

# Analysis of Nanostructured Materials Ph.D. Course\*

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*The Ph.D. student course includes four areas oriented on analytical training in the field of nano-scale materials. The first one is focused on the computer modeling of nano-structured systems using the molecular simulation in Cerius<sup>2</sup> modeling environment, the second deals with nano-scale surface analysis using Atomic Force Microscopy, and the third brings advanced information about crystal structure analysis using single-crystal and powder X-ray diffraction methods. The last area is oriented on analysis of materials by electron microscopy techniques. The Ph.D. student analytical course includes both theory and applications (training) of individual analytical procedures for various nano-structured materials (for example, nanotubes, intercalated and grafted clays, graphite, silicon wafers, polymer/clay nano-composites, and metallic thin multilayer materials).*

## INTRODUCTION

THE Ph.D. COURSE is consequence of long research collaboration between the Central Analytical Laboratory and Department of Physics of the Technical University of Ostrava and Faculty of Mathematics and Physics of the Charles University in Prague. The mutual research program is oriented on nano-scale materials, above all intercalated materials and the analysis of resulting supramolecular structures. Ph.D. students participate in this research and therefore, the primary object of the program is to improve the training conditions of Ph.D. students by enabling them to use research facilities and labs at both institutions. The Ph.D. program is divided into the following areas: (1) Computer modeling of nano-structured systems, (2) Nano-scale surface analysis using Atomic Force Microscopy, (3) Crystal structure analysis using X-ray diffractions, (4) Analysis of materials by electron microscopy techniques.

## COMPUTER MODELING

The molecular mechanics and molecular dynamics simulation in the Cerius<sup>2</sup> modeling environment is a very powerful tool in determination of crystal structures of various materials (namely, if the standard procedure, like X-ray single-crystal diffraction, is difficult to apply) and in prediction of their properties. Therefore,

application of molecular modeling is useful for solution of the following problems in the field of analysis of nano-scale materials:

- Visualization of the crystal structure of materials and their atomic-scale surface. It is very important, e.g., for interpretation of atomic force microscopy images.
- Complex structure analysis of materials (in combination with experimental results obtained from X-ray powder diffraction, NMR-spectroscopy, IR/Raman spectroscopy and atomic force microscopy). The use of this method enables us to investigate relatively large scale of materials.
- Understanding of the structure-properties relationship as a crucial factor in design of new materials.

Complex structure analysis of materials is based on the molecular simulation procedure which is a method of optimization of bonding geometry and molecular and crystal packing using energy minimization. Energy is described using empirical force field [1]. The total energy of the system is expressed as a sum of bonding interactions (analytical expressions describing the covalent bonds) and non-bond interactions (Van der Waals, hydrogen bond and electrostatic interactions). The strategy of modeling means: the building of the initial models, the set up of energy expression, the choice and test of the force field, the determination of rigid fragments and the set up of the fixed and variable structure parameters during energy minimization. This strategy should be always based on the available experimental data. In order to reach

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the global minimum of the system the molecular dynamics will be used to overcome the local potential barriers. Molecular dynamics allows the introduction the kinetic energy and corresponding temperature into the system. The atom vibrational velocities are assigned randomly using Gaussian distribution and atomic trajectories are calculated solving Newton's equations. In the Cerius<sup>2</sup> system the Ewald summation method [2] is used to calculate the Coulombic energy, and the Lennard-Jones functional form is used for Van der Waals energy calculation. Charges are calculated using Qeq method (Charge equilibration approach) [3]. The temperature during dynamic simulations is kept fixed using Berendsen thermostat [4].

