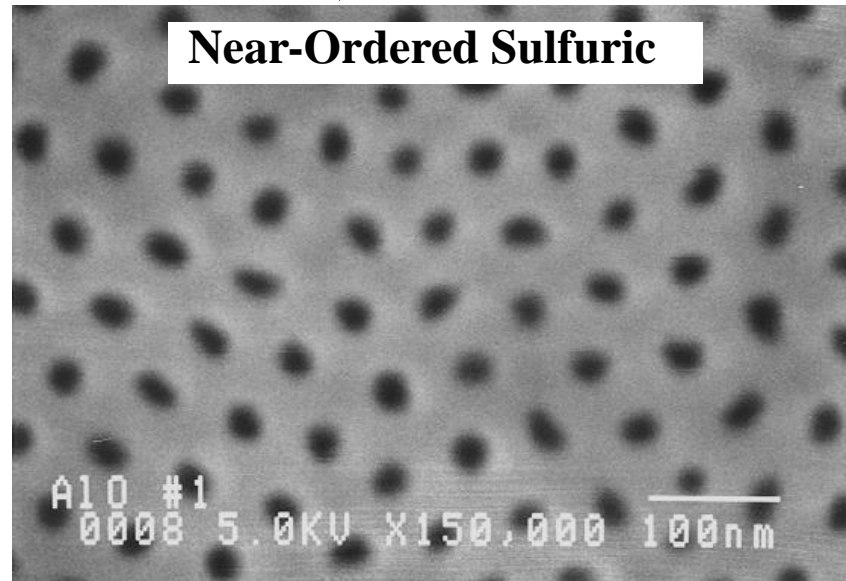
- In 1995, Japanese group found that pores will self-order under the right anodization conditions.
- The two most important conditions are narrow voltage ranges and long anodization times.



