Recent Progresses in Nanometer Scale Analysis of Buried Layers and Interfaces in Thin Films by X-rays and Neutrons

Krassimir STOEV* and Kenji SAKurai**†

*Canadian Nuclear Laboratories, 286 Plant Road, Chalk River, Ontario, K0J 1J0, Canada
**National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

In the early 1960s, scientists achieved the breakthroughs in the fields of solid surfaces and artificial layered structures. The advancement of surface science has been supported by the advent of ultra-high vacuum technologies, newly discovered and established scanning probe microscopy with atomic resolution, as well as some other advanced surface-sensitive spectroscopy and microscopy. On the other hand, it has been well recognized that a number of functions are related to the structures of the interfaces, which are the thin planes connecting different materials, most likely by layering thin films. Despite the scientific significance, so far, research on such buried layers and interfaces has been limited, because the probing depth of almost all existing sophisticated analytical methods is limited to the top surface. The present article describes the recent progress in the nanometer scale analysis of buried layers and interfaces, particularly by using X-rays and neutrons. The methods are essentially promising to non-destructively probe such buried structures in thin films. The latest scientific research has been reviewed, and includes applications to bio-chemical, organic, electronic, magnetic, spintronic, self-organizing and complicated systems as well as buried liquid-liquid and solid-liquid interfaces. Some emerging analytical techniques and instruments, which provide new attractive features such as imaging and real time analysis, are also discussed.

Keywords Thin films, multilayers, buried interfaces, surface and interface analysis, X-ray reflectivity, grazing-incidence X-ray analysis, neutron reflectivity

(Received December 10, 2019; Accepted February 26, 2020; Advance Publication Released Online by J-STAGE March 6, 2020)
1 Introduction

Nanostructures are becoming increasingly important for developing new technologies. Nanostructures offer a vast range of functionalities and physical effects, which can be used to design and optimize new devices. In many cases, nanostructures are prepared as multilayers. The structure, composition, and chemistry of layered materials are different from that of bulk materials. Also, most of the exotic properties and functions of the multilayer nanostructures are determined by the structures of the interfaces, i.e., the combination of the materials connected at the interface as well as the degree of chemical separation, the physical shape such as roughness, etc. In this respect, development of new nanostructure devices necessitates the development of methods to analyze the nano-layers and the interfaces between the nano-layers (i.e., buried layers and interfaces). These methods have to be non-contact and non-destructive, so the sample can be preserved, used, and analyzed with other methods.

Thin film, or the surface/interface region, is usually defined in a broad range, from sub-monolayer atomic layer up to several thousand atomic layers. Based on their depth inside the material, the following regions can be defined: (i) top surface (first 3 nm); (ii) near surface (3 – 10 nm), (iii) thin film (10 – 100 nm), (iv) coating (100 – 1000 nm), and (v) bulk material (>1000 nm). This definition of regions is somewhat arbitrary, and does not take into account the surface and interface roughness, which could be up to 0.5 – 3 nm or more. The above definitions will change depending on the probing wavelength. From a viewpoint of properties related to practical applications, probing specific depth and/or specific thickness is significant, for example:

- Wettability, catalytic reactions, and solderability are influenced by a single atomic monolayer
- Oxidation, passivation, corrosion, tribology, surface treatment, optical properties, electrical contacts, and electronic gates are influenced by tens of hundreds of atomic layers
- Diffusion, colors and some of the work functions of thin layers are influenced by hundreds to thousands of atomic layers

In this respect, there is a need for methods to analyze buried layers and interfaces that can cover all of this depth range in terms of penetration, sensitivity and resolution.

Another important reason for the need to develop new methods is strong demands for understanding the complex nanostructures embedded in the nano-layers, such as particles, dots, lines, etc. Such structures present new challenges for analysis methods, because it requires not only depth resolution, but also nanoscale horizontal spatial resolution.

In addition, there is a need to have methods capable of analyzing samples on-line during the preparation or during the use of the nano-layers. This will allow for studying time evolution and processes in buried layers, structures and interfaces, such as inter-diffusion of nano-layers, changes in the volume/thickness/density of nano-layer with temperature, pressure, and humidity, changes in the interface area between the nano-layers, etc. Development of on-line real time analytical techniques is also very useful for optimizing the properties and production process of nanolayers and nanostructures.