Applications and training involve:

1. Visualization of the crystal structure of silicon, graphite, and phyllosilicates (mica, montmorillonite), and atomic-scale surface of different sections through their structures to calculate interatomic distances.
2. Determination of the interlayer region structure of montmorillonite developed after intercalation with polar molecules of octadecylamine in dependence on the concentration of guest molecules using molecular simulation procedure. Different arrangement of octadecylamine molecules leads to the different interlayer spacing and conditions for possible

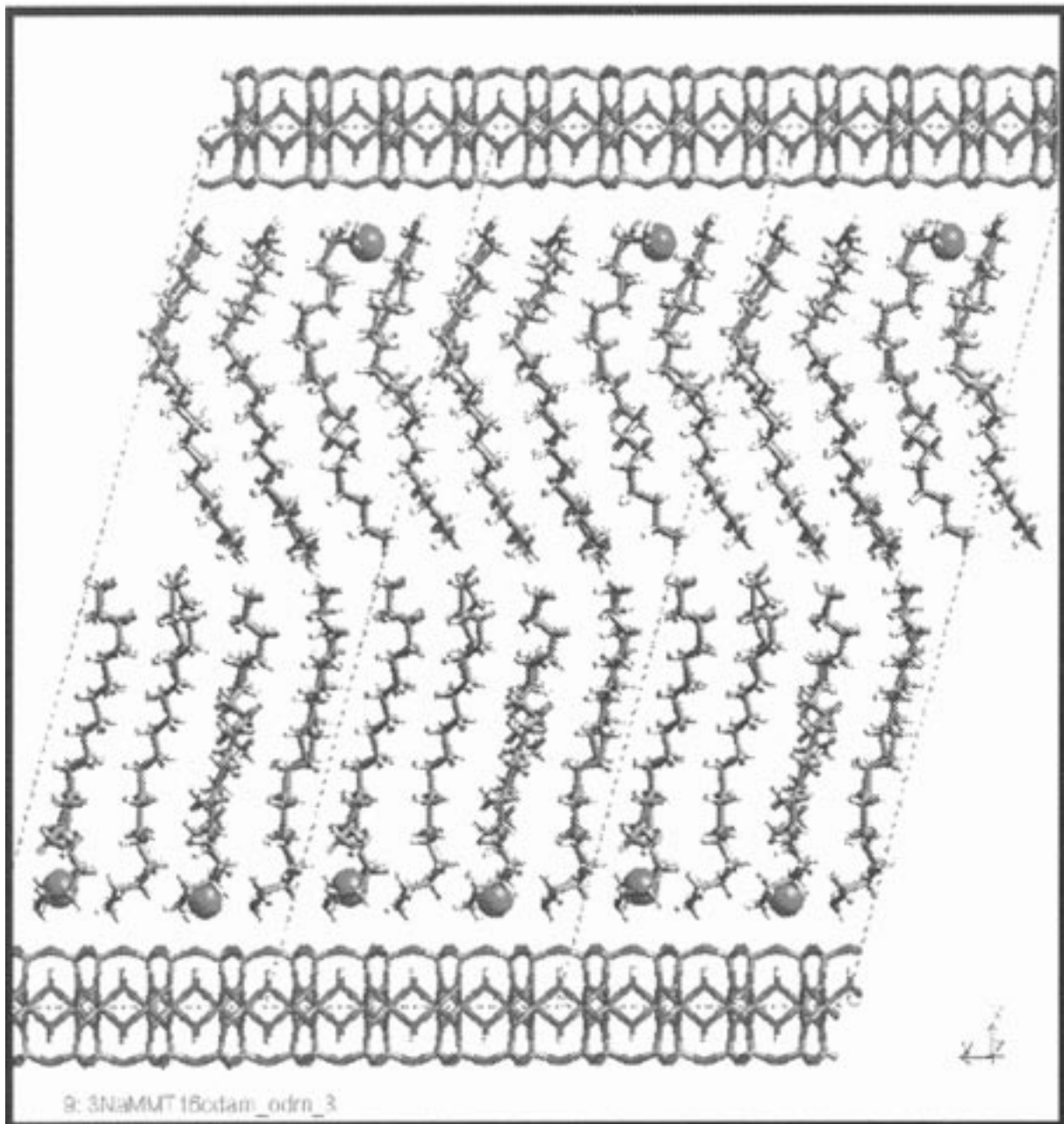


Fig. 1. Determination of the interlayer structure of montmorillonite intercalated with polar molecules of octadecylamine.

