Surfaces, Interfaces, and Thin Films: Characterisation at the Nanometre Scale

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Dr. Ovidiu D. Gordan & Dr. Raul D. Rodriguez
1. Photons vs. electrons: Basic considerations for achieving surface/interface sensitivity

2. Extending the photon energies towards the vacuum ultraviolet region: Ellipsometry using synchrotron radiation

3. Special ways of achieving surface/interface sensitivity in Raman and reflectance anisotropy spectroscopy

4. High resolution photoemission and X-ray absorption fine structure measurements
Semiconductor Physics – Activities in Chemnitz

Surface Science:  
Photoemission Spectroscopy (UPS and XPS)  
X-ray Absorption Fine Structure (NEXAFS)  
Auger Electron Spectroscopy (AES)  
Low Energy Electron Diffraction (LEED)  
Inverse Photoemission  
Kelvin Probe (CPD)

Growth:  
(Organic) Molecular Beam Deposition in Ultra-High Vacuum  
(Metal-Organic) Vapour Phase Deposition  
Spray coating

Electrical Measurements:  
Current-Voltage (IV)  
Capacitance-Voltage (CV)  
(Deep Level) Transient Spectroscopy

Optical Spectroscopy:  
Raman Spectroscopy (RS)  
Spectroscopic Ellipsometry (SE)  
Infrared Spectroscopy (IR)  
Reflection Anisotropy Spectroscopy (RAS)  
Photoluminescence and UV-vis

Nanoscale Characterization:  
- Micro-Raman spectroscopy and imaging  
- Atomic force microscopy  
- Kelvin probe force microscopy, current sensing  
- AFM  
- Tip- and surface-enhanced Raman spectroscopy (TERS and SERS)  
- ANSYS: finite element simulation package Matlab
Organic field-effect transistors

Electrically driven organic lasers

Organic semiconductors

Organic/Inorganic Microwave Diodes

Plastic solar cells

Metal

Organic Interlayer

GaAs(100)

Organic-modified Schottky Diodes
First OVPD-OLED

Structure of the large area OVPD-OLED device

First large area OVPD-OLED displaying the Logo of TU Braunschweig processed on a substrate size of 35 x 50 mm².
Avinash Agarwal et al., Alternatives to SiO$_2$ as Gate Dielectrics for Future Si-Based Microelectronics, 2001 MRS Workshop Series (2001)
Scanning Tunneling Microscopy

STM Basics

Tunneling current
\[ I \sim e^{\kappa z} \]
VERY sensitive to changes in z!

Scanning Tunneling Microscopy

(G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel, Phys. Rev. Lett. 49, 57 (1982)).
Moving atoms one at a time...
Monatomic Regular Steps on Si(111)-3°

After 30sec. x 2times of flash

Monatomic layer on each step (0.3 nm/layer)
Equidistant terraces
Atomically straight edges
Experimental slope ~
Nominal value of wafer

9.0nm

5.7nm
Atomic force microscopy (AFM)
AlAs QDs in InAs matrix.
Ion milling with cooling.

We can see the stripes!

Lattice period (50±4) nm
Optical Spectroscopy

- Reflected
- Incident
- Transmitted
- (Absorbed)
- Scattered (Raman, Brillouin...)
- Luminescence
Light – Matter Interaction

Dielectric Function

\[ \varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega) \]

describes light – matter interaction

Refractive index:

\[ \tilde{n}(\omega) = \sqrt{\varepsilon(\omega)} = n + i\kappa \]

with \( n \) real part of refractive index (refraction !) and \( \kappa \) the so-called extinction coefficient (absorption).

Absorption coefficient:

\[ \alpha = \frac{2\omega\kappa}{c} \]

Light intensity as function of distance \( x \) travelled in a medium:

\[ I(x) = I_0 \exp(-\alpha x) \]
Energy $E / \text{eV}$

$1 \text{ eV} = 1,602 \times 10^{-19} \text{ J}$

$1 \text{ nm} = 10^{-9} \text{ m} = 10 \text{ Å}$

<table>
<thead>
<tr>
<th>UV</th>
<th>IR</th>
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<tbody>
<tr>
<td>410</td>
<td>700</td>
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<tr>
<td>495</td>
<td>620</td>
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<tr>
<td>560</td>
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</table>