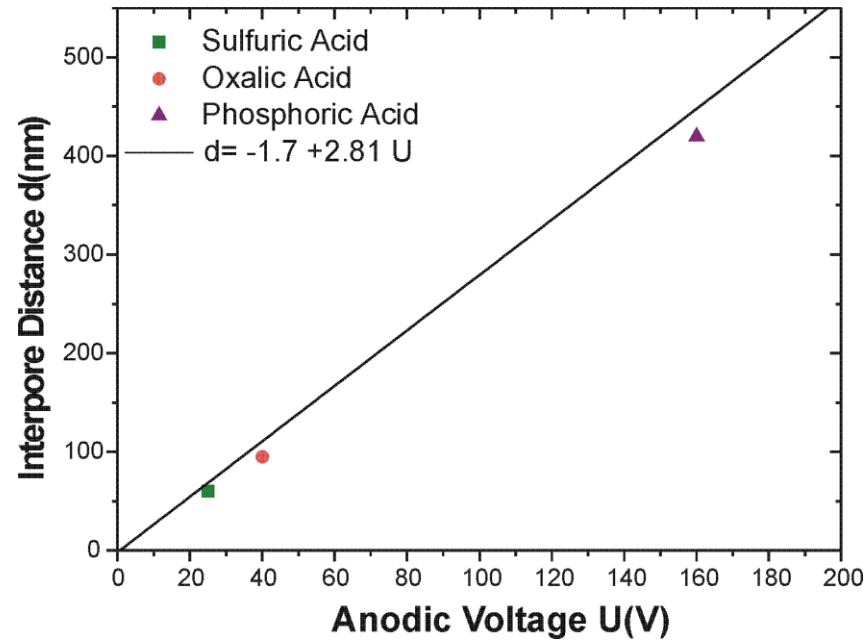
Ordered Nano-Templates



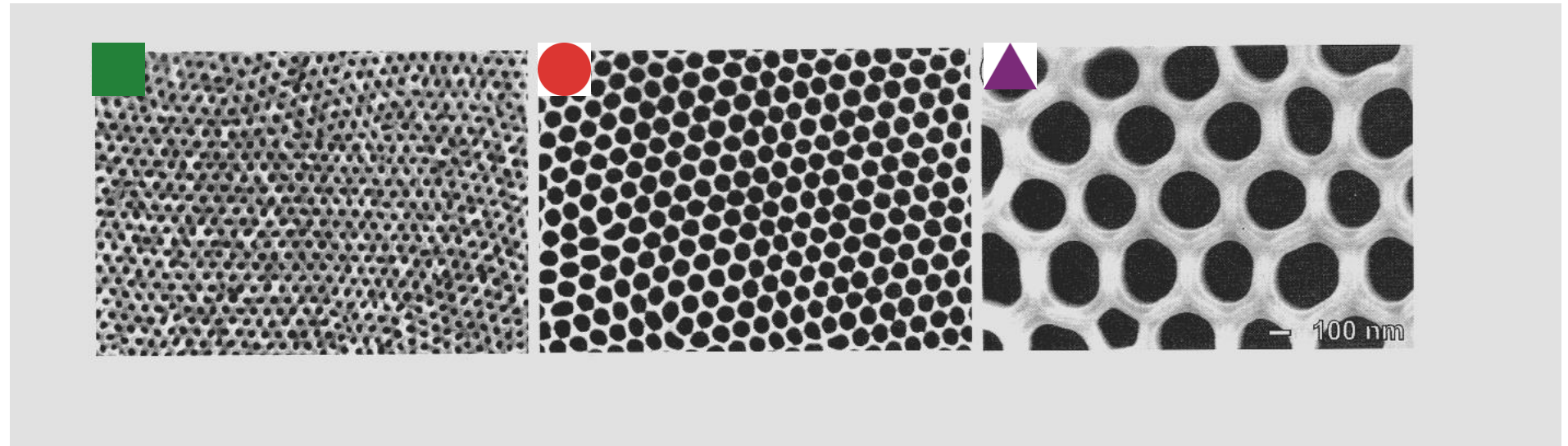
- Tunable diameters and spacings from 20 nm to 500 nm.
- Polycrystalline structure: ordered micron-sized domains, defects at grain boundaries.
- Low temperature growth produces unordered 4-10 nm arrays.



Ordered Growth of Porous Template



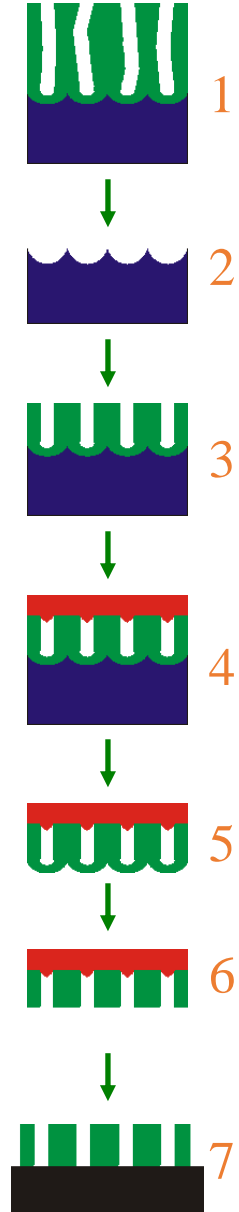
- Ordered pore arrays obtained in three different electrolytes for long anodization times and appropriate voltages (specific for each electrolyte).
- Polycrystalline structure with perfectly ordered domains a few microns in size. Defects occur at grain boundaries.