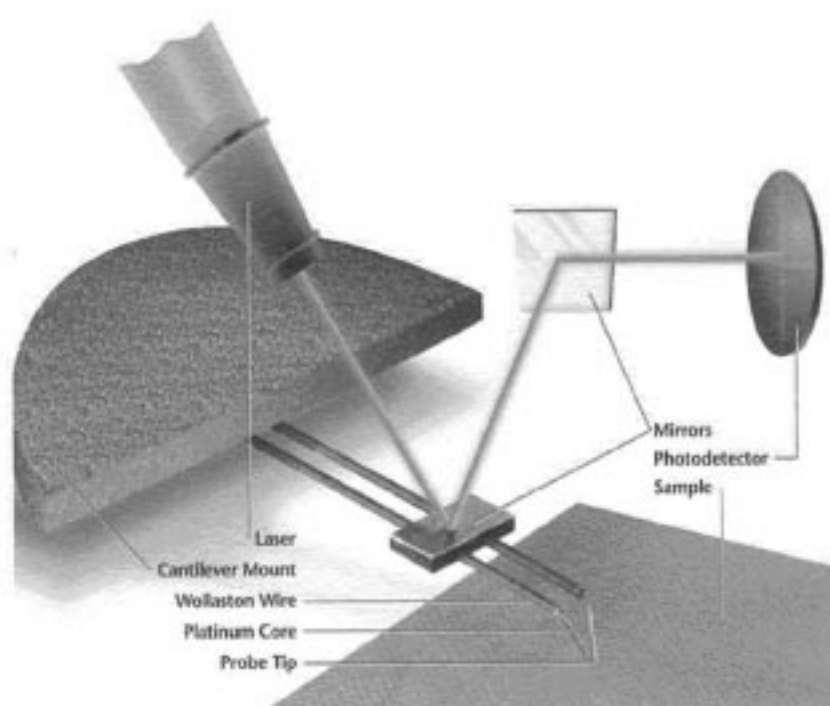


Fig. 2. Scheme of AFM arrangement.

formation of clay nano-particles can be predicted. The mutual interaction of host layers,  $\text{Na}^+$ -cations and octadecylamine molecules leads also to the unusual charge distribution in the intercalated structure with the positive charge on the silicate layers for high concentrations of octadecylamine molecules and both interlayer species ( $\text{Na}^+$ -cations and polar molecules of octadecylamine) participate in the host-guest charge transfer (Fig. 1).

### ATOMIC FORCE MICROSCOPY

The atomic force microscopy probes the surface of a sample with a sharp tip, which is attached to

the end of a cantilever which is 100 to 200  $\mu\text{m}$  long. Forces between the tip and the sample surface (Van der Waals, magnetic, electrostatic) cause the cantilever to bend, or deflect. A detector measures the deflection of the cantilever as the tip is scanned over the sample, or the sample is scanned under the tip. The measurement cantilever deflections allow a computer to generate a map of surface topography (Fig. 2). AFMs can be used to study insulators and semiconductors as well as electrical conductors [5].

#### Contact AFM

Contact AFM mode, the simplest AFM method, is the most commonly used method of imaging with atomic force microscopy, involving the least instrument variables for the gathering of

