Local Anodic Oxidation with AFM: A Nanometer-Scale Spectroscopic Study with Photoemission Microscopy

Laboratorio Nazionale TASC-INFM, Trieste  
*Università degli Studi di Modena e Reggio Emilia

A. Locatelli  
Sincrotrone Trieste, ELETTRA
Location of TASC and Elettra
TASC-INFM National Laboratory

- **Tecnologie Avanzate e NanoSCienza** (Advanced Technology and Nanoscience)
- Director: Giorgio Rossi
- www.tasc.infm.it

- 99 Researchers (13 Professors, 47 Scientists, 28 PhD students, 11 other)
- 17 Technicians, 9 Administrative staff
TASC Laboratories

- AD - Analytical Division
- AMD - Advanced Material and Devices group
- HAS - He Atom Scattering
- IPES - Inverse Photoemission laboratory
- MBE - Materials Division
- NED - Nanoscale Electronic Devices
- OxMBE - Oxide MBE
- PLL - PhotoLum Laboratory
- SSR - Surface Structure and Reactivity Group
- TEM - Transmission Electron Microscopy
- XSTM and low-temperature STM of nanostructures
TASC Facilities

- Class 1000 Cleanroom
- Optical Lithography
- Metal deposition
- Dielectric films deposition
- AFM and AFM lithography
- X-Ray Diffraction
TASC Beamlines at Elettra

- ALOISA - Advanced Line for Overlayer, Interface and Surface Analysis
- APE - Advanced Photoemission Experiment
- BACH - Beamline for Advanced diCHroism
- BEAR - Bending magnet for Emission Absorption and Reflectivity
- GAPH - Gas Phase Photoemission
- LILIT - Laboratory for Interdisciplinary Lithography
Beamlines at Elettra

TASC BL @ Elettra:
ALOISA
APE
BACH
BEAR
GAPH
LILIT

Spectromicroscopy:
ESCA Microscopy
Nanospectroscopy
Spectromicroscopy
IR Microscopy
Microfluorescence
TwinMic
Motivation

Why XPS?
- chemical state information
- surface sensitive
- ease of quantification
- (in general) nondestructive
Photoelectron Mean Free Path

Motivation

Why XPS?

- chemical state information
- surface sensitive
- ease of quantification
- (in general) nondestructive
Motivation

Why XPS?
- chemical state information
- surface sensitive
- ease of quantification
- (in general) nondestructive

Why spectromicroscopy?
- semicond. nanostructures: self-organized islands (dots)

Motivation

Why XPS?
- chemical state information
- surface sensitive
- ease of quantification
- (in general) nondestructive

Why spectromicroscopy?
- semicond. nanostructures: self-organized islands (dots)
- carbon nanotubes

Motivation

Why XPS?
- chemical state information
- surface sensitive
- ease of quantification
- (in general) nondestructive

Why spectromicroscopy?
- semicond. nanostructures: self-organized islands (dots)
- carbon nanotubes
- catalysis, chemical waves

Motivation

Why XPS?
- chemical state information
- surface sensitive
- ease of quantification
- (in general) nondestructive

Why spectromicroscopy?
- semicond. nanostructures: self-organized islands (dots)
- carbon nanotubes
- catalysis, chemical waves
- surface magnetism (XMCD)

The SPELEEM at Elettra

Spectroscopic photoemission and low energy electron microscope

Main features
- Photon flux $10^{17}-10^{18}$ cm$^{-2}$ s$^{-1}$
- Best Energy resolution 0.2 eV
- Lateral resolution 25 nm
The SPELEEM at ELETTRA

Spectroscopic photoemission and low energy electron microscope
Local Anodic Oxidation (LAO)

Commonly used model:
- Water electrolysis
  \[ \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \, . \]
- OH\(^-\) groups (or O\(^-\)) migrate towards the substrate-oxide interface.
- Oxide penetration induced by the intense local electric field (>10\(^7\) V/cm).

Versatile tool at relatively low cost
High lateral resolution but small area
Local Anodic Oxidation (LAO)

The penetration depth is 1.0-1.5 times the oxide height.

After oxidation.

Oxide removal with HF 10%, 30 s.

The penetration depth is 1.0-1.5 times the oxide height.
LAO on GaAs/AlGaAs

Before oxidation:
- Surface states
- 2DEG
- GaAs/AlGaAs heterostructure

After oxidation:
- Surface states
- Oxide
- 2DEG
- GaAs/AlGaAs heterostructure
Quantum Point Contact

Setup for Lithography on GaAs
LAO oxide consists of SiO₂
Properties similar to those of thermally grown SiO₂

GaAs LAO-Oxide: Desorption

Before exposure to x-rays

After hours of exposure

$h v = 130 eV$

We observe a linear relation between exposure time and height reduction. A dependence on other oxidation parameters (bias, writing speed) could not be detected.

Thermal stability

Each annealing step: 10 minutes in N₂ atmosphere

The Knotek-Feibelman mechanism

This Auger decay leads to a final state with two vacancies in the valence band weakening the bond between Ga or As and O.

Spectra From GaAs LAO-Oxide

Chemistry of the GaAs LAO-Oxide

- Photon assisted partial desorption of the AFM-grown oxide was observed.
- The AFM-oxide is mainly composed of Ga$_2$O, with a small fraction of Ga$_2$O$_3$ and As-oxides.
- The shape of the Ga peak does not change with exposure time (early stage of desorption), however, Ga-oxides do desorb.
- All As-oxides desorb completely. No As-oxides detected after some hours of exposure.
- The As-oxides are located only at the surface.
- Evidence for the presence of unoxidized GaAs in the LAO-oxide.
- Chemical composition does not depend on writing bias.

The microscopical dynamics of LAO
LAO on III-V Heterostructures

Chemical composition of LAO oxide

- Aluminium observed at the surface of the LAO oxide
- No Al in the regions not oxidized with LAO
- The other oxide lines do not show remarkable differences between the relative concentration of the components in each core level.

G. Mori et al.: submitted to Nucl. Instr. and Meth. B
The effect of X-ray exposure

- The X-ray exposure is removing the Ga oxides faster than the Al ones resulting in a surface enrichment with Al.
- The Al oxides are more stable to X-ray exposure than Ga oxides

G. Mori et al.: submitted to Nucl. Instr. and Meth. B
The effect of X-ray exposure

\[ N_{Ga} (t) = N_{Ga}^0 \cdot e^{-\frac{t}{\tau_{Ga}}} \]

\( N_{Ga}^0 \) is the number Ga atoms at the surface before exposure
\( \tau_{Ga} \) is the probability that a Ga atom is desorbed and is replaced by an underlying Al atom.

Assuming that the Ga atoms desorbs much faster that the Al ones

\[ N_{Al} (t) \approx N_{Al}^0 + N_{Ga}^0 \cdot \left( 1 - e^{-\frac{t}{\tau_{Ga}}} \right) \]

With this simple model we can calculate \( R(Al/Ga) \) for any exposure time.

G. Mori et al.: submitted to Nucl. Instr. and Meth. B
The effect of X-ray exposure

Initially:
\[ R(\text{Al/Ga}) = 0.34 \pm 0.10 \]
\[ \tau_{\text{Ga}} = 560 \pm 60 \text{ min} \]

We are able to quantify the effect of X-ray exposure on the surface chemical composition of the LAO oxide.

G. Mori et al.: submitted to Nucl. Instr. and Meth. B
Shallow Oxidations

Average oxide height:
Area A: 1.9 ± 0.7 nm
Area B: 1.3 ± 0.3 nm

Ratio Al / Ga:
Area A: 1 / 3
Area B: 1 / 13
Al 2p: 260 min
Ga 3d: 300 min

Al content depends strongly on oxide height

Variation in AlAs layer thickness

- 2 nm AlAs
  - Oxide height 9.0 ± 1.0 nm
  - Ratio Al / Ga: 0.5
  - Al 2p: 220 min
  - Ga 3d: 300 min

- 5 nm AlAs
  - Oxide height 8.9 ± 0.9 nm
  - Ratio Al / Ga: 1.3
  - Al 2p: 260 min
  - Ga 3d: 230 min

Refined Model

- Diffusion of oxygen-rich ions plus substrate ions
- Homogeneous mixing of components
- Ratio Al / Ga:
  - 0 for $h < d_{GaAs}$
  - $(h - d_{GaAs}) / d_{GaAs}$ for $d_{GaAs} < h < d_{GaAs} + d_{AlAs}$
  - $d_{AlAs} / (h - d_{AlAs})$ for $h > d_{GaAs} + d_{AlAs}$

Comparison with Experiment

Summary

- Investigation of chemical properties of LAO nanostructures on epitaxial GaAs/AlAs/GaAs layers.
- Presence of Al-oxides in the surface layers of the LAO nanostructures detected.
- Classical model of LAO process has to be revised.
- More general model is proposed which includes the diffusion of ionized substrate atoms to the surface.
- Good agreement between model and experiment is observed.