Photoelectron spectroscopy on semiconductor nanostructures

S. Heun
Sincrotrone Trieste
Motivation

Why spectro-microscopy?

- (semiconductor) nanostructures
  - lithography
  - self-organization
- devices
- laterally inhomogeneous surfaces
- segregation at defects
- alloying (silicide formation)
- 2-compound growth on surfaces
- ...

Pb/W(110)
Pb 5d
hv = 64 eV
Outline

Spectromicroscopy at Elettra

- ESCA - microscopy
  Example: Nanotubes

- SPELEEM
  Example: Nanocrystals

Both experiments in collaboration with Y. Watanabe (NTT Japan).
Location of Elettra
Elettra Beamlines

Operational:
1. Super ESCA
2. ESCA Microscopy
3. VUV Photoemission
4. X-ray Diffraction
5. X-ray Small-angle Scattering
6. Surface Diffraction (ALOISA)
7. Gas-Phase Photoemission
8. Mammography (SYRMEP)
9. Spectromicroscopy

Under commissioning or construction:
10. Circular Polarized Light
11. Deep Lithography (Microfabrication)
12. Proximity Photolithography (LILIT)
13. Materials Science
14. XAFS
15. Advanced Dichroism (BACH)
16. Dichroich Photoemission (APE)
17. Soft X-ray Optical Spectroscopy
18. XRD II
19. Nanospectroscopy
20. Inelastic UV Light Scattering
21. Powder Diffraction
Photon optics is demagnifying the beam: **scanning instrument**
1. Whole power of XPS in a small spot spectroscopy mode.
2. Flexibility for adding different detectors.
3. Limited use for fast dynamic processes.
4. Lower resolution than imaging instruments.

Electron optics to magnify irradiated area: **imaging instrument**
1. High lateral resolution (20 nm).
3. Excellent for monitoring dynamic processes.
4. More difficult to operate.
5. Sensitive to rough surfaces.
Photoelectron Mean Free Path

Flux density in a 0.01 µm² spot ~ 1 - 5*10⁹ ph/sec.

Lateral Resolution

Lateral resolution of SPEM using 60 nm / 200 µm zone plate fabricated in CXRO-Berkeley (Dr. E. Anderson).

AFM and SPEM images of assembled directionally grown SmFe$_2$ films on a Mo buffer, fabricated by pulsed laser deposition. (Project of Dr. J. Vogel et al., Louis Neel Lab, Grenoble, Feb. 99)

Carbon Nanotubes

• highly one-dimensional structure

• specific electronic structure expected at tips, where graphene cylinders are semi-spherically closed

• application as field emitters

Suzuki et al, APL 76 (2000) 4007: work function changes after Cs-deposition

Choi et al, APL 75 (1999) 3129
Bower et al, APL 77 (2000) 830: Multi-walled carbon nanotubes aligned perpendicular to Si substrate grown by CVD method length: 10 µm, diameter: 30 nm
Integral PES

PES: electronic structure
(work function, VB, core levels)

NTT: smaller work function at tip
larger density of states at $E_F$
slight band bending

Two different kinds of samples:
(a) aligned (b) unaligned

Experiment:
Laterally resolved PES on nanotube side and tip in cross-section (core levels, VB, work function)

Results:
• At tips larger density of states near Fermi-Edge
• Cs concentration along the tube axis

The SPELEEM at ELETTRA

Spectroscopic photoemission and low energy electron microscope

lateral resolution: 22nm
energy resolution < 0.5 eV

Lateral Resolution of XPEEM

Evaluated spatial resolution in XPEEM mode: 22nm

Images from a Field Effect Transistor (FET) at different binding energies. Photon energy $h\nu = 131.3$ eV.

Sample from M. Lazzarino, L. Sorba, and F. Beltram, Laboratorio TASC-INFM, Trieste, Italy

Energy Resolution of XPEEM

Energy resolution better than 0.5 eV

Pb/W(110)

Nanocrystals formed during strained-layer epitaxy
• Quasi zero-dimensional nature (quantum dots)
• Semiconductor lasers and memory applications
• No lithography: cost-effective fabrication of devices

Problems:
• Size fluctuations: need for nano-scale spectroscopy
• Segregation and interdiffusion observed for Ge/Si and for InAs/GaAs

Purpose of this work:
• Determination of the elemental composition of the nanocrystals
• Photoelectron spectroscopy with high lateral resolution
• Electronic structure of a single InAs nanocrystal

InAs / Se / GaAs after capping and decapping.