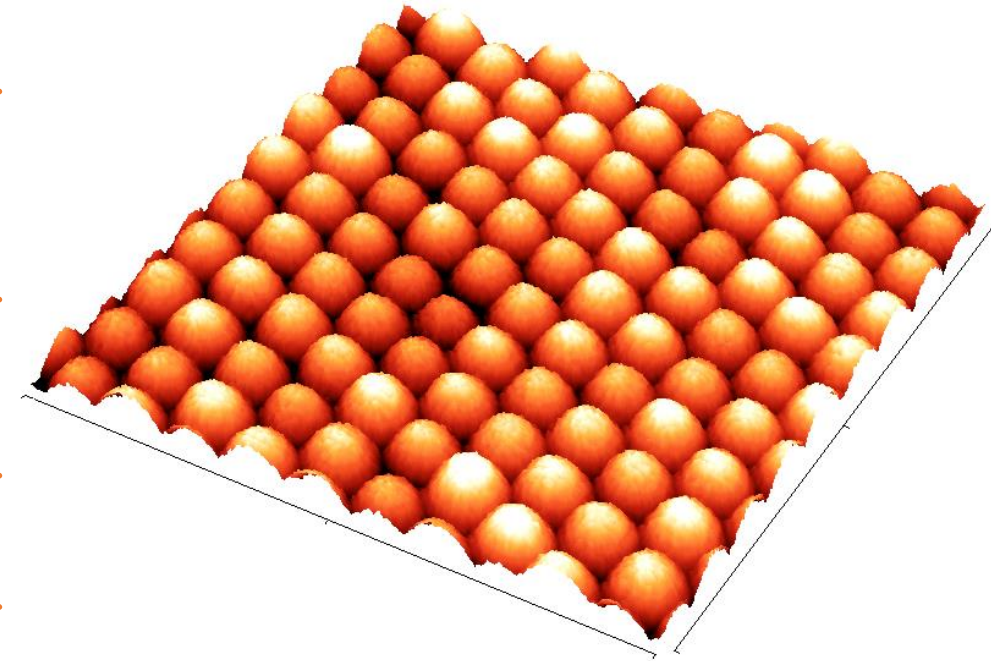
Mask Processing

To create an ordered through-hole mask:

1. Anodize for a long time allowing pores to order.
2. Chemically remove the alumina in a mixture of phosphoric and chromic acid.
3. Anodize for a short time (now pores are ordered).
4. Coat top surface of alumina with a polymer (collodion) to protect it from further processing.
5. Remove Al Substrate in a saturated HgCl_2 solution.
6. Remove the barrier layer in 5 wt.% Phosphoric Acid.
7. Remove collodion and place alumina on desired substrate.



AFM of Unopened
Barrier Layer
(1 μm x 1 μm)



Pattern Transfer Techniques

1. Etching Processes

Fluorine Beam

Transfer mask pattern via etching into substrate for ordered arrays of trenches.

Ion Beam

Transfer mask pattern via ion etching into substrate for ordered arrays of trenches or pillars.

2. Growth Processes

Sputtering and Thermal Deposition

Transfer mask pattern via deposition onto substrate for ordered arrays of dots.

F-Etched Array of Si(001) Nano-Holes

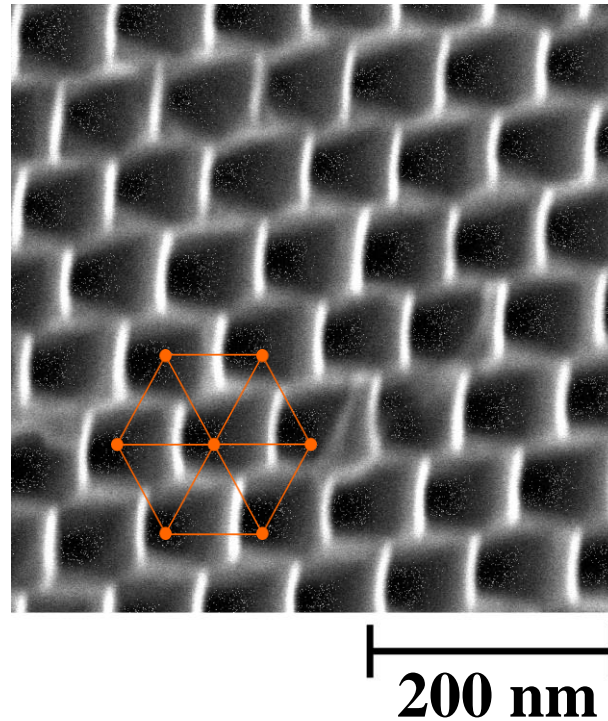
SAMPLE: ~500nm thick Free-Standing AAO/Si(001)

F-ETCH: 1 min. 20 sec.

