# PHYSICS - NANOENGINEERING

# DR. PIOTR SITAREK

# SURFACE PHYSICS

# Surface physics

(selected materials for seminar)

## Dr. Piotr Sitarek

Institute of Physics
Wrocław University of Technology

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# Preface

The present course book contains selected materials supplementing the lectures in Surface Physics. It is designed for students of Nanoengineering studying in English. The problems are presented from the experimental point of view.

The course book starts from the introduction to ultrahigh vacuum and surface preparation/growth and through the presentation of real surfaces and their structure focusing on different scattering and optical techniques for surface/interface examination.

In the author's aim each part can be read individually. The problems which should be discussed are introduced. To help students in preparation of their presentation the supporting questions are expressed. Each chapter has its own references and literature parts. The reference part lists a sourced which were used by the author. The literature part contains a list of textbooks which could be helpful for the student. Student has to find which textbook is most understandable and useful for him.

The teacher should decide how many students are presenting each part and if it should be divided into more meetings. Below please find some advice which can be helpful in presentation preparation.

**Advice for speakers**

- speech should be about 30 minutes long,

- the remained time (about 15 minutes) is left for additional discussion,

- please follow remarks contained in these materials,

- questions which you should answer are emphasized in the text by italics,

- some important terms, which you should concern, are bolded,

- during preparation of the speech please discuss with the teacher its structure.

# Contents

**Seminar 1**

# Ultrahigh vacuum (UHV).

# Techniques for preparation of well-defined surfaces and interfaces

The surface of a solid is a small number of atomic layers where the top one is in contact with surrounding atmosphere or, in an ideal case, the vacuum. A solid interface usually separates two solids being in very close contact. From the experimental and technical points of view the preparation of a clean and well-defined surface becomes possible only after the development of ultrahigh vacuum techniques. [1]



The preparation of a well-defined surface with negligible contamination requires ambient pressure below $10^{-10}$ Torr (approx. $10^{-8}$ Pa). To obtain such a low pressure several different vacuum pumps have to be connected to the UHV chamber - fig.1.1. Each pump can usually operate over a limited pressure range.
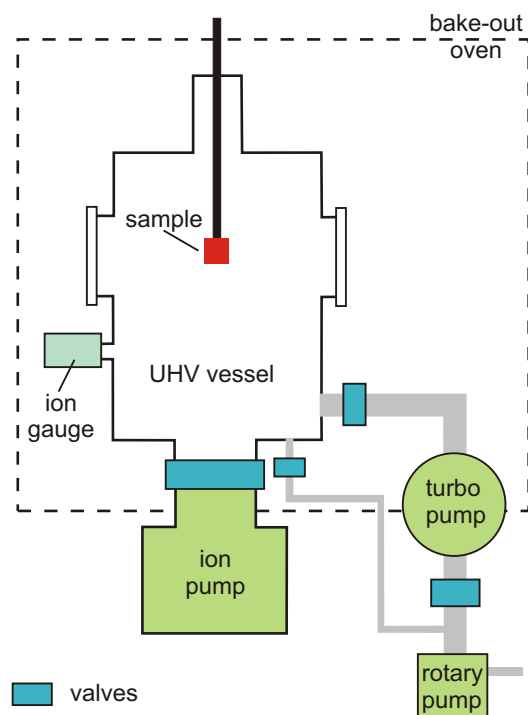
**Figure 1.1.  Schematic view of UHV system.**

1.  *Describe the model UHV system. List the most often used vacuum pumps. Explain the operation of: rotary pump, turbo-molecular pump and ion pump. What is their pressure limit? How to measure the pressure in a chamber?*

Cleavage in UHV is a simple way to prepare a clean surface, which is in general stoichiometric but may also contain step defects. Cleavage is only possible along certain crystallographic directions which are determined by the geometry of chemical bond.

2.  *Explain what cleavage is. Why is it usually performed in UHV? Why may only brittle materials be treated in such a way? What materials can be cleaved?*

Comparing to cleavage the ion bombardment and annealing has no limitation to the certain materials and to the certain crystallographic surface planes. We are using noble gas ions to bombard and sputter off all contaminants (and usually topmost atomic layers) from the

## Seminar 1

surface and next anneal the surface to remove adsorbed noble gas atoms and to recover surface crystallography.

3.  *Explain the ion bombardment and annealing method for surface cleaning. What ions can be used? What analytical methods are usually used to control surface cleaning?*
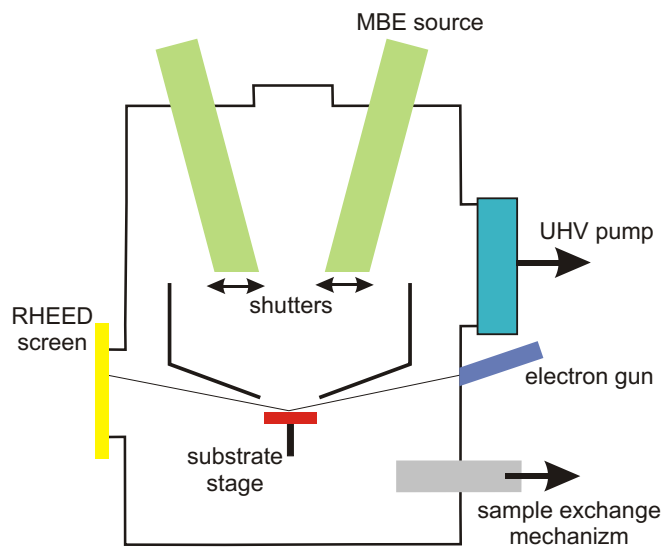


**Figure 1.2 Diagram of a typical MBE system growth chamber.**

The surface preparation methods described above can be used with freely obtained crystals. The most versatile technique for preparing clean and well-defined surfaces and interfaces is molecular beam epitaxy technique (MBE) which works in UHV regime. The monocrystalline films obtained from MBE may be grown on the substrate which is the same material - homoepitaxy, or different material - heteroepitaxy.

4.  *Describe the MBE technique of crystal growth. What are homo- and hetero-epitaxial growths? How is it possible to deposit one material on the other without the loss of surface quality? How to control the crystalline quality during MBE growth?*

Chemical vapor deposition is chemical reactions which transform gaseous molecules, called precursor, into a solid material, in the form of a thin film, on the surface of a substrate. The process, usually under standard pressure conditions, is widely used to fabricate semiconductor devices. Usually the precursors are organic and according to this the technique is called metal-organic chemical vapor deposition (MOCVD).
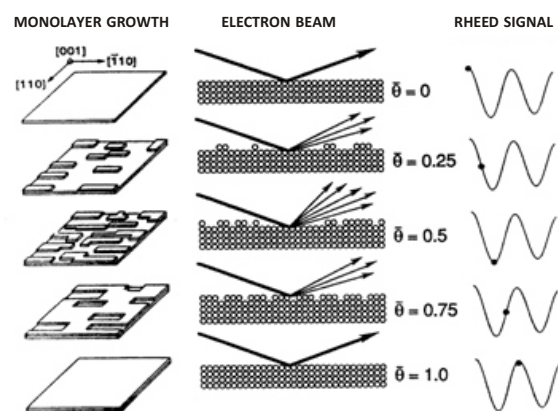


**Figure 1.3 Illustration of the mechanism for RHEED during growth of a monolayer.**

## Seminar 1

### *5. Show the basics of MOCVD growth technique.*

**References**

[1]  Hans Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer-Verlag Berlin Heidelberg, 2001.

**Bibliography**

1.  Harald Ibach, *Physics of Surfaces and Interfaces*, Springer-Verlag Berlin Heidelberg, 2006.
2.  Hans Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer-Verlag Berlin Heidelberg, 2001 (chapter 2).
3.  Andrew Zangwill, *Physics at Surfaces*, Cambridge University Press, 1988.
4.  John T. Yates, Jr., *Experimental innovations in surface science*, Springer-Verlag New York, Inc. 1998.

# Techniques for examining surfaces.
# Quasi-elastic scattering techniques

To examine the surface it is possible to exploit many experimental techniques and their modifications. Let's concentrate on the most often used methods. All experimental methods can be divided into two groups: **scattering experiments** and **microscopic experiments**.

In scattering experiments a particle is an incident on the sample, and another particle (not necessarily the same) is detected after the interaction with the sample. The probe will be formed from a particular type of the particle, and will typically have a well defined energy and often a well defined wave-vector. The response may be either the same or a different particle, and, depending on the detection system, its energy or its wave vector. If we understand the nature of the scattering, then we can interpret the experiment and deduce the corresponding characteristics of the sample.

*1. Group an experimental methods for surface investigation. Explain the basics of scattering experiments. List a few (the most popular) scattering experimental techniques.*

The common electron-based diffraction techniques are **Low Energy Electron Diffraction** (LEED) and **Reflection High-Energy Electron Diffraction** (RHEED). The theory of LEED and RHEED concentrates on elastic scattering, where the energy of the outgoing electron is the same as that of the incoming electron. As with all surface diffraction techniques, the analysis is based in terms of the surface reciprocal lattice. Both methods are applied to check crystallographic quality of the freshly prepared surface or to investigate a new atomic surface structure.

There are two aspects to diffraction techniques. The first, and simplest, is that the positions of the spots in a pattern give the symmetry and size of the unit mesh, i.e. the surface unit cell. The second, and much more subtle effect, is that the position of atoms in the mesh is not determined by this qualitative
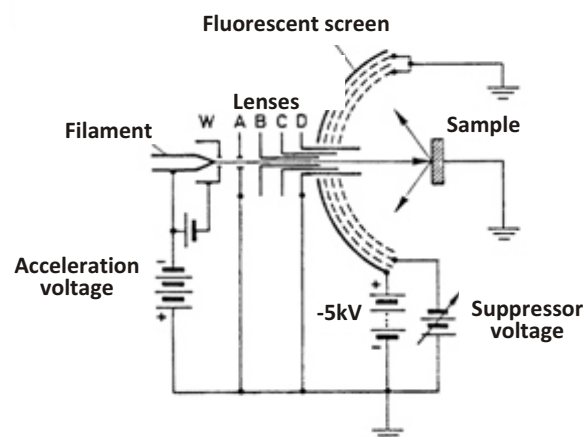


**Figure 2.1 Schematic of three-grid LEED system. [1]**

## Seminar 2

pattern but requires a quantitative analysis of the intensities. The LEED technique gives us the opportunity to get all above information.