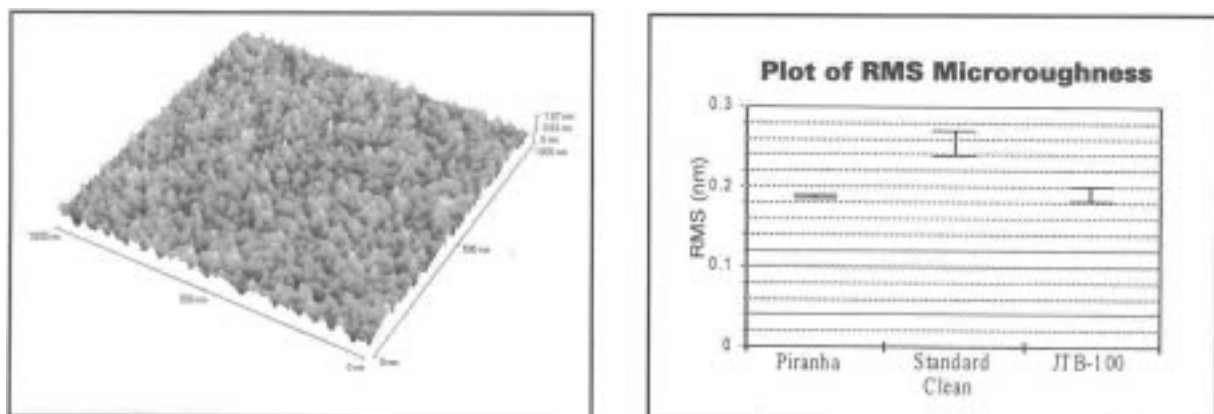


Fig. 3. AFM microroughness analysis of silicon wafer.

topographic information, even to atomic-level resolution [6]. In the contact AFM mode, the probe tip scans across the sample surface, coming into direct physical contact with the sample. As the probe tip scans, varying topographic features cause deflection of the cantilever. The amount of motion of the cantilever, or the force it applies to the sample, can then be used in a feedback loop to control the Z piezo, maintaining constant cantilever deflection. In this way, topographic data is obtained.

#### *Non-contact AFM*

In the non-contact AFM mode, the cantilever is oscillated near the surface of a sample at its resonant frequency. The spacing between the tip and surface is on the order of tens to hundreds of angstroms. As the probe gets closer to the sample surface, the attractive force between the tip and sample will change the oscillation amplitude and phase of the probe tip. The changes in amplitude and in phase can be detected and used by the feedback loop to produce topographic data. Amplitude detection is the non-contact method usually used for high-amplitude oscillation. Phase detection is the method usually used when the oscillation amplitude is relatively small and/or higher sensitivity is needed for stable feedback. Non-contact AFM method is ideal for scanning soft and adhesive samples, for example polymers, because scanning takes place without any physical contact between the probe tip and sample surface. This mode can also produce high-resolution images of hard materials, such as silicon, where tip contact would blunt the probe tip—resulting in poor lateral resolution and damage to the probe. Most AFMs can now be used at very low loading forces and hence, even on a hard substrate, damage to the tip can be minimised. This method is also well suited for scanning materials that exhibit a strong attractive force with the probe tip. Non-contact scanning can increase lateral resolution on some samples while maintaining high Z resolution.

Applications and training involve:

1. Determination of micro-roughness and surface profile measurement of silicon wafer before and after polishing in the nano-scale (Z) and micron-scale (X,Y) (Fig. 3).
2. Dopant analysis. The selective chemical etching of Si containing an impurity profile is used to obtain AFM surface topography related to the local carrier concentration.
3. Comparison of nano-scale surface images of mica single-crystal sections with models of corresponding sections through the mica structure.
4. Determination of particle size of very fine montmorillonite and iron oxide powders (nanoscale).