In order to understand the processes and the properties of the buried layers and interfaces, one needs to obtain information about their geometrical arrangements, chemical composition, structural and crystalline state of the materials, etc. In general terms, analyzing buried nano-layers and interfaces means determining their properties, or the time evolution and changes in their properties, such as:

- Mechanical properties and processes: thickness, roughness, clusters/particles dimensions and distribution, friction, fracture, strength, strain, stress, deformation properties, fatigue resistance, wear, etc.
- Physical properties and processes: density, crystallization, physical inter-diffusion, dielectric and magnetic properties, energy density, etc.
- Chemical properties and chemical processes/pheno mena of interest: elemental and molecular composition of the layers, size and orientation of individual molecules, adhesion, corrosion, passivation, interfacial interactions, chemical diffusion, barrier properties (also known as transport properties), etc.
- Optical properties and processes: refractive indices, spectral reflectivity and transmittance, optical absorption properties, etc.

It is not possible to obtain all this information using only one measurement method, and that is why several different methods are usually applied when comprehensive characterization of a multilayer structure is required. For example, the thickness of the nanolayer can be evaluated by many different techniques, such as scanning electron microscopy (SEM), atomic force microscopy (AFM), surface plasmon resonance, quartz crystal microbalance, optical ellipsometry, X-ray and neutron reflectivity, etc., but these techniques do not provide information about the internal chemical structure of the nanolayer. Examples of techniques capable of determining the internal chemical structure of a nanolayer are attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) depth profiling, transmission electron microscopy with energy-dispersive X-ray fluorescence analysis, (TEM+EDX), total reflection X-ray fluorescence analysis (TXRF), etc. With respect to characterizing the internal structure of buried layers and interfaces, the analytical methods can be grouped as:

- Elemental analysis of buried layers and interfaces. Methods such as TXRF, OES, etc.
- Molecular analysis of buried layers and interfaces. Methods based on mass spectroscopy or infrared spectroscopy.
- Crystal structure of buried layers and interfaces. Methods such as X-ray, neutron and electron diffraction.

There are several reviews and books,1–4 that present classifications of the surface and interface analyzing techniques. Below are listed the main surface and interface analysis techniques, closely following the classification presented in Ref. 1:

A. Electron detection methods:

A.1. X-ray photoelectron spectroscopy (XPS). Additional information about the XPS method can be found in Ref. 1, 4 – 15.

A.2. Auger electron spectroscopy (AES). Additional information about the AES method can be found in Ref. 1, 4, 5, 12, 13.

A.3. Electron energy-loss spectroscopy (EELS) and appearance potential spectroscopy (APS). Additional information about the EELS and APS methods can be found in Ref. 1, 4, 16, 17.

A.4. Electron microscopy, including scanning electron microscope (SEM), energy-filtering transmission electron microscope (EF-TEM), scanning tunneling microscopy (STM), etc. Additional information about these microscopic methods can be found in Ref. 1, 4, 18 – 21.
A.5. Low-energy electron diffraction (LEED). Additional information about the LEED method can be found in Ref. 1, 4, 22, 23.

B. Ion detection methods:
B.1. Static and dynamic secondary ion mass spectrometry (SIMS). Additional information about SIMS method can be found in Ref. 1, 4, 24, 25.
B.2. Electron impact secondary neutral mass spectrometry (EI-SNMS). Additional information about the EI-SNMS method can be found in Ref. 1, 4.
B.3. Laser secondary neutral mass spectrometry (Laser-SNMS). Additional information about the Laser-SNMS method can be found in Ref. 1, 4.
B.4. Rutherford backscattering spectroscopy (RBS). Additional information about the RBS method can be found in Ref. 1, 4.
B.5. Low-energy ion scattering (LEIS). Additional information about the LEIS method can be found in Ref. 1, 4.
B.6. Elastic recoil detection analysis. Additional information can be found in Ref. 1, 4.
B.7. Nuclear reaction analysis. Additional information can be found in Ref. 1, 4.
B.8. Field ion microscopy. Additional information can be found in Ref. 1, 4.