There are different types of LEED apparatus in regular use. The "normal-view" arrangement has the LEED gun and screen mounted on a UHV flange. Most new systems are of the "reverse-view" type, where the gun has been miniaturized, and the pattern is viewed through a transmission screen and a viewport.

*2. Show and describe the LEED apparatus. What types of LEED are in regular use?*

*3. Present the example of the LEED patterns. Explain the Ewald sphere construction. Explain how to "read" the LEED patterns. What is important in the pattern and what information can we get from it?*
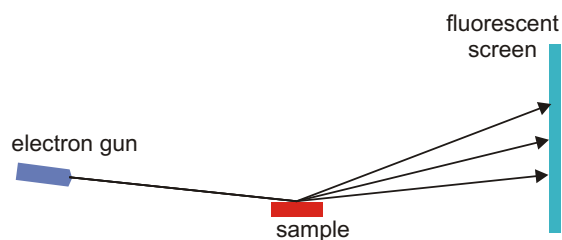


**Figure 2.2 Schematic of the experimental setup for RHEED.**

The second important electron diffraction technique described here in RHEED. High energy electrons with energies between 10 and 100 keV are incident under grazing angles (3 - 5 degree) onto the surface. RHEED technique may be also used in-situ to monitor the surface crystallography in an MBE experiment. The glancing angle geometry has many practical advantages over LEED, especially in the ease of the access around the sample. Or it can utilize an electron gun approaching electron microscope quality, and produce finely focused diffraction spots over a wide angular range. The glancing angle geometry of RHEED means that the reciprocal lattice rods are closely parallel to the Ewald sphere near the origin. This means that the low angle region often consists of streaks, rather than spots.

*4. Show and discuss the differences between RHEED and LEED techniques. Are there any advantages of RHEED over LEED?*

*5. Present an example of RHEED patterns.*

*6. Explain the term "in-situ" monitoring.*

**References**

[1] Hans Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer-Verlag Berlin Heidelberg, 2001.

## Seminar 2

**Bibliography**

1. Harald Ibach, *Physics of Surfaces and Interfaces*, Springer-Verlag Berlin Heidelberg, 2006.
2. H. Bubert and H. Jenett (editors), *Surface and thin film analysis*, Viley-VCH Verlag GmbH 2002 (chapter 2.4).
3. Hans Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer-Verlag Berlin Heidelberg, 2001 (Panel VIII).
4. Andrew Zangwill, *Physics at Surfaces*, Cambridge University Press, 1988.
5. John T. Yates, Jr., *Experimental innovations in surface science*, Springer-Verlag New York, Inc. 1998.

**Seminar 3**

# Techniques for examining surfaces.
# Inelastic scattering techniques

The previous part describe the techniques which concentrate on elastic scattering, where the energy of the outgoing electron is the same as that of the incoming electron. Here we will concentrate on **inelastic scattering** techniques.

There are three main analytical techniques that use electron emission in inelastic manner. **Ultra-violet Photoelectron Spectroscopy** (UPS) uses ultra-violet radiation as the probe, and collects electrons from the valence band, whereas X-ray Photoelectron Spectroscopy (XPS) excites a core hole with X-rays. The third technique is **Auger Electron Spectroscopy** (AES), which can be excited by (X-ray) photons or, more usually, electrons. In general, XPS and AES are used for species identification, and core level shifts in XPS can also give chemical state
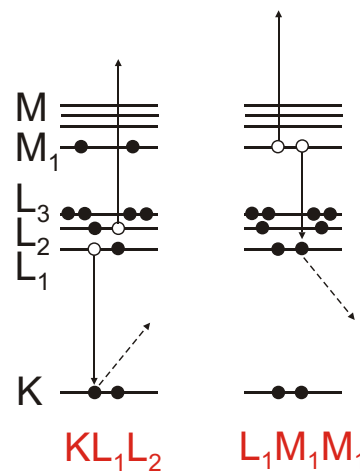


**Figure 3.1 Explanation of the Auger process. A primary electron produces an initial hole in a core level and the escaping electron is indicated by broken arrow; another electron is deexcited from a higher shell. The deexcitation energy is then transferred to a third electron, which leaves the system as an Auger electron.**

identification. AES is predominantly used to check surface cleanliness of the freshly prepared surface under UHV conditions. Another application is in the study of surface chemical composition. UPS is the main technique for determining the band structure (also of solids) and can also identify surface states. The surface sensitivity depends primarily on the energy of the outgoing electron.

*1. Describe the inelastic scattering of electrons (or the other particles).*

*2. Explain the basics of ultra-violet photoelectron spectroscopy.*

*3. Explain the Auger process. Explainin detail (how to produce electrons, what energy they have, how to collect Auger electrons, etc.) how to use AES to investigate surface. Give examples.*

## Seminar 3

Apart from electrons we can also use ions in surface investigations. The technique which uses a primary ion beam is **Secondary Ion Mass Spectroscopy** (SIMS). The ion beam has a typical energy between 1 and 10 keV. Due to the transferred energy neutral atoms, molecules and ions (secondary ions) are emitted from the surface and next analyzed. The obtained spectrum (mass spectrum) yields information about the chemical composition of the surface e.g. adsorbed layers. SIMS method is very useful in thin film studies.
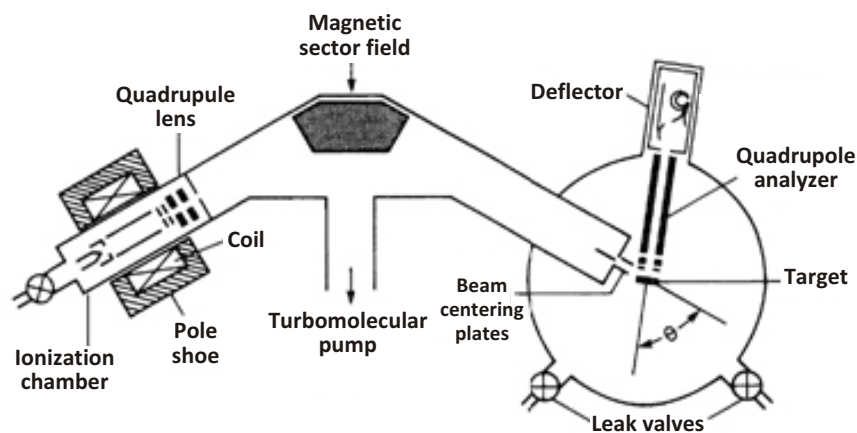


**Figure 3.2 Schematic view of SIMS setup. [1]**

*4. Explain the basics of SIMS technique. Show and describe the setup for SIMS measurements.*

*5. How are secondary ions analyzed? How does mass spectrometer work?*

*6. Give some examples of SIMS spectra.*

**References**

[1] Hans Luth, Solid Surfaces, Interfaces and Thin Films, Springer-Verlag Berlin Heidelberg, 2001.

**Bibliography**

1. Harald Ibach, *Physics of Surfaces and Interfaces*, Springer-Verlag Berlin Heidelberg, 2006.
2. H. Bubert and H. Jenett (editors), *Surface and thin film analysis*, Viley-VCH Verlag GmbH 2002 (chapter 2.2 - AES, chapter 3.2 - SIMS).
3. Hans Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer-Verlag Berlin Heidelberg, 2001 (Panels III and IV).
4. Andrew Zangwill, *Physics at Surfaces*, Cambridge University Press, 1988.
5. John T. Yates, Jr., *Experimental innovations in surface science*, Springer-Verlag New York, Inc. 1998.

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**Seminar 4**

# Techniques for examining surfaces.
# Electron microscopy techniques

There is now a wide range of techniques available for studying surfaces on a microscopic scale. To see as much as we can we have to switch from classical optical microscopy to electron microscopy. Electron microscopy has revolutionized our understanding of materials by completing the processing-structure-properties linked down to atomistic levels. It can be categorized into fixed beam, scanned beam and scanned probe technique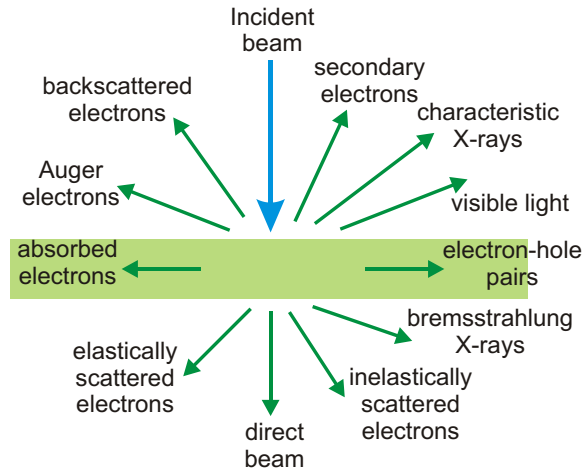s. A typical fixed beam technique is **Transmission Electron Microscopy** (TEM) which can also be used for Reflection Electron Microscopy (REM). The great virtue of fixed beam techniques is that the information from each picture element (pixel) is recorded at the same time, in parallel. This leads to relatively rapid data acquisition, and the ability to study dynamic events, often in real time, e.g. via video recording.
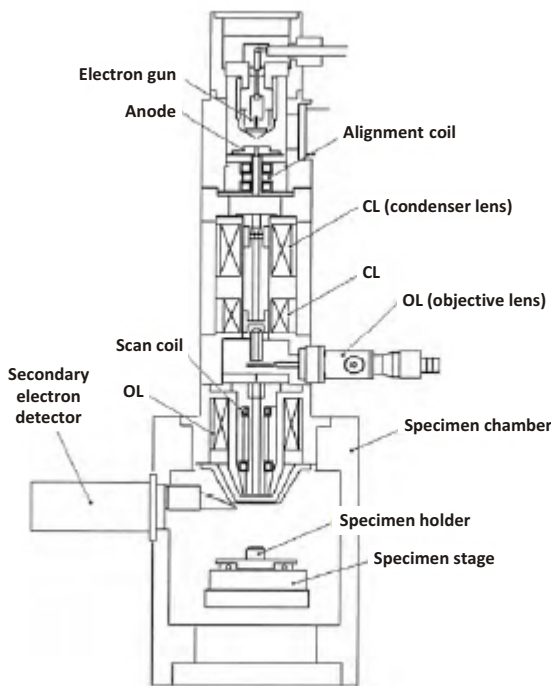


**Figure 4.1 Different signals generated when high-energy beam of electrons interacts with a thin specimen.**

In contrast, data in a scanned beam technique, such as **Scanning Electron Microscopy** (SEM) - fig.4.2, is collected serially, point by point. This makes the instrument ideally adapted for computer control and computer-based data collection, but can have a corresponding disadvantage; the need to concentrate a very high current density into a small spot means that not all forms of information can be obtained rapidly, that there will be a substantial signal to noise ratio problems, and that the beam can cause damage



**Figure 4.2 Schematic setup of SEM. [2]**

**Seminar 4**

to sensitive specimens. Another disadvantage is that at elevated temperatures defects may migrate across the surface and this migration may be too fast to be imaged by the scanning microscope methods. In that situation diffraction techniques (e.g. electron diffraction techniques) can still provide information about the surface i.e. the mean concentration of defects or the mean shape of islands.