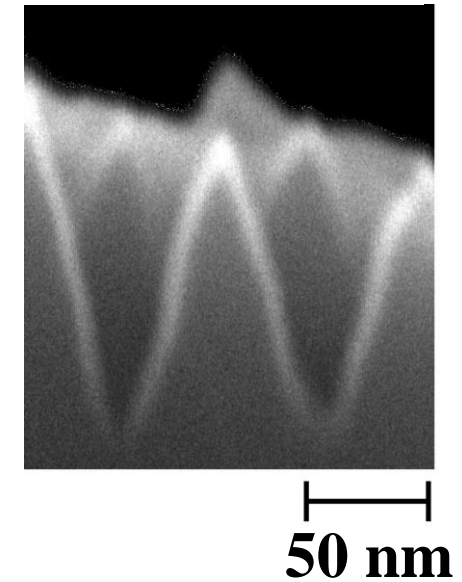
$T_{\text{SUB}} = 250^{\circ}\text{C}$

PORES: Width 70 nm, Depth 100-120 nm

TOP DOWN VIEW



X-SECT. VIEW



- Walls are ~30 nm thick (near top).

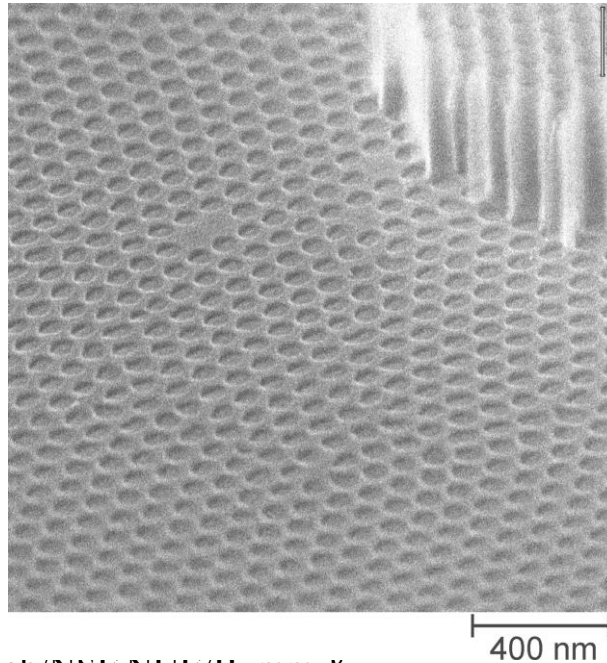
Ion Etched Array of GaAs Nano-Holes

SAMPLE: ~500nm thick Free-Standing
AAO/GaAs(100)

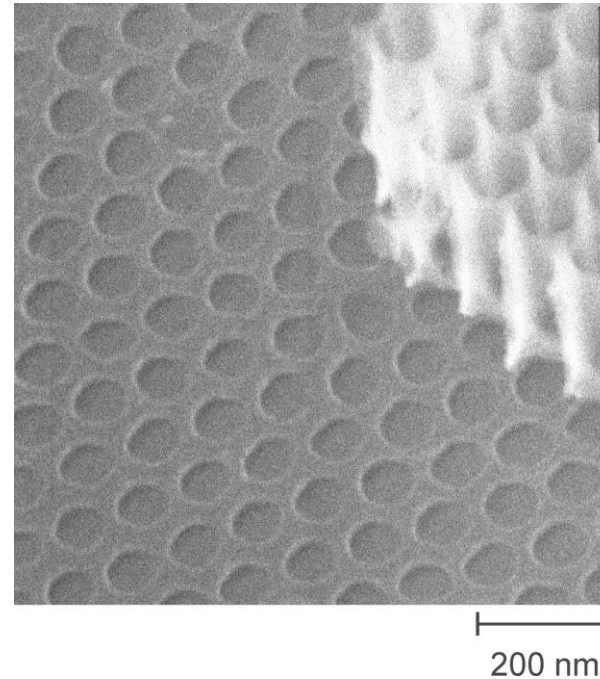
ION BEAM: 500 eV Ar⁺, 0.05 mA/cm²
Time = 2hrs. 12min.