## X-RAY DIFFRACTION

The primary aim of crystal structure analysis using X-ray diffraction is to obtain detailed information about the position of the individual atoms in the structure of a solid crystalline materials. Then, interatomic distances, bond angles, and other features of the molecular geometry that are of interest, such as the planarity of a particular group of atoms, the angles between planes, and conformation angles around bonds can be calculated. Frequently the resulting three-dimensional representation of the atomic contents of the crystal establishes a structural formula and geometrical details hitherto completely unknown. This information is of primary interest to most chemists, biologists, mineralogists and material scientists who are concerned with the relationship of structural features to chemical and physical properties. Precise molecular dimensions may be determined for a substance whose structure has been established already. Such results are more likely to be of interest to those a theoretical bent with, differences between arrangements owing to atomic substitutions, molecular strain, deformation of basic structure units and the interaction between molecules. This part of our advanced course is oriented on the last topic, and therefore, splits into the following sessions:

- *Single-crystal refinement of the structure.* After measuring of the intensity reflections (50 to 100 or more per atom) the ‘trial structure’ parameters, representing atomic positions, occupation and temperature factors may be refined to obtain the best fit of observed and calculated structure factors. Two basic methods for refinement are included: Fourier methods and the least squares procedure [7, 8].
- *Rietveld refinement of the crystal structure using powder diffraction data.* For many substances it has not been possible to find crystals that are suitable for single-crystal diffraction studies. Therefore, the Rietveld refinement method can be used to obtain a detailed information about the position of the individual atoms in the structure. Refinement is conducted by minimizing the sum of the weighted, squared differences between observed and calculated intensities at every step in a digital powder pattern. The Rietveld procedure can be also used for quantitative phase analysis if the powdered sample is the multi-phase mixture. The Rietveld method requires: (1) accurate powder diffraction intensity data, (2) a starting model that is reasonably close to the actual crystal structure(s) of the material sample, and (3) a model that accurately describes shapes and widths of the Bragg profiles in the powder pattern.
- *Grazing Angle X-ray powder diffraction analysis (GA XRD).* This powder diffraction technique is becoming a powerful technique for the analysis of thin films structures. In the grazing inci-

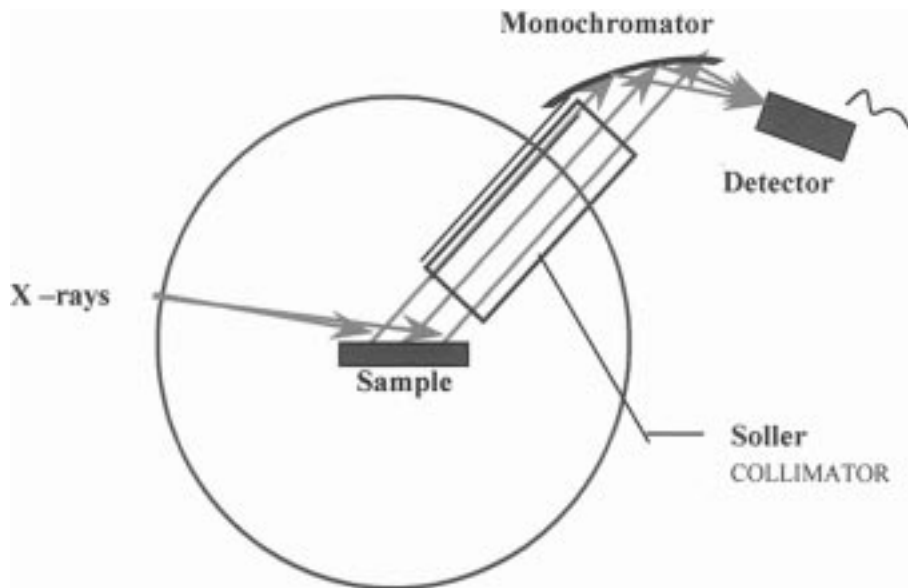


Fig. 4. GA XRD experimental setup with parallel beam geometry.

dence geometry (Fig. 4), the incident X-rays impinge on the surface of the sample (characterized by linear absorption coefficient  $\mu$ ) at small angles  $\gamma$  and penetration depth  $t$  of monochromatic parallel beam can be calculated from relation:

$$t = \frac{[(\sin \gamma \cdot \sin(2\theta - \gamma))]}{[\mu \sin \gamma + \mu \sin(2\theta - \gamma)]}$$

Penetration depth does not depend on the diffraction angle  $2\theta$  at low values of  $\gamma$  and thickness of thin films growing on substrates can be determined if GA XRD patterns for different  $\gamma$  angles are taken and reflections belonging to the film and substrate materials are identified.