Scanning Auger Microscopy (SAM) is the child of AES and SEM. A fine primary beam is used, scanned sequentially across the sample as in SEM, and the emitted electrons are energy analyzed as in AES.

The basic principle of scanning techniques is to focus an electron beam (usually 2 - 10 keV) on the surface under study and next to collect secondary electrons, which typically form a large proportion of the emitted electrons. The intensity of the emitted signal, in SEM, determines the brightness of the observed spot. The formation of the topographical image is due to the local variations of the electron emissivity of the surface.

*1. How can you categorize electron microscopy techniques? What are their advantages and disadvantages? Why du we use electrons instead of light?*

*2. Present the basic principles of SEM. Describe setup details.*

*3. What type of images can we get? Give examples.*

The first TEM was built by Max Knoll and Ernst Ruska in 1931. TEM is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen next the image is magnified and focused onto an imaging device.

Imaging methods in TEM utilize the information contained in the electron waves exiting from the sample to form an image. The projector lenses allow for the correct positioning of this electron wave distribution onto the viewing system. At smaller magnifications TEM image contrast is due to the
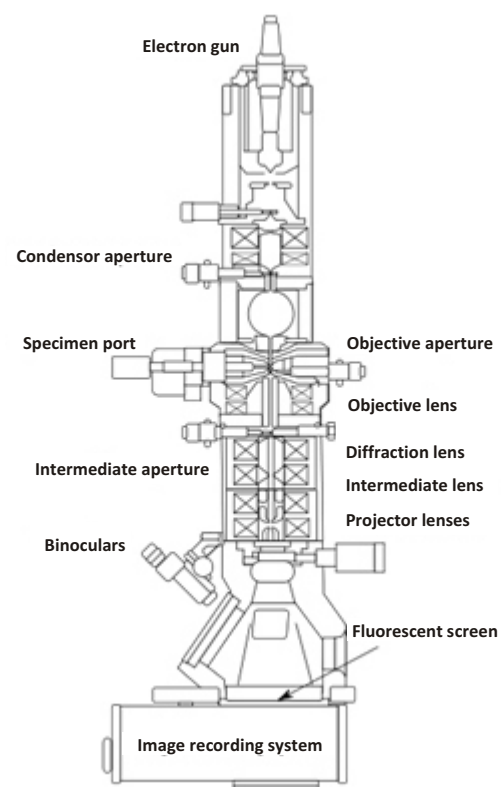
**Figure 4.3 Schematic setup of TEM. [1]**

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## Seminar 4

absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of the observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

### 4. Present the basic principles of TEM. Describe details of TEM setup.

TEM (as any other technique) has also some disadvantages. Many materials require extensive sample preparation to produce a sample thin enough to be electron transparent. There is potential that the sample may be damaged by the electron beam, particularly in the case of biological materials.

### 5. What kind of samples are usually under investigations. Introduce the specimen preparation.

### 6. What type of images can we get? Give TEM image examples.

Using electrons in surface investigations we have to remember about another problem - we get two-dimensional images of three-dimensional specimens, viewed in transmission. Our eyes and brain routinely understand reflected light images but are ill-equipped to interpret TEM images and so we must be cautious.

### 7. Introduce the problem of image simulation. TEM image in 3D.

**References**

[1] Hans Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer-Verlag Berlin Heidelberg, 2001.

[2] Weilie Zhou and Zhong Lin Wang (editors), *Scanning Microscopy for Nanotechnology*, Springer 2006.

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1.  Hans Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer-Verlag Berlin Heidelberg, 2001 (Panels V and VI).
2.  Weilie Zhou and Zhong Lin Wang (editors), *Scanning Microscopy for Nanotechnology*, Springer 2006 (chapters 1 and 4).
3.  David B. Williams and C. Barry Carter, *Transmission Electron Microscopy*, Springer, 2009.
4.  Harald Ibach, *Physics of Surfaces and Interfaces*, Springer-Verlag Berlin Heidelberg, 2006.
5.  John T. Yates, Jr., *Experimental innovations in surface science*, Springer-Verlag New York, Inc. 1998.

# Techniques for examining surfaces.
# Scanning tunneling microscopy

The scanning tunneling microscope (STM) was developed by Binning and Rohrer in 1982. It delivers pictures of a surface with an atomic resolution. The STM has become the most important method to observe and investigate defects on surfaces. The advantages of STM are: the nature and shape of the defects is identified from the images, their atomic structure can be seen directly, and their motion on the surface can be tracked.
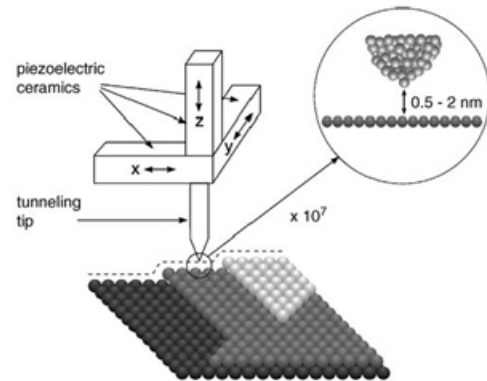


**Figure 5.1 Schematic diagram showing the principle of STM.[2]**

The basis of the STM is the quantum mechanical tunneling process and its extreme sensitivity on the width of the tunnel gap. A sharp metallic tip (ideally terminated by a single atom) is immersed into the evanescent electron wave functions outside the solid surface. For small tunneling voltages, the tunneling current is proportional to the density of those electrons in the tail that have their energy at the Fermi-level. As the electron density decreases exponentially with the distance, the tunnel current also decreases exponentially with the distance. In the standard mode of operation, the tunnel current is held cons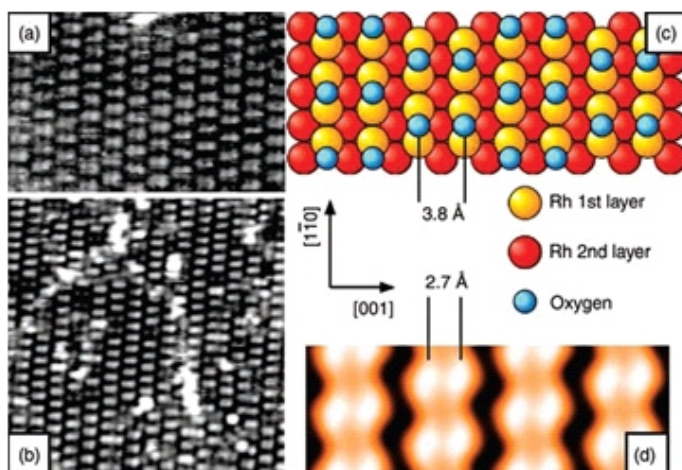tant by a feedback loop, so that the tip follows the contour of constant density of electrons at the Fermi-level. An alternative mode of operation is the constant height modus. The latter is employed in particular for fast scans (video frequency) over small and mildly corrugated surface areas. [1]

An electron in one lead of the junction has a nonvanishing probability to pass the potential barrier between the two sides and to tunnel into the



**Figure 5.2 (a) Rh(1 1 0) surface (11.5nm x7.5 nm, I = 1 nA, VB = 0.13 V), (b) STM image after dosing oxygen and annealing at 270 K (20nmx20 nm, I = 1 nA, VB = 0.42 V. (c) Structural model of the c(2x4)-O. (d) Simulated STM image (I = 0.05 nA, VB = 0.13 V). [2]**

## Seminar 5

other lead. However, this process is highly influenced by (i) the distance between the leads, (ii) the chemical composition of the surface and tip, (iii) the electronic structure of both the systems, (iv) the chemical interactions between the surface and the tip atoms, (v) the electrostatic interactions of the sample and tip. The main problem, from the theoretical point of view, is that the order of importance of all these



**Figure 5.3 The schem of AFM operation.**

effects depends generally on the distance and therefore on the tunneling conditions.
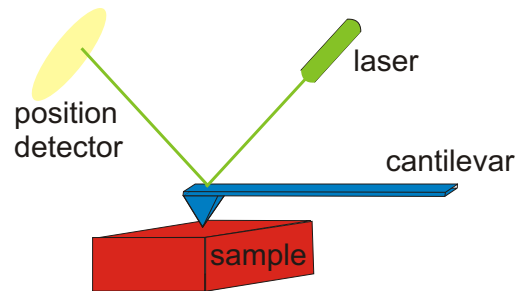
*1. Explain basics of STM. Describe STM setup. What is a "tip"? How is it made? Describe basic modes of working with STM.*

*2. What can we investigate using STM? What are the disadvantages of STM? Is the UHV always necessary?*

*3. Give examples of STM images. How to examine STM images?*

The Atomic Force Microscope (AFM) originally suffering from a lower, non-atomic resolution has now a lateral resolution comparable to the STM, and has found a widespread application in the investigation of insulator and soft matter surfaces.