PORES: Width 50 nm, Depth 50-60 nm

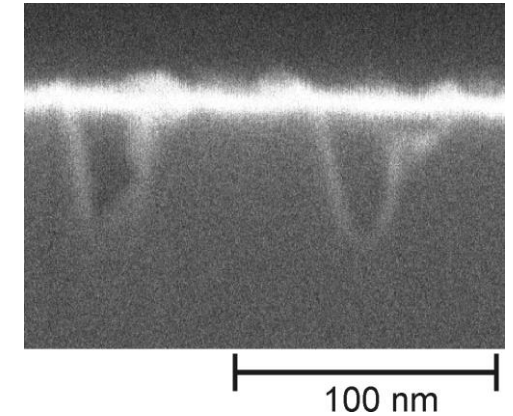
OBLIQUE VIEW



~TOP DOWN VIEW



X-SECT. VIEW

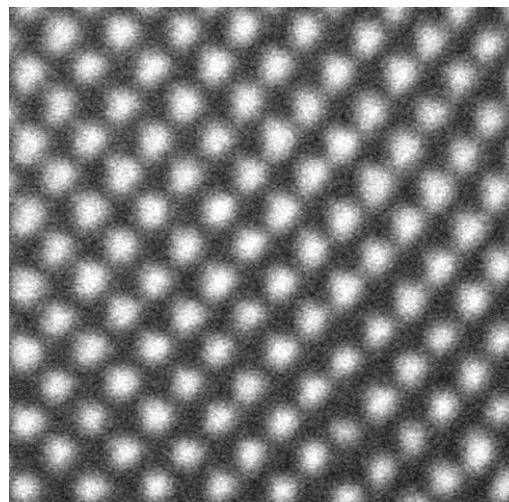


OU NanoLab/NSF NUE/Bumm &
Johnson

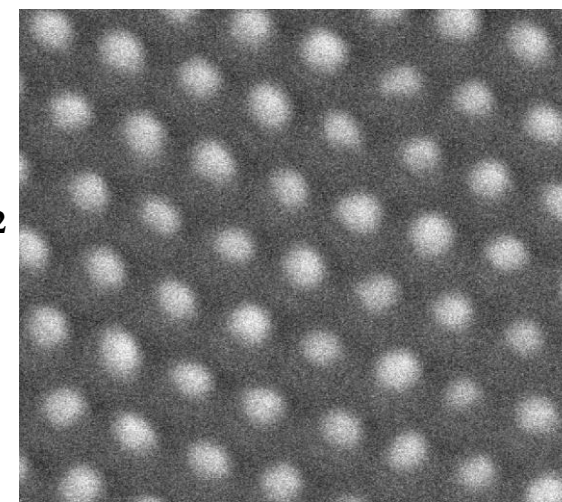
Thermally Evaporated Nano-Dots: MgF_2

SEM Top Views