Wavelength $\lambda / \text{nm}$
Penetration depth

\[ I(z) = I_0 e^{-\frac{2\pi k}{\lambda} z} \]

\[ \delta_p = \frac{\lambda}{4\pi k} \quad \text{Information depth} \]

\[ k \quad \text{extinction coefficient} \]

\[ z \quad \text{depth} \]
Raman Spectroscopy

- Information about atomic arrangement
  - Chemical/molecular analysis
  - Crystallinity
  - Polymorphism
  - Phase

- Non-destructive
  - Photon

- Phonon frequency depends on elastic constant of chemical bond and atom mass

- Applied to any optically accessible sample
- Solid, liquid, gas, transparent, non-transparent, bio-applications
- Microscopic spatial resolution
- Confocal analysis
Handheld Raman spectrometer

Identification and use with:
• Narcotics & illicit street drugs;
• Explosives & chemical warfare agents;
• Hazardous materials & chemical spills;
• Pharmaceutical IQ/OQ/PQ quality;
• Gemstone authentication, etc.

Fig. 2. Raman spectrum of ammonium perchlorate explosive through black plastic bag using a portable Raman station.
Forgery detection on an Arabic illuminated manuscript by micro-Raman and X-ray fluorescence spectroscopy
Medical applications

Graphs showing SERS intensity (a.u.) vs. Raman shift (cm⁻¹) for targeted and nontargeted conditions. The targeted graph shows distinct peaks at specific Raman shifts, indicating the presence of a tumor. The nontargeted graph shows a more uniform response.

Images illustrating the use of an 885-nm laser beam over a tumor and the liver. Arrows indicate the 885-nm Laser beam and the locations of the tumor and liver.
Intensity of the $G^+$ band / a.u.
Raman spectroscopy: Key technique for the analysis of CNT

<table>
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<th>cm$^{-1}$</th>
<th>Tentative type</th>
<th>Diameter / nm</th>
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<tbody>
<tr>
<td>829 nm</td>
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<tr>
<td>1569.1</td>
<td>S</td>
<td>1.5</td>
</tr>
<tr>
<td>1553.8</td>
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<td>1565.9</td>
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Raman Spectroscopy

1) Illuminate sample with laser

2) Measure intensity of scattered light at each $v_{ph}$

$L_\text{spot} \approx 2000 \text{ nm}$

Nanoparticle $\approx 40 \text{ nm}$
Still we have contributions from a sample region comparable in size to the laser spot but...
Sample signal comparable in size to the tip!

The key: Excitation of localized surface plasmons at the tip apex confines and amplifies the electromagnetic field.

TERS: Tip-enhanced Raman Spectroscopy
Tip-enhanced Raman Spectroscopy

TERS

Tip Approached
Tip retracted

G^+
G^-
D
2D

Intensity / cts
Raman shift / cm⁻¹

Tip-enhanced Raman Spectroscopy

TERS

Tip Approached
Tip retracted

G^+
G^-
D
2D

Intensity / cts
Raman shift / cm⁻¹
Transistors

Technology generation: $L \rightarrow L/\sqrt{2}$

“Moore’s Law”

“Transistorized” PBS, Nov. 8, 1999

www.pbs.org/transistor/
21st Century Electronics: Transistors at the nano/molecular scale

Texas Instruments
~2000

~100 nm

~10 nm
~2015

Source
Gate
Drain

electron flow

?
The Scale of Things

- 1 meter (1m)
- 1 mm (10^{-3} m)
- 1 µm (10^{-6} m)
- 1 nm (10^{-9} m)
- 1 pm (10^{-12} m)

- human hair (100 µm)
- wavelength of light (< 1µm)
- 248 nm - DUV lithography
- transistor (100 nm - 2000)
- biomolecules (10’s nm)
- Silicon atom (0.118 nm)
Putting it in Scale

- Simple molecules <1 nm
- DNA proteins ~nm
- Bacteria ~1 μm
- Red blood cell ~5 μm (SEM)
- Diatom 30 μm

- Semiconductor nanocrystal (CdSe) 5 nm
- Nanometer memory element (Lieber) $10^{12}$ bits/cm² (1 Tbit/cm²)
- SOI transistor width 0.12 μm
- Circuit design Copper wiring width 0.2 μm
- IBM PowerPC 750™ Microprocessor 7.56mm x 8.799mm 6.35 x $10^8$ transistors
Surface Area

One intrinsic benefit is the increased surface area available in nanoparticles.

N = total atoms; n = surface atoms
J-V characteristics of organic modified Schottky diodes
Crystal structure

Diamond & Zincblende lattices – two interpenetrating fcc sublattices one displaced from the other by $\frac{1}{4}$ of the distance along the diagonal of the cell ($a\sqrt{3}/4$)