*4. What are main differences between STM and AFM?*
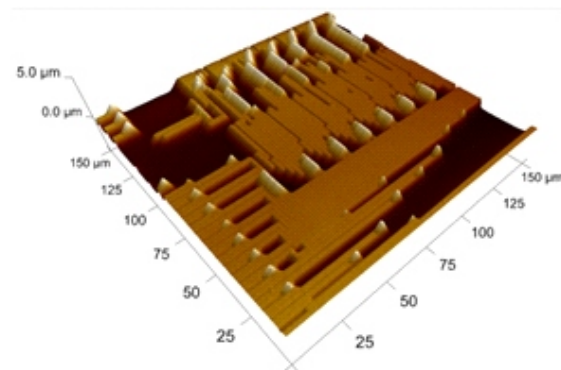
*5. Give examples of AFM images.*



**Figure 5.4 Part (150 x 150 m) of pentium procesor core. (J.Rebis - Wikipedia)**

**References**

[1] Hans Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer-Verlag Berlin Heidelberg, 2001.

[2] Michael Bowker and Philip R. Davies (editors), *Scanning Tunneling Microscopy in Surface Science, Nanoscience and Catalysis*, WILEY-VCH Verlag GmbH, 2010.

## Seminar 5

**Bibliography**

1. Hans Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer-Verlag Berlin Heidelberg, 2001 (Panels V and VI).

2. H. Bubert and H. Jenett (editors), *Surface and thin film analysis*, Viley-VCH Verlag GmbH 2002 (chapter 5.1 - AFM, chapter 5.2 - STM).

2. Michael Bowker and Philip R. Davies (editors), *Scanning Tunneling Microscopy in Surface Science, Nanoscience and Catalysis*, WILEY-VCH Verlag GmbH, 2010 (i.e. chapter 4).

3. Harald Ibach, *Physics of Surfaces and Interfaces*, Springer-Verlag Berlin Heidelberg, 2006.

4. John T. Yates, Jr., *Experimental innovations in surface science*, Springer-Verlag New York, Inc. 1998.

**Seminar 6**

# Surface crystallography

The periodic structure of crystalline, as for bulk materials, reduces the electronic degrees of freedom from 1023 per cm3 to the degrees of freedom in a single unit cell - in the number a dozen or so.

At surfaces the reduction in the degrees of freedom by periodicity is not so spectacular. Near surfaces, material properties usually differ from the bulk and the surface unit cell contains more atoms than the corresponding unit cell of the bulk structure. For example, the surface cell of the clean (111) surface of silicon contains 49 atoms in one atom layer and the restructuring involves 4-5 atom layers! [1]

Assuming above a better understanding on an atomic level is very important and impossible without the knowledge of the crystallographic structure of the studied medium.

A surface crystallography is an excellent introduction to get acquainted with the structure of the surface.

We know that the positions of surface atoms differ from the bulk because of the broken symmetry and the broken bonds. These modifications are called:

- **relaxations** - if the surface unit cell remains the same as truncated bulk and

- **reconstructions** - if the surface unit cell is different. The lattice of an adsorbed phase with a unit cell larger than the surface cell of the truncated bulk is called a **superlattice**, the associated structure a **superstructure**.
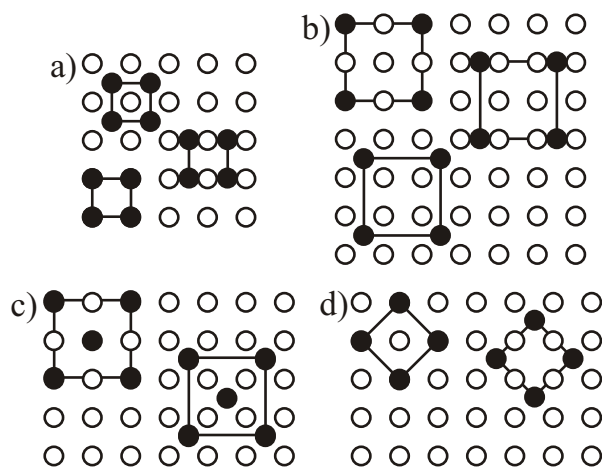


Figure 6.1 Examples of 2D surface structures.
a) p(1x1), b) p(2x2), c) c(2cx2), d) $(\sqrt{2}x\sqrt{2})R45^{o}$, denoted according to the Wood nomenclature.

*1. Explain why arrangement of atoms on the surface differs from its arrangement in bulk. Explain terms: relaxation and reconstruction, related to the broken symmetry of truncated bulk. Give examples (see fig. 1.1). Explain the trivial notation.*

Let's consider bulk material. From solid state physics we learned that different materials (metals or semiconductors) crystallize in well known structures: face-centered cubic (fcc), body cubic centered (bcc), diamond, zincblende or wurtzite. The surface reconstruction of any bulk structure depends on how the structure was terminated (what direction - see fig. 6.2).

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## Seminar 6

### 2. Visualize examples of surfaces for structures truncated in different directions (see e.g. fig. 6.2). Give examples also for real surfaces.

The large diversity in the structures of bare surfaces is surpassed by the diversity of structures of adsorbates covered surfaces. Adsorbates can have different effects on the structure of the substrate surface. They may



**Figure 6.2 {111}, {100}, and {100} surfaces of fcc-crystals; bottom row displays side view.**

- saturate the dangling bonds and then restore the unreconstructed surface (reconstruction isn't necessary),

- cause a restructuring of the substrate (for strongly bonded adsorbates),

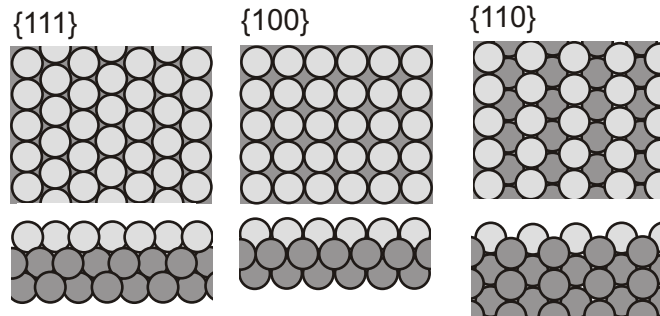- leave the substrate surface largely unaltered and locally form superlattices.

### 3. Present examples of different surface superlattices formed by adsorbates.

The concept of the reciprocal lattice was devised to tabulate two important properties of crystal planes: their slopes and their interplanar distances. Reciprocal space is also called Fourier space, k- space, or momentum space in contrast to real space or direct space.

The reciprocal space lattice is a set of imaginary points constructed in such a way that the direction of a vector from one point to another coincides with the direction of a normal to the real space planes and the separation of those points (the absolute value of the vector) is equal to the reciprocal of the real interplanar distance.



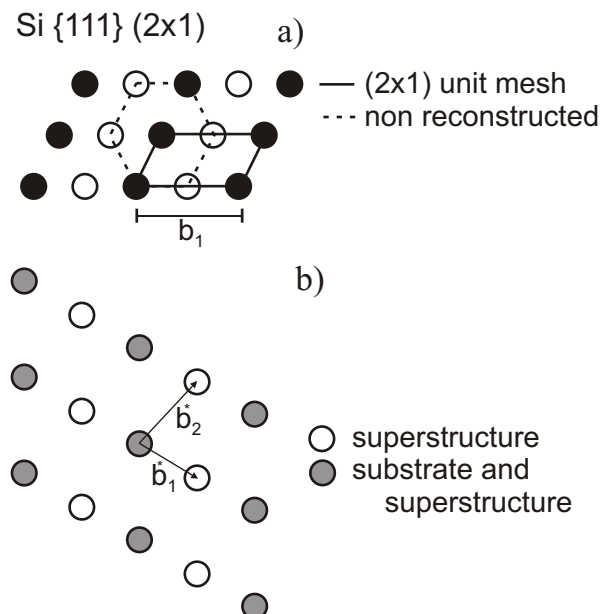### 4. Explain the terms real space and reciprocal space. Visualize and explain how to construct the reciprocal space.

**Figure 6.3 Example of surface superlattice in real (a) and reciprocal space (b) for (2x1) unit mesh of a Si {111} surface.**

## Seminar 6

**References**

[1] Harald Ibach, *Physics of Surfaces and Interfaces*, Springer-Verlag Berlin Heidelberg, 2006.

**Bibliography**

1.  Harald Ibach, *Physics of Surfaces and Interfaces*, Springer-Verlag Berlin Heidelberg, 2006 (chapter 1).
2.  Hans Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer-Verlag Berlin Heidelberg, 2001.
3.  Andrew Zangwill, *Physics at Surfaces*, Cambridge University Press, 1988.

**Seminar 7**

# Defects at surfaces and their observation

The crystal surfaces can be divided into the idealized perfect ones, which do not exhibit any lattice defects and the real, imperfect ones, where all the defect types (vacancies, impurities or intrusions, stacking faults, etc.) are present (see Fig. 7.1). Usually as a perfect surface we imagine a lattice plane revealed by the ideal cleavage of a single crystal into two parts, parallel to the crystallographic plane, without changing the atomic configuration in either of the resulting parts. In practice the total elimination of lattice defects is not possible. In order to avoid the number of defects/ impurities the measurement should be carried out under ultrahigh vacuum conditions. To illustrate the importance of this restriction one may note that at a pressure of $10^{-6}$ Torr a monolayer of oxygen is formed on a metal surface (about $10^{15}$ atoms per $cm^2$) in one second. Under the vacuum conditions of $10^{-9}$ Torr this time extends to one hour. [1]
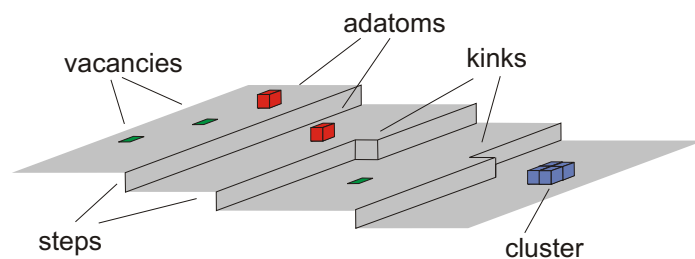


**Figure 7.1 Different types of surface defects.**

All surface imperfections cause all important surface quantities, as binding energy or electronic states.