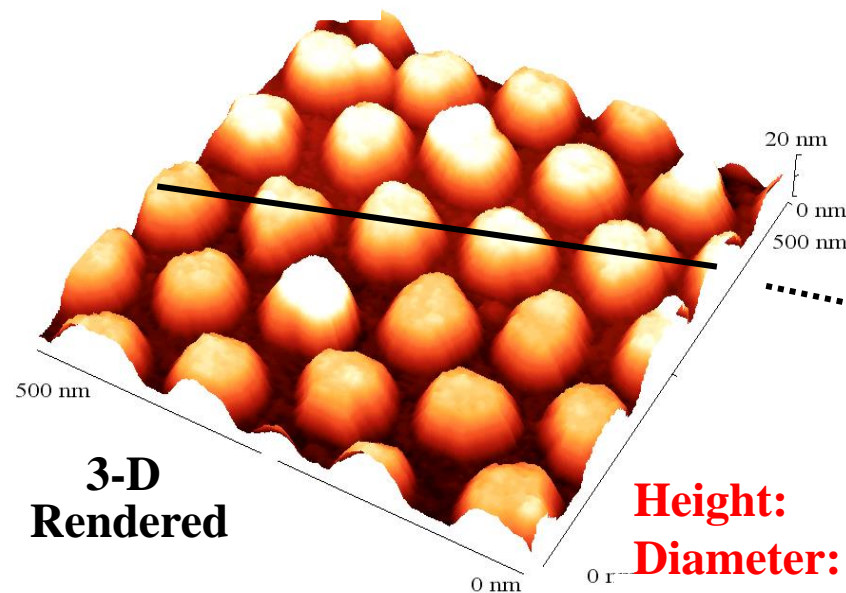
MgF_2 dots/Si



Au dots/ SiO_2



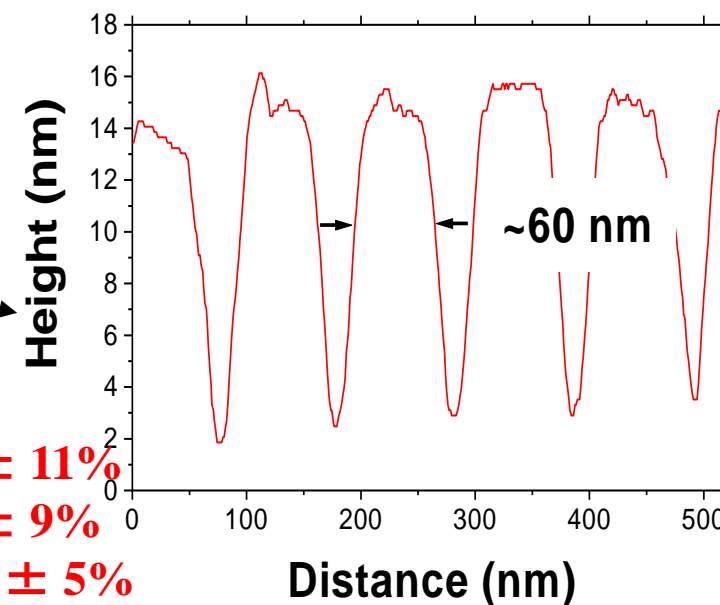
AFM Views



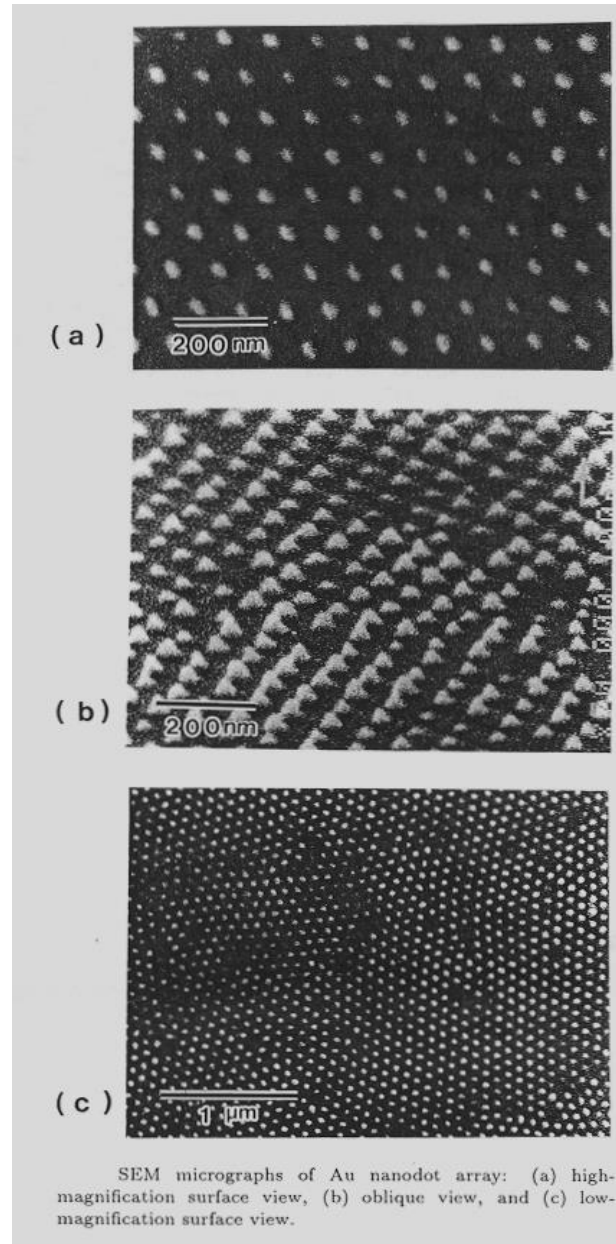
3-D
Rendered

Height: $12 \text{ nm} \pm 11\%$
Diameter: $60 \text{ nm} \pm 9\%$
Spacing: $110 \text{ nm} \pm 5\%$