Applications and training involve:

1. Single-crystal refinement of the crystal structures of two protolothionites (micas) 1M and 3T in the  $C2/m$  and  $P3_112$  space groups using SHELX program. Refinements are based on single-crystal diffraction data including experimental corrections [9]. Using resulting atomic positions, the bond lengths and angles, and deformation characteristics of coordination polyhedra are calculated.
2. Rietveld refinement of the crystal structures of pyrite, marcasite and their mixture. Refinements are based on powder diffraction data taken from natural iron disulfides.
3. Analysis of iron oxide thin films using depth-resolved GA XRD. By varying the grazing incidence angle  $\gamma$  the X-ray penetration depth

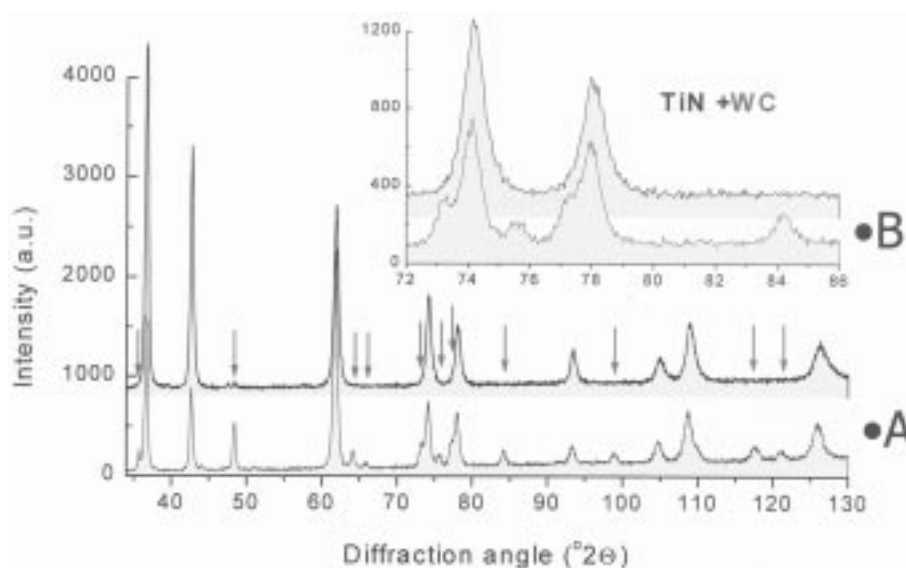


Fig. 5. Depth-resolved GA XRD patterns of tin and WC thin layer for  $\gamma = 2^\circ$  (A) and  $\gamma = 6^\circ$  (B)

is varied from tens to several thousand Angstroms, slightly larger than the film thickness. A measurements are realized on Co doped  $\text{Fe}_3\text{O}_4$  thin films.

4. Analysis of X-ray depth profiling of TiN and WC thin layer using GA XRD method for  $\gamma = 2^\circ$  (A) and  $\gamma = 6^\circ$  (B) (Fig. 5).

## ELECTRON MICROSCOPY

The electron microscope is a device that forms magnified images by means of electrons. The electrons are usually accelerated to between 50 and 100 kV (transmission microscopy) and to between 5 and 50 kV (scanning microscopy). The microscope magnifies in two or three stages by means of electromagnetic or electrostatic lenses. The electron microscope makes use of the wave properties of the moving electron.

### Transmission microscope

The best known electron microscope is the magnetic transmission microscope, where the image is formed by electrons which have passed through the specimen. It is composed of the following major sections: electron gun, condenser lens, projector lens, viewing screen, photographic, recording system.