*1. What can you tell about perfect and real surfaces? Are there any conditions when we can treat surface as an perfect one?*

*2. Why do defects (imperfections) appear on surfaces? List and characterize different types of defects which can be found on real surface.*

One can classify the surface defects according to their dimensionality. Zero-dimensional or point defects involve **adatoms**, **ledge adatoms**, **kinks** and **vacances**. An one-dimensional or line defect is the **step** in which the ledge separates two terraces from each other, boundaries between different domains of adsorbate structures, **dislocations** and also non-structural defects as the boundaries between magnetic or ferroelectric domains. [2] A two- or three-dimensional compound of a few identical or different atoms on surfaces is called a **cluster**. In the case of an ensemble of many atoms we can say about **island**.

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*3. Can you classify defects according to their dimensionality? Is this characterization sufficient? What can you say about i.e. intersitials and anti-site defects? What are dislocations?*

At the beginning the experimental investigation of defects was very difficult. The only possibility of defect observation was **decoration** of steps and point defects by large Z-elements (mostly Au) and imaging the decorated defects in an electron microscope. The images produced in that way presented defects which cannot change the position with time after decoration (these defects were also chemically inactive).

*4. Explain what decoration of defects is. What disadvantages does it have?*

A classical diffraction experiment concerns vicinal surfaces with regular step arrays. Such a surface has two periodicities, one is the atomic periodicity of the flat terraces, and the other one is the periodic array of steps and terraces. Diffraction therefore requires constructive interference with respect to both periodicities. Low energy electron diffraction (LEED) has been shown to be very sensitive to the presence of surface steps and other types of defects, including domain structures.

Diffraction techniques are mainly employed in the cases where the defects exist merely on a very short time scale or move rapidly about on the surface (scanning microprobe techniques are not efficient). Each type of defect gives rise to a particular diffraction pattern according to the structure of the defect and its embedding into the surface matrix. This specific diffraction pattern can be used to identify the nature of the preponderant surface defect and to analyze its shape, size and concentration.

*5. What are the advantages of diffraction techniques in surface defects investigations? Give examples.*

The invention of the scanning tunneling microscope (STM) and the other scanning microprobes gave the possibility of detailed defect investigations. Not only that line and point defects have become visible objects, it was also possible to track their motion as they migrate across the surface. The advantages of STM are: the nature and shape of the defects are identified
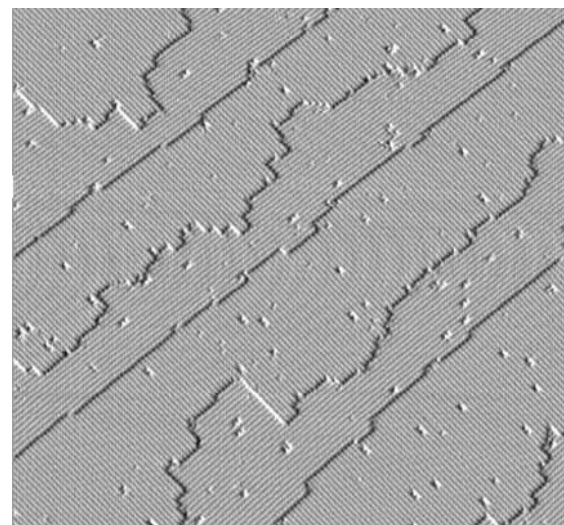


**Figure 7.2 STM image of a Si(100) surface with steps. [4]**

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from the images, their atomic structure can be seen directly, and their motion on the surface can be tracked. The scanning microscopy techniques have also disadvantages. One of them is that at elevated temperatures defects may migrate across the surface and this migration may be too fast to be imaged by the scanning microscope methods. In that situation diffraction techniques (e.g. electron diffraction techniques) can still provide information about the surface e.g. the mean concentration of defects or the mean shape of islands. [3]

6. *List an advantages and disadvantages of STM technique (and other scanning microprobes) to surface defects investigations.*

7. *Give examples of using STM to surface defect investigations.*

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[1] A. Kiejna and K.F. Wojciechowski, *Metal Surface Electron Physics*, Elsevier Science Ltd. 1996.

[2] Hans Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer-Verlag Berlin Heidelberg, 2001.

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**Seminar 8**

# Charge distribution at surfaces and interfaces

In the solids, the simplest model for the quantum states of electrons in a metal is the particle-in-a-box model. The model neglects all explicit electron-electron interactions. According to the Pauli-principle, the single electron states are occupied by one electron up to a maximum energy, the Fermi-level. While the **particle-in-a-box** model is reasonably realistic concerning the electron charge distribution near the surface, it cannot predict the **work function** or, alternatively the depth of the potential well.

*1. Explain in a few words the bases of particle-in-a-box model. What is a work function?*

A more realistic representation of the electron distribution at the surface of a simple metal is provided in the framework of the uniform positive background or **jellium model**. In this model the positive
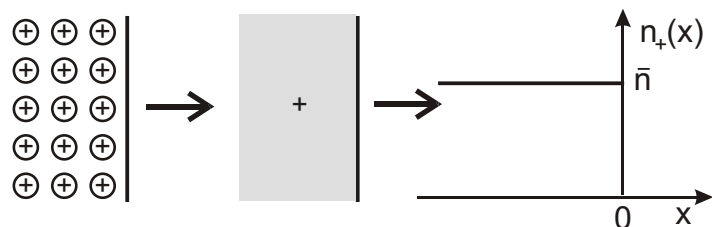


**Figure 8.1 The jellium model - positive charge distribution.**

charge of point ions is smeared out uniformly over the volume of the crystal forming a sort of metallic jelly (fig.8.1). The next step is to include electron-electron interactions. [1]

In the above expression we have placed the jellium edge at x - 0, i.e. at the location of



**Figure 8.2 Illustration to the Smoluchowski effect.**

surface (fig.8.1). An interesting question is, if the jellium edge is located in the same position as a barrier? First we have to distinguish between the **physical** and **geometric surface**. The first one will denote the location of the barrier while the second, the place where the positive charge background terminates. The application of the jellium model and the regard of the charge neutrality condition leads to the solution of the problem stated above: the physical and geometrical surfaces of real metal are shifted one relative to the other. [2]
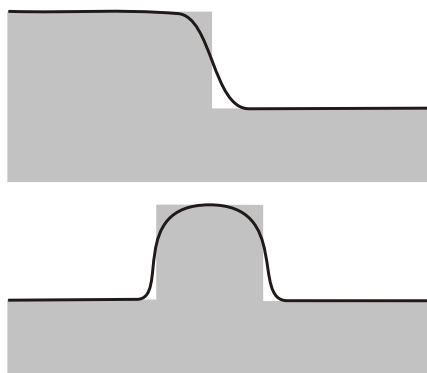
*2. What is jellium model? What are its advantages and limitations.*

*3. Define physical and geometric surface. Why are there shifted one relative to the other?*

The work function of a metal depends on the crystallographic structure of the surface - the more open the structure, the lower is the work function. Furthermore, a rough morphology

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leads to the reduction of the work function. This reduction is known as the **Smoluchowski-effect**. The density of electrons on the surface cannot follow the sharp contour of the jellium-edge at a step site - fig.8.2 (a) or at a single adatom - fig.8.2 (b). The result of the above is a dipole moment pointing with the positive end away from the surface leading to a reduction of the work function.

### *4. Explain the Smoluchowski effect. What is the reason for the reduction of metal work function?*
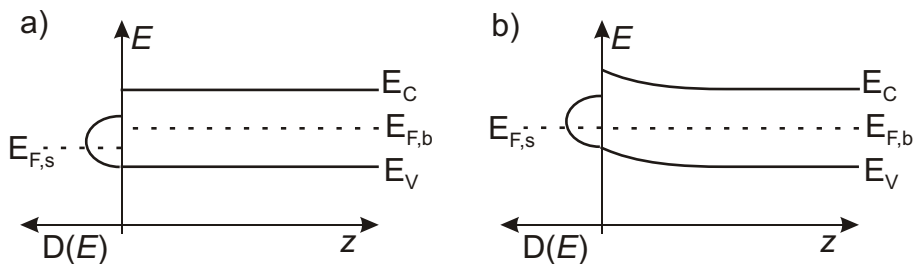


**Figure 8.3 Bands bending close to the surface, a) before equalizing of Fermi levels from the surface and bulk, b) after that.**

Inside the semiconductor bulk, the Fermi level is determined by the neutrality condition - it is near the center of the band gap for undoped material, near the conduction and valence bands for *n* and *p* doped material, respectively. Equilibrium between the surface and the bulk requires that the Fermi level in the surface and in the bulk must be at the same energy. This is realized by bending the bulk band structure near the surface (fig.8.3). Since the interface must remain neutral as a whole and the density of surface states is large, the shift within the surface state band in negligible, the Fermi level is pinned by the surface states.
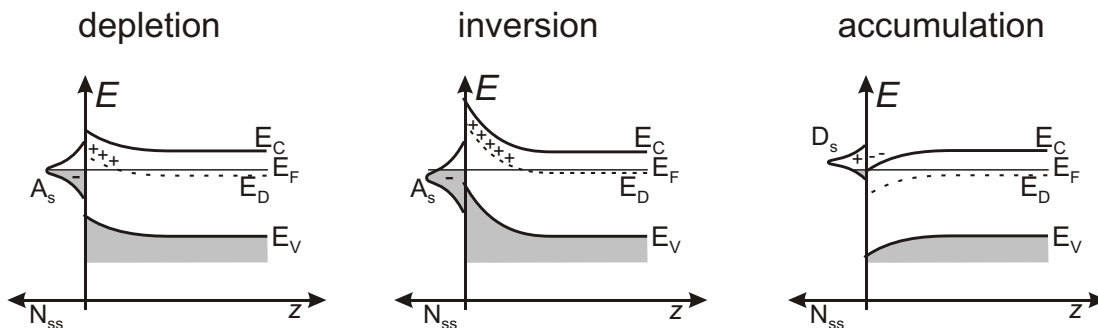


**Figure 8.4 Schematic plot of bands in *n*-type semiconductor. $A_s$ and $D_s$ are surface acceptors/donors, $N_{ss}$ is carriers density (after [3]).**

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*5. Why is semiconductor surface charged? (Is surface states density high?)*

*6. Explain why energy bands in bulk material bends near the surface? What is Fermi level pinning effect?*

*7. What is space-charge layer? Classify the space-charge layers.*

Comparing to the clean surface more important are surfaces in *p-n* junction and at the metal semiconductor interface. A potential diagram of a metal/semiconductor interface with an *n*-doped semiconductor is shown in fig. 8.5. The band bending is determined by the work function of the metal $W_F$, the potential drop    across the microscopic interface, the electron affinity of the semiconductor   , and the position of the Fermi level in the semiconductor relative to the conduction band edge $E_c$.