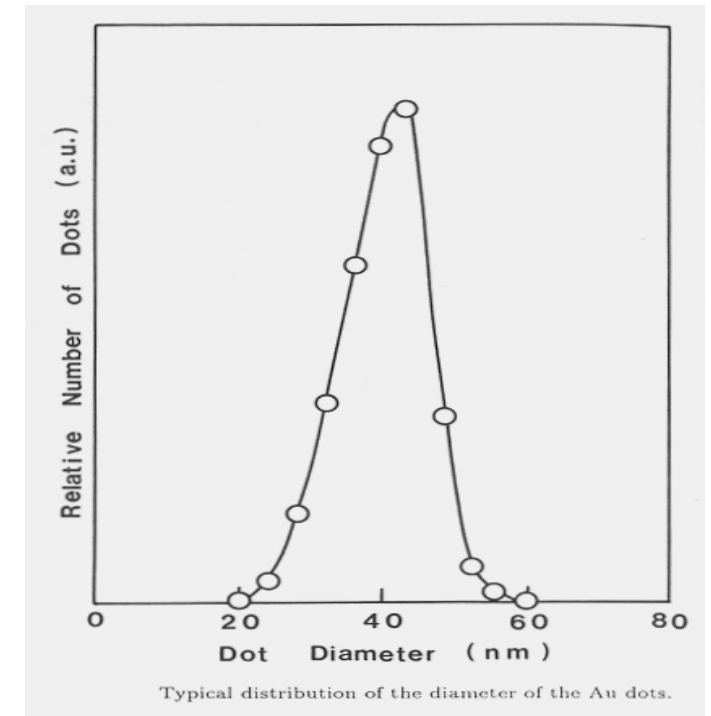
Line Scan



Thermally Evaporated Nano-Dots: Gold



- Porous alumina used as an evaporation mask to grow quantum dots.

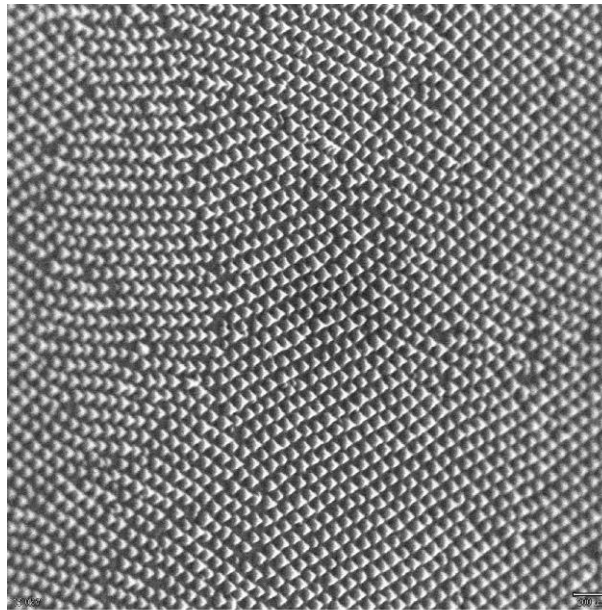


H. Masuda *et al.*, *Jpn. J. Appl. Phys.* **35**, L126 (1996).

Ion Etched Array of GaAs Nano-Pillars

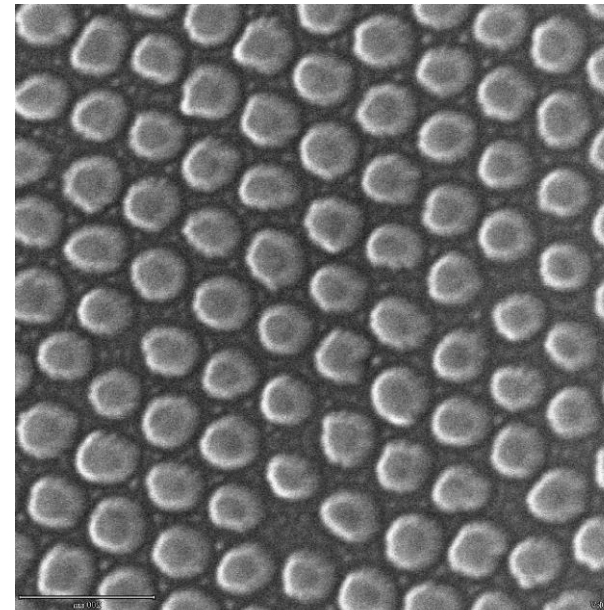
SAMPLE: ~20nm thick Fe dots on GaAs(100).
ION BEAM: 500 eV Ar⁺, 0.05 mA/cm²
Time = 17 min.
PILLARS: Width 50 nm, Height 50 nm