C. Photon detection techniques:
C.1. Total reflection X-ray fluorescence (TXRF) and standing wave X-ray fluorescence. Additional information about TXRF method can be found in Ref. 1, 4, 26.
C.2. Energy dispersive and wavelength-dispersive X-ray spectroscopy. Additional information about XRF methods can be found in Ref. 1, 4, 27, 28.
C.3. Glancing-incidence X-ray methods for surface and interface analysis:
• Glancing-incidence X-ray reflectivity (XRR)\(^{36-31}\)
• Glancing-incidence X-ray diffuse scattering\(^{12-35}\)
• Glancing incidence resonant X-ray scattering\(^{36}\)
• Glancing-incidence X-ray diffraction (XRD)\(^{37,38}\)
• Glancing-incidence X-ray absorption fine structure (XAFS)\(^{39-44}\)
C.4. Optical emission spectroscopy (OES). Additional information about the OES method can be found in Ref. 1, 4, 45.
C.5. Surface analysis by laser ablation or sputter depth profiling. Additional information about this method can be found in Ref. 1, 46.
C.6. Ion-beam spectrochemical analysis. Additional information about this method can be found in Ref. 1, 4.
C.7. Infra-red spectroscopy:
• Reflection absorption infra-red spectroscopy (RAIRS)\(^{1,4}\)
• Attenuated total reflection (ATR)\(^{1,4}\)
• Surface enhanced infrared absorption spectroscopy (SEIRA)\(^{1,4}\)
• ATR Fourier transform infrared spectroscopy (ATR-FTIR)\(^{1,47}\)
C.8. Surface Raman spectroscopy, including surface-enhanced Raman scattering. Additional information about Raman spectroscopy methods can be found in Ref. 1, 48, 49.
C.9. Optical reflectivity and ellipsometry. Additional information about these methods can be found in Ref. 1, 4, 50 - 55.
C.10. Sum-frequency generation (SFG) spectroscopy.

---

| Method          | Type of information              | Maximum depth of analysis/μm | Spatial resolution/μm |
|-----------------|----------------------------------|------------------------------|-----------------------|
| XPS             | Elemental + chemical             | 10                           | 3                     |
| AES             | Elemental + chemical             | 10                           | 0.02                  |
| EELS            | Elemental + chemical             | 10                           | 0.002                 |
| TEM             | Elemental                        | 2000                         | 0.005                 |
| LEED            | Crystal                          | 10                           | 0.0001                |
| SIMS            | Chemical                         | 3                            | 0.005                 |
| EI-SNMS         | Elemental                        | 5                            |                       |
| Laser-SNMS      | Elemental                        | 3                            | 0.005                 |
| RBS             | Elemental                        | 2000                         | 5                     |
| LEIS            | Elemental                        | 3                            | 1000                  |
| TXRF            | Elemental                        | 20                           | 1000                  |
| XRF             | Elemental                        | >2000                        | 100                   |
| XRR             | Thickness, density               | 1000                         | 1000                  |
| XDS             | Chemical                         | 1000                         | 1000                  |
| XRD             | Crystal                          | >2000                        | 1000                  |
| XAFS            | Chemical                         | 1000                         | 1000                  |
| OES             | Elemental                        | 1000                         | 10                    |
| Raman           | Chemical                         | 300                          | 100                   |
| RAIRS           | Chemical                         | 3                            | 1000                  |
| ATR-FTIR        | Chemical                         | 1000                         | 100                   |
| AFM             | Chemical                         | 1                            | 0.05                  |
| SEM             | Elemental                        | 200                          | 0.05                  |

Additional information about the RBS method can be found in Ref. 1, 4, 56 - 58.

C.11. Soft X-ray appearance potential spectroscopy. Additional information about this method can be found in Ref. 1, 4.

C.12. Inverse photoemission spectroscopy. Additional information about this method can be found in Ref. 1, 4.

D.1. Atomic force microscopy (AFM). Additional information about the AFM method can be found in Ref. 1, 4.
D.2. Scanning near-field optical microscopy. Additional information about this method can be found in Ref. 1, 4.

E.1. Neutron reflectivity.\(^{59,63}\)
E.2. Neutron diffraction and scattering.\(^{64-68}\)

The above described different methods for analysis have different depth of analysis and spatial resolution, which are summarized in Table 1. This review will focus mainly on the X-ray based and neutron-based methods, but other methods will be discussed as well. Grazing incidence X-ray and neutron techniques share the same theoretical principles, and are often discussed together in many books and reviews.\(^{30,60-73}\) Grazing incidence X-ray and neutron methods for characterization of thin films and buried layers, structures, and interfaces are of high importance, because: (i) they are non-destructive; (ii) they have a high penetration ability (up to