*8. Show and explain the potential diagram of a metal/semiconductor interface. What is Schottky barrier?*

The most important application of space-charge layers is field-effect devices. Since their conduction process involves one kind of carriers, field-effect transistors are called **unipolar**. Two major classes of field-effect transistors are: metal semiconductor field-effect transistors (MESFET) and metal-oxide semiconductor field-effect transistors (MOSFET).
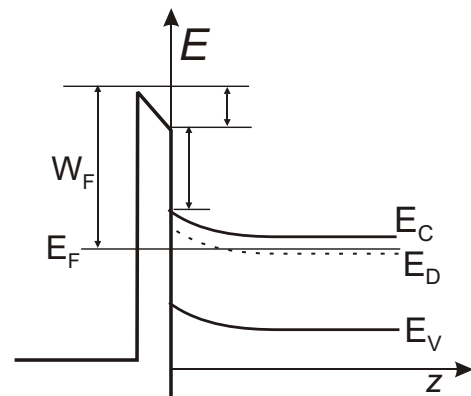


**Figure 8.5 Potential diagram of a metal/semiconductor interface with an *n*-doped semiconductor (after [1])**

*9. Why do we call MESFET's and MOSFET's unipolar? What is their band diagram? Do you know any bipolar transistors?*

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**Seminar 9**

# Optical Techniques

Optical tools for surface and interface analysis have become very prominent within the last twenty years due to their steadily increasing sensitivity and their possibilities for in situ operation. Optical techniques have some advantages over non-optical ones determined by their (usually) non-perturbing character, reliability and ease of use. They can be applied under vacuum as well as under and ambient conditions.

At the moment there are many different optical methods and their modifications which can be applied to investigate surfaces and interfaces. Here we will deal with some of the most popular techniques. Some of them will be discussed in other chapters. Mentioning linear optical techniques we can talk about: **spectroscopic ellipsometry** (SE), **surface differential reflectivity** (SDR), **reflection anisotropy spectroscopy** (RAS), transmission spectroscopy, photoluminescence spectroscopy, raman spectroscopy and **surface plasmon polariton spectroscopy**. Depending on the medium under study the above methods may require an infrared or visible light. Expecially in infrared region some of these techniques may be combined with a **Fourier-transform infrared** (FTIR) spectrometer.

Spectroscopic ellipsometry is a sensitive optical tool for studying various surface properties and processes which occur on surfaces. It can be used to monitor *in situ*: sample preparation, surface temperature, adsorption and growth. [1]



**Figure 9.1 Schematic sketch of an ellipsometer.**

The basic equation in SE connects the complex dielectric function of the crystal with the angle of incidence     and    - the ratio of the reflection coefficient in p-polarization to that in s-polarization. For the two-phase model of a crystal–vacuum interface we can write:

$$\sin^2 \quad 1 \quad \tan^2 \quad \left[ \frac{1}{1} \right]^2 .$$

*1. List the most popular optical methods for surface/interface investigations.*

*2. Introduce the basics of the spectroscopic ellipsometry method. Show SE setup. What is measured using SE? Present and discuss examples.*

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Surface differential reflectivity relies on the comparison of the reflectance of a clean semiconductor and the one of the same semiconductor (or other substrate) after adsorption of gas atoms or molecules. SDR is a powerful method to investigate ultrathin films and/or adsorbed species. [2] In SDR one obtains the relative difference in reflectivities measured at nearnormal incidence in p-polarization given by

$$\frac{R_{pp}}{R_{pp}} = \frac{R_{pp}^{clean} - R_{pp}^{ads}}{R_{pp}^{ads}},$$

where $R_{pp}^{clean}$ and $R_{pp}^{ads}$ are the reflectivities of the clean and adsorbate-covered surfaces, respectively, and the double subscript pp means that both the incident light and the reflected light are p-polarized.

### 3. Explain the basics of surface differential reflectivity. Present an examples.

Another surface sensitive method is reflectance anisotropy spectroscopy. [4] It relies on the comparison of the reflectance of light in normal incidence, when the light polarization is rotated from one to the other main axis of the surface. If the semiconductor bulk is isotropic, the measured signal carries information on the optical anisotropy of the surface only.

It is a very good method to investigate ultrathin films or adsorbed on the surface species. RAS can be used to distinguish between the properties of the adsorbate film and those of the substrate. [5] Being originally developed for the study of semiconductor surfaces, more recently RAS has been extended to probe the surface optical properties of metals and to monitor the growth of molecular assembly on metal surfaces.
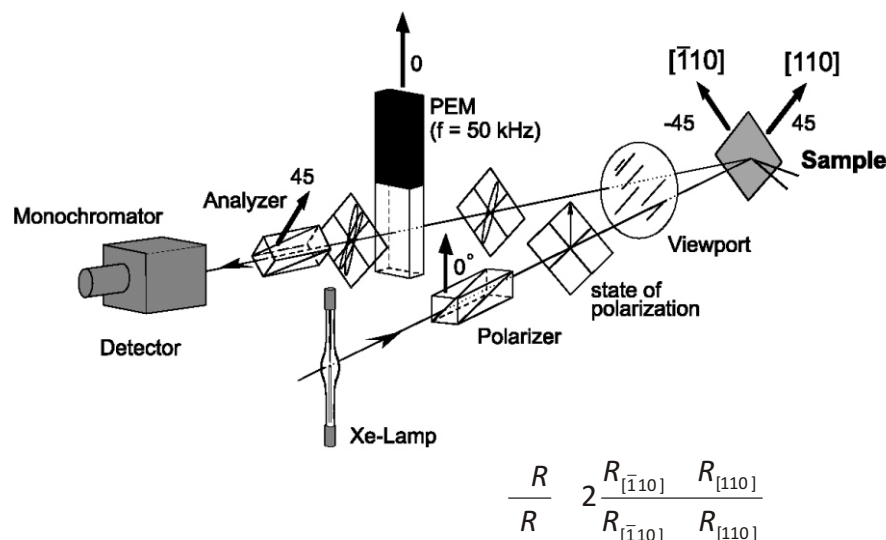


$$\frac{R}{R} = 2\frac{R_{[\bar{1}10]} - R_{[110]}}{R_{[\bar{1}10]} + R_{[110]}}$$
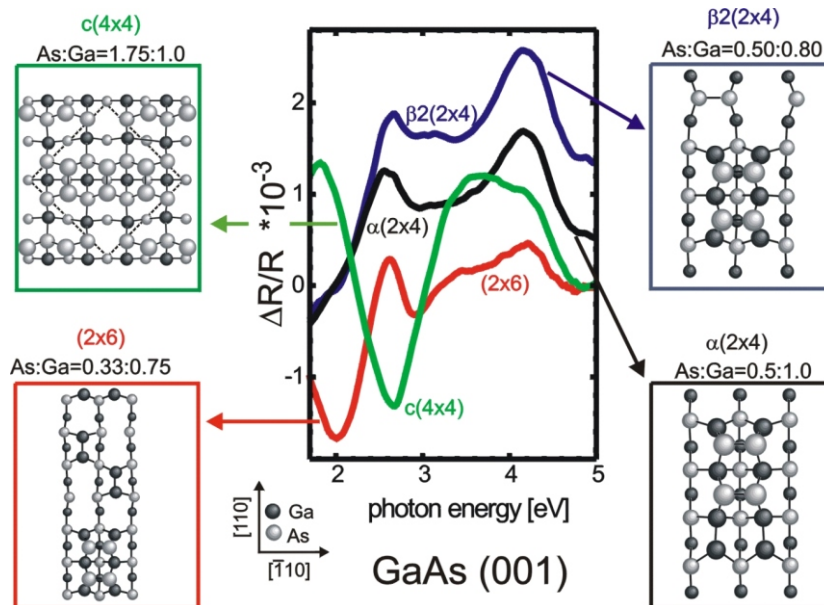
**Figure 9.2 RAS setup. [3]**

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**Figure 9.3 RAS spectra and surface correlation for GaAs(001) surfaces. [3]**

4. *Explain the basics of reflectance anisotropy spectroscopy. Describe in details the RAS setup. Explain how it can be used in-situ. Present some examples of RAS spectra.*

5. *List and briefly describe other optical methods appropriate for metal surface investigations.*

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[4] D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, J. Vac. Sci. Technol. A 6, 1327 (1988).

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## Seminar 10

# Optical techniques. Raman spectroscopy

In Raman spectroscopy, the spectrum of light inelastically scattered by a sample is measured. When the light is scattered from a molecule, most photons are elastically diffused (have the same energy of the incident ones) however, a small fraction of the light (approximately 1 in $10^7$ photons) is scattered at energies different from (usually lower) the incident light energy.

The above process is called **Raman scattering**. The frequency of the incident light is usually in the visible region and the frequency shift observed in scattering corresponds to vibrational or rotational transitions of the material. Raman spectra are widely used for the identification of chemical compounds in the sample as well as for the study of vibrational dynamics. The surface properties can be extracted from Raman spectra when they are distinguishable from those in the bulk.

## *1. What can we study using Raman spectroscopy? How can we investigate surface properties?*

As a result, the frequency of the scattered light,  ' is different from the frequency of the incident light,  . From energy conservation in a scattering process of incident photons, we can write [1]

$$\hbar\,' \quad \hbar \quad \hbar$$

where    is the frequency of the elementary excitation. The minus sign in the above equation implies the creation of excitation (**Stokes scattering**), whereas the plus sign corresponds to annihilation (**anti-Stokes scattering**) - see fig.10.1.
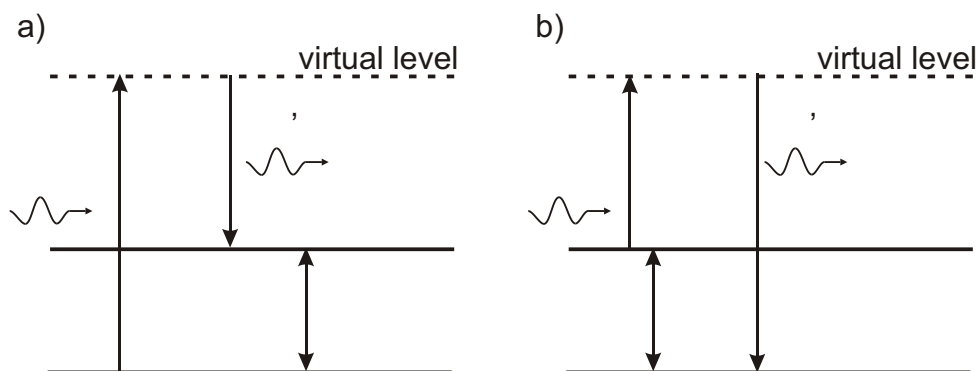
**Figure 10.1 Energy level diagram for (a) Stokes Raman scattering, (b) anti-Stokes Raman scattering.**
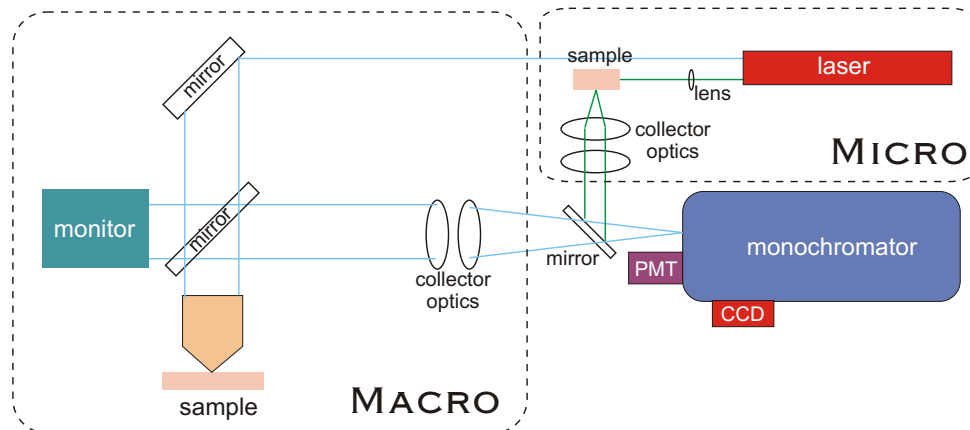
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**Figure 10.2 Schematic diagram of a Raman spectroscopy apparatus operating both in micro- and macroarrangements.**

### 2. Explain the Raman scattering process. Distinguish between Stokes and anti-Stokes Raman scattering.

### 3. What can you say about mutual intensities of anti-Stokes and Stokes lines?

The Raman spectra can be measured using a dispersive or Fourier-transform spectrometers. Dispersive spectrometers use grating monochromators and are preferable in the visible spectral range. Fourier-transform spectrometers calculate the spectrum from the interference pattern and are preferable in the infrared spectral range.

### 4. Present the Raman spectroscopy setup. What type of spectrometers can be used to measure Raman spectra? What are their preferable spectral ranges?

### 5. Give some examples of Raman spectra with reference to surface properties investigations.

It was discovered that Raman scattering from some molecules adsorbed on a metal surface has an enormously large cross-section. This phenomenon was named **surface-enhanced Raman scattering** (SERS). [1] Till now SERS has been observed for a large variety of molecules adsorbed on the surfaces of relatively few metals (silver, copper and gold) for different morphologies and physical environments. Possible mechanisms responsible for these features can be broadly classified as electromagnetic and chemical.

### 6. What is SERS? Can you explain the basics of this phenomenon?

The main limitation of Raman scattering for applications in the domain of the nanotechnologies is its low spatial resolution. [2] To enhance the Raman spectroscopy resolution it was combined with the **near-field spectroscopy** technique. The high resolution Raman spectroscopy was named **near-field Raman spectroscopy**.

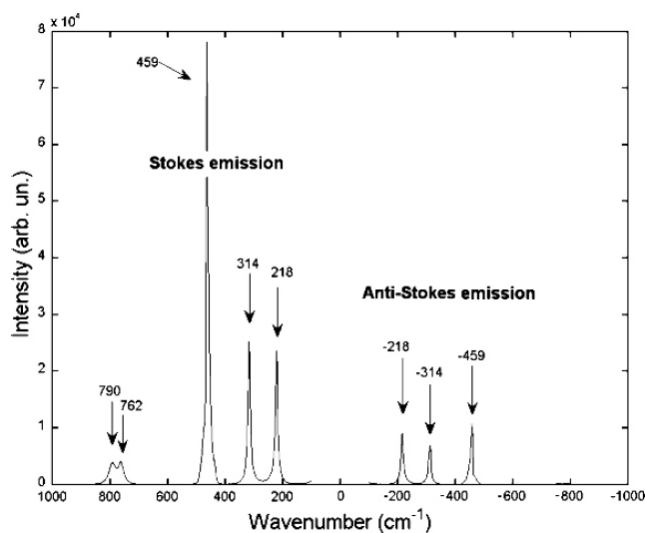## 7. Present the basics of near-field Raman spectroscopy.



**Figure 10.3 Stokes and anti-Stokes Raman emission of CCl₄ at room temperature, excited by the 514.5 nm line of an Ar laser. [2]**

**References**

[1] Vladimir G. Bordo and Horst-Günter Rubahn, *Optics and Spectroscopy at Surfaces and Interfaces*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2005.

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**Seminar 11**

# Optical Techniques.

# Electromodulation spectroscopy

To explore various physical properties of new materials and based on them semiconductor heterostructures and their surfaces (interfaces) a number of optical characterization methods have been applied. Most of the these methods require special experimental conditions such as low temperature or special sample preparation. For practical applications, it is advantageous to use techniques, which are simple and at the same time provide a lot of valuable information. Such are modulation spectroscopy techniques. [1,2]



**Figure 11.1 Spectra of MBE grown InGaSb/GaSb QW structure measured at 10K from different spectroscopic methods.**
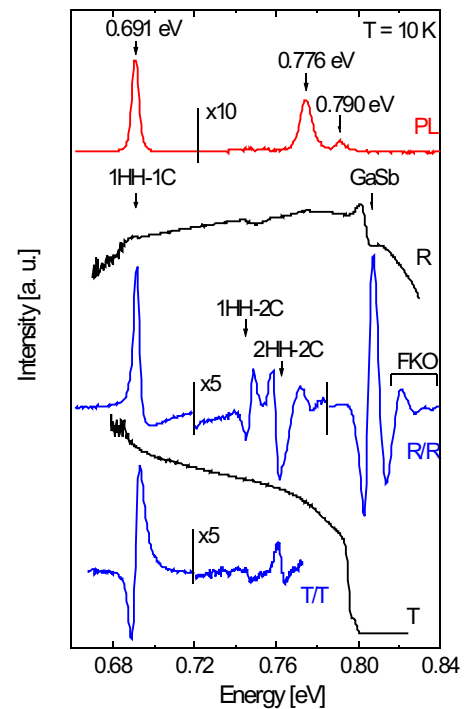
Modulation techniques take the advantage of the application of a small periodic perturbation to a physical property of the investigated sample. The change in the optical function (reflectivity or absorption) is only a small fraction of its unperturbed value, typically 1 part in $10^4$ or less. The most widespread are the methods based on modulation of the electric filed - **electromodulation** (EM) methods. Electromodulation can be classified into three categories depending on the relative strengths of characteristic energies (i.e. **electro-optic energy** or **broadening** energy): the low-field regime, the intermediate-field regime and high-field regime. Previously the most popular method was electroreflectance. Now we have to deal mostly with **photoreflectance** (PR) and **contactless electroreflectance** (CER).

1. *Characterize briefly modulation techniques. What are their advantages over other optical spectroscopic methods?*

2. *What is electromodulation? Define electro-optic energy or broadening. Distinguish between three categories in which the electromodulation can be classified.*

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The electromodulation techniques are based on the modulation of the electric field. In photoreflectance spectroscopy the varying parameter is the internal (built-in) electric field. Modulation of the electric field in the sample is caused by photo-excited electron-hole pairs created by the pump source (usually laser) which is chopped with a given frequency. The photon energy of the pump source is generally above the band gap of the semiconductor being under study.
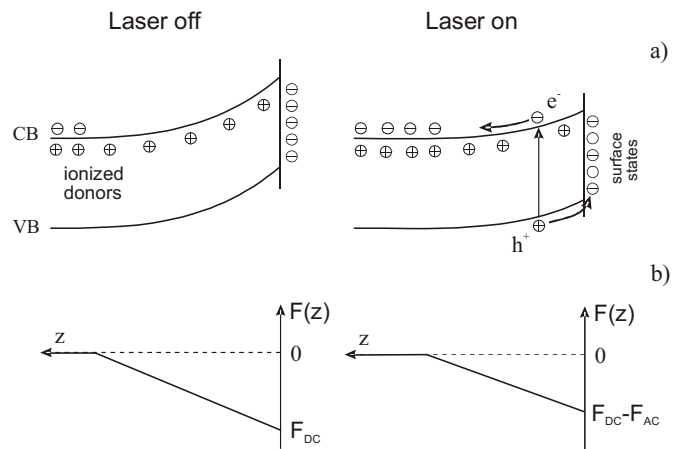


**Figure 11.2 Schematic representation of the photoreflectance effect - part a, and the photoinduced changes in the surface bulit-in electric field - part b, for an n-type semiconductor.**

Photoexcited electron-hole pairs are separated by the built-in electric field, with the minority carrier (holes in this case) being swept toward the surface. At the surface, the holes neutralize the trapped charge, reducing the built-in field from $F_{DC}$ to $F_{DC}-F_{AC}$, where $F_{AC}$ is a change in the built-in electric field (fig. 11.2b).