OBLIQUE VIEW



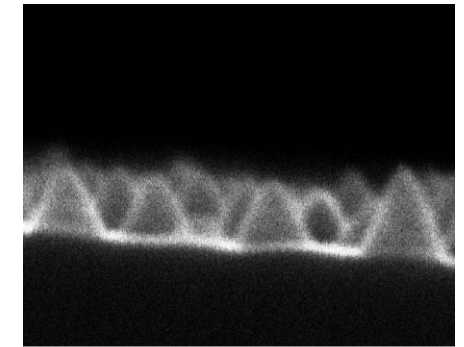
800 nm

TOP DOWN VIEW



800 nm

X-SECT. VIEW



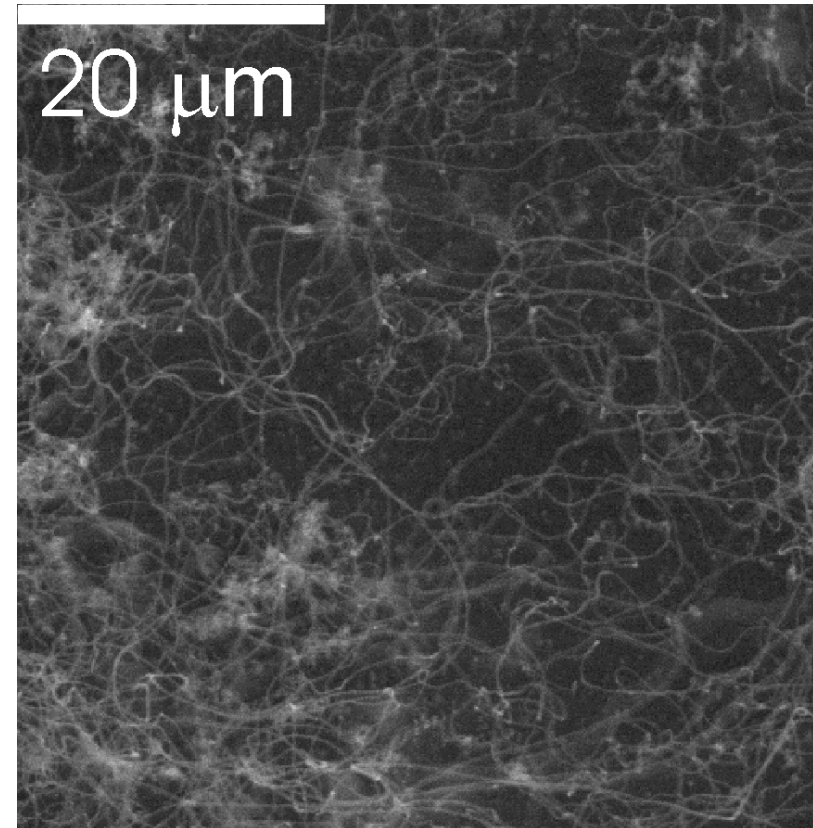
200 nm

Note: No Fe
remaining.

Evaporated Catalyst Dots For Carbon Nanotube Growth

SAMPLE: ~20nm thick Fe catalyst dots on 100nm Ti/Si
GROWTH: CVD using Methane gas at 500 Torr, 800°C
NANOTUBES: Multi-walled tubes, ~10s of microns long

TOP DOWN VIEW



- Collaboration with Dr. Shen Zhu of Marshall Space Flight Center.

Remarks

Conclusions

Fabricated ordered, arrays of nanostructures using porous alumina templates as masks:

- Arrays of 50 nm wide trenches in Si and GaAs by atom-beam and sputter etching.
- Arrays of 50 nm dots of various materials onto substrates by evaporation and sputtering.
- Arrays of nano-pillars in Si and GaAs by etching nano-dot arrays.

Future

- Make pores smaller (to 5 nm) using sulfuric acid electrolytes and low temp. anodization.
- Seed for carbon nanotube growth.
- Explore optical, electrical, and magnetic properties of nanostructures.
- Explore ways to transfer single or arbitrary dot/trench patterns.
- Fabricate such nanostructures *in situ* in multichamber MBE system.