### Image formation

In the transmission electron microscope, the image is formed by the scattering of electrons during their passage through the specimen. The absence of the scattered electrons produces the lighter or darker appearance of each spot in the image. Three types of electrons emerge after transit through the specimen:

1. Unscattered electrons are those that did not interact with the atoms of the specimen. They traverse it without deviating from their trajectory.
2. Elastically scattered electrons interacted with the nuclei of atoms in their path. The interaction is especially strong with heavy nuclei. The number of elastically scattered electrons is proportional to the  $4/3$  power of  $Z$ , the atomic number of the atoms. The elastically scattered electrons did not lose kinetic energy but changed their direction significantly.
3. Inelastically scattered electrons interact with the electrons of the atoms in their path. They

emerge within a narrow angle but have given up some of their energy. Their numbers is proportional to the  $1/3$  power of  $Z$ . Elastically scattered electrons are removed, to a large extent, by the limiting aperture in the gap of the objective lens. Inelastically scattered electron cause chromatic aberrations. They are focused in a plane other than the image plane of the unscattered electrons. They degrade the image.

### Scanning microscope

While in the standard transmission electron microscope the total area under observation is irradiated at the same time by the electron beam, only a single element of this area is irradiated at any one time by the probe in the scanning electron microscope (SEM). This probe is a very fine electron beam that has been demagnified by magnetic lenses. It scans the specimen in a television type raster. The finer the probe, the higher is the resolution of the microscope. The signal originating from each element while it is under irradiation modulates the electron beam of a display tube. The display tube beam is deflected synchronously with the probe scan. The SEM can operate in a number of different modes that will supply different information about the specimen.

The SEM can make create surface images from [10–12]:

- *secondary electrons* from the surface of a thick specimen collected by a collector mounted on the side, facing the specimen
- *backscattered electrons* from the surface collected by a ring electrode mounted below the exit aperture of the lens
- *transmitted electrons* through the specimen.

Applications and training include:

1. TEM observation of the carbon nanotube materials and estimation of the range of nanotube diameter.
2. TEM observation of carbon thin films treated under different temperatures. The distribution of crystallite sizes is determined using TEM images.
3. SEM observation of the surface of chemical etching of silicon wafers to compare images obtained with the AFM observations.
4. SEM and TEM observation of the thin oxide/carbon friction layer which is formed on the surface of the multiphase friction composite.

## REFERENCES

1. P. Comba, T. W. Hambley, *Molecular Modeling*, VCH-Verlagsgesellschaft mbH., Weinheim, New York (1995).
2. N. Karasawa, W. A. Goddard III, *J. Phys. Chem.*, **93**, 1989, p. 7320.
3. A. K. Rappe W. A. Goddard III, *J. Phys. Chem.*, **95**, 1991, p. 3358.
4. H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, J. R. Haak, *J. Chem. Phys.*, **81**, (1984), 3684.
5. Explorer<sup>TM</sup> Instrument Operation Manual ThermoMicroscopes, 2000

6. A Practical Guide to Scanning Probe Microscopy, *ThermoMicroscopes, Park Scientific Instruments*, TOPOMETRIX, 2000.
7. H. Stout, L. H. Jensen, *X-ray Structure Determination*, The Macmillan Company, London, 1968.
8. J. P. Glusker, K. N. Trueblood, *Crystal Structure Analysis*, Oxford University Press. New York, 1985.
9. Z. Weiss, M. Rieder, L. Smrcok, V. Petříček, S. W. Bailey, Refinement of the crystal structures of two protolithionites., *Eur. J. Mineral.* **5**, 1993, p. 493.
10. R. M. Besancon, *The Encyclopedia of Physics*, 2nd Edition, Oxford University Press, New York. 1974.
11. D. B. Williams, *Practical Electron Microscopy in Materials Science*, Verlag Chemie International, Deerfield Beach, 1984.
12. G. Thomas, *Transmission Electron Microscopy*, J. Wiley& Sons, New York, 1980.

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