*3. Explain the basics of PR spectroscopy - the built-in electric field modulation. Describe the model set-up for PR measurements. What quantity is measured?*
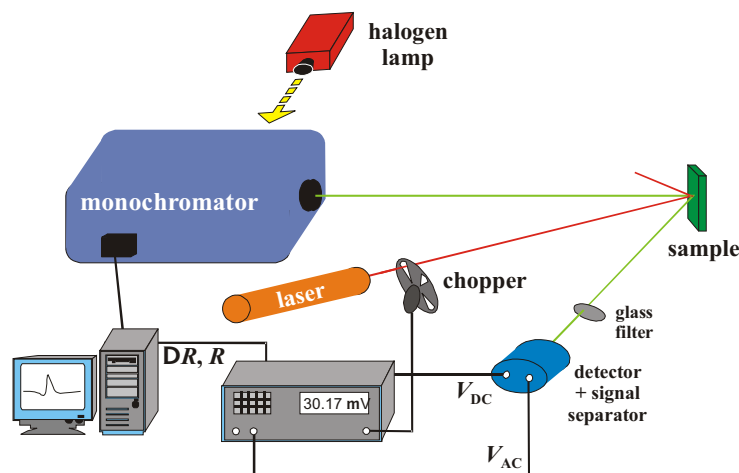


**Figure 11.3 PR setup.**

The method of electric field modulation in PR by an additional light source drives to the fact that PR is a contactless method. The sample doesn't require any special mounting. After

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measurements the surface stays as good as before it. It is even possible to measure PR in the growth chamber during the growth process [3].

The most important disadvantage of PR is that it is not possible to exclude the photovoltaic effect from both the pumping and probe beams. These pump beams may produce photovoltage of the value which may be even about 40% of Fermi level pinning.

Another contactless EM technique is contactless electroreflectance. The mechanism of modulation is very easy. Instead of placing the sample in the electrolytes (electrolyte ER) or evaporation on the sample ohmic contacts the sample is placed in a capacitor-like sample holder. The condenser-like sample holder consists of two electrodes. The bottom electrode on which the sample is fixed is usually made from metal. The top electrode is transparent. Usually to make the top electrode a thin, transparent and conductive metal coating on transparent substrate is used. Another idea to make the top electrode is to use a metal grid. The distance between the top electrode and the sample surface is about 0.1 mm. Ac voltage of 1-2 kV peak-to-peak is applied to the capacitor. If necessary it is possible to apply dc bias voltage.

One of CER disadvantages compared to the PR technique is mounting of the sample, which is crucial to get any result. Another disadvantage of CER is that due to the high screening by the surface electric field sometimes it is not easy to get a response from deeper lying parts of the investigated structure - we get the information from the region very close to the surface.
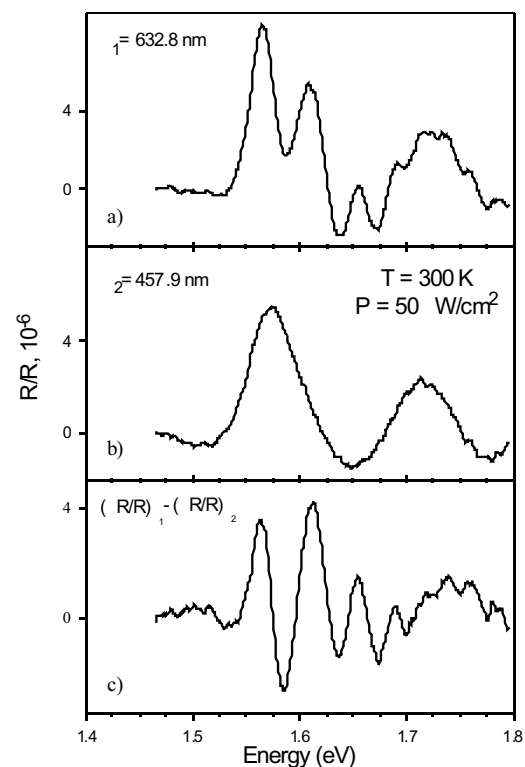
**Figure 11.4 PR spectra for $Al_{0.11}Ga_{0.89}As$ layers obtained with using following pump beams: a) 632.8 nm line of the He-Ne laser, b) 457.9 nm line of the $Ar^+$ laser; c) the difference between the two former spectra giving the Franz-Keldysh oscillations connected with the electric field at the $Al_{0.11}Ga_{0.89}As$/GaAs inteface (after Sitarek et al. 1999).[1]**

4. *What is a source of modulation in CER spectroscopy?*

5. *List advantages and disadvantages of PR and CER.*

## Seminar 11

PR and CER are usually used to study energies of direct bandgap optical transitions present in the investigated structure, but both methods are also very sensitive to the semiconductor surface/interface condition and quality. A detailed lineshape analysis lets us not only get optical transition energies and their broadening parameters (which usually tell us about structure quality) but also: calculate the value of the electric field, investigate the influence of annealing, processing and growth. All surface/interface investigations are usually possible in the intermediate-field regime, when PR and CER spectra have oscillation behavior - we can observe so called **Franz-Keldysh oscillations** (FKO).

*6. What are Franz-Keldysh oscillations? When can we observe FKO in PR/CER spectra? What can we estimate analyzing FKO?*

*7. Give examples of surface/interface electric field investigations using PR or CER technique.*

The PR has been used to the in situ study of the Fermi level pinning behavior of *n*- and *p*-type GaAs (001) surfaces in the ultrahigh-vacuum environment of a molecular beam epitaxy chamber [4]. PR has been also used to study the effects of in situ substrate cleaning processes in GaAs homoepitaxial structures [5].

*8. Show examples of the influence of annealing, processing or growth on the surface/interface using PR or CER technique.*

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## Seminar 12

# Optical Techniques.

# Surface Photovoltage Spectroscopy

The surface photovoltage (SPV) method is a well-established contactless technique for the characterization of semiconductors, which relies on analyzing illumination-induced changes in the surface voltage. The **photovoltaic effect** at metal-semiconductor and semiconductor-semiconductor junctions is at the heart of semiconductor devices which convert light to electricity (e.g. photodetectors). [1]

*1. Explain briefly the photovoltaic effect. What are metal-semiconductor and semiconductor-semiconductor junctions?*

*2. Introduce the basic concepts of surface photovoltage.*

Let's concentrate on the SPV induced at the free surface of a semiconductor sample with a grounded Ohmic back contact. SPV measurements are non-trivial because the surface potential is a built-in potential, rather than an external potential. SPV cannot be measured simply with some form of voltmeter. In the case of a free surface, the application of any contact for indirect electrical measurements of the built-in
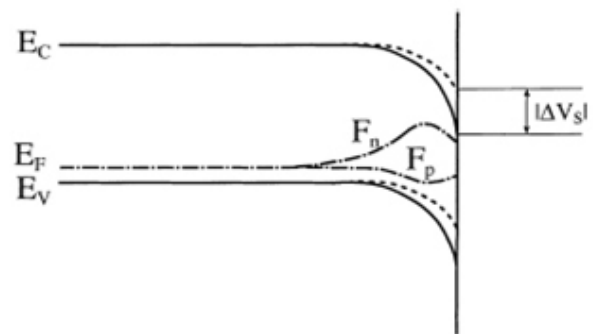


**Figure 12.1 Schematic band diagram of a surface space charge region under depletion: Solid lines -equilibrium. Dashed lines - under illumination. [1]**

voltage may invariably alter the surface properties. Due to the above, it is necessary to apply elaborate techniques for measuring the surface potential or its changes.

*3. Present the experimental methods permitting SPV measurements.*

*4. Explain the principles of Kelvin probe method.*

*5. Explain the principles and practical usage of MIS structure method (metal-insulator-semiconductor - MIS).*

Some information about important semiconductor properties as: the semiconductor bandgap energy and the type or its (surface and bulk) defect states, may be extracted using a simple analysis of the SPS spectra (SPV as a function of incident photon energy).

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### 6. Give examples of SPS spectra obtained for different materials. How is the bandgap energy determined from SPS spectra?

With the advent of crystal growth techniques, allowing the production of high quality semiconductor heterostructures, the surface photovoltage spectroscopy (SPS) method found some additional applications. Now it is also used to study electronic states in: heterostructures, quantum wells, quantum dots and superlattices.
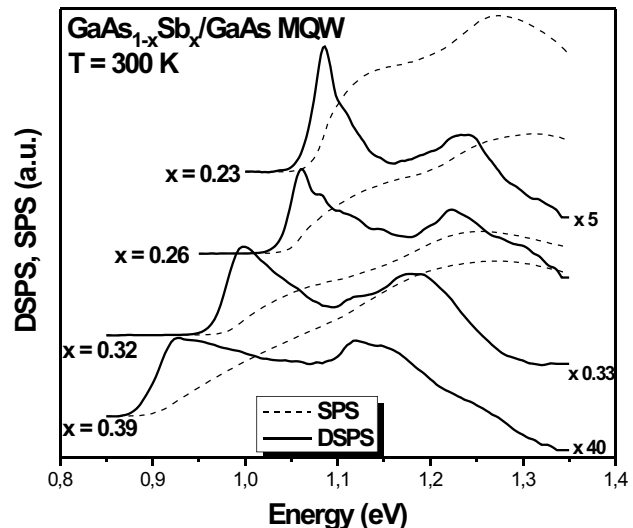


Figure 12.2 SPS (and its derivative) spectra for different samples. [3]

### 7. Give examples of SPS spectra obtained for different low-dimensional heterostructures.

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