Typical island size: 50 nm.
Typical island height: 20 nm.
Typical island density: $25 \mu \text{m}^{-2}$

nanocrystals have square base oriented along $<110>$

Island Size Distribution

Sampled area: 20 μm²  
Nanocrystal density: 25 μm⁻²  
Average diameter: 53 nm

Core Level Spectra

Integral photoemission spectra from a 3 µm² area, obtained by integration of a series of SPELEEM images.

Good agreement with literature values ↑ samples not changed by capping / decapping

$E_b = 17.4 \text{ eV}$

$E_b = 20.1 \text{ eV}$

$\nu = 52 \text{ eV}, \text{ FoV} = 2 \mu\text{m}$

nanocrystal height from their shadow length: 22 nm

Laterally resolved core level spectroscopy

Integral spectrum

Laterally resolved spectra

(a) Ga 3d / In 4d
hv = 52 eV

(b) Ga 3d / In 4d
hv = 52 eV

Indium on substrate ↑ SK growth mode
Gallium on nanocrystals

Selenium on the nanocrystals

Valence band and work function data:
Further evidence for the presence of Selenium at the surface of the nanocrystals

Se 3d core level spectra

- Ga$_2$Se$_3$: zincblende structure with ordered Ga vacancies.
- A: Se with no Ga vacancy as nearest neighbor
- B: Se with one Ga vacancy as nearest neighbor
- B species closer to the surface than A species
- clean Se/GaAs: A / B = 1.51

Here: intensity ratio A / B = 2.26
 aument in B species after deposition of InAs
 aument in some material moved from surface to nanocrystals

From LEEM: volume of nanocrystals: 6 x 10$^5$ nm$^3$ per µm$^2$
2 ML InAs correspond to 6 x 10$^5$ nm$^3$ per µm$^2$
SK growth mode
 aument in nanocrystal volume is greater than expected
 aument in additional material from another source (Ga$_2$Se$_3$)

Discussion

- Reaction between InAs and $\text{Ga}_2\text{Se}_3$
- No GaAs reaction (growth at 200°C)

- Formation of a quaternary unlikely (As and Se from different chemical groups)
- Alloying on cation sublattice (strain minimization)
- Phase separation on anion sublattice (like in $\text{InAs}_x\text{Sb}_{1-x}$)

- No bulk inclusions of $\text{Ga}_2\text{Se}_3$ in the InAs nanocrystals (10% lattice mismatch)

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Summary

• During heteroepitaxy, the InAs reacts with the Ga$_2$Se$_3$.

• Phase separation on anion sublattice, alloying on cation sublattice.

• A wetting layer of In$_x$Ga$_{1-x}$As is formed covered by (In$_y$Ga$_{1-y}$)$_2$Se$_3$.

• (In$_y$Ga$_{1-y}$)$_2$Se$_3$ covered nanocrystals are formed on this surface.

Conclusions

ESCA microscope:
• Easy to use
• Cross section possible
• 100 nm lateral resolution
• 300 meV energy resolution

SPELEEM:
• Multi-method instrument
• Structural information
• Chemical information
• 20 nm lateral resolution
• 500 meV energy resolution
Nanospectroscopy beamline

Now under commissioning!

The Nanospectroscopy Beamline
The SPELEEM at ELETTRA
**Source:**
Sasaki type undulator, 10 cm periods
elliptical and linear polarization
20 - 1000 eV @ 2 GeV (5 eV @ 1 GeV)
240 μm x 40 μm source dimension

**Monochromator:**
20 - 1000 eV (2 VLS plane gratings)
< 20 eV + 0. order (spherical grating)
$E/\Delta E > 4000$

**Spot:**
High photon flux density ($10^{14}$ ph/sec/μm²)
Spot as small as possible (2 μm x 2 μm)
Constant divergence
Variable photon density
Uniform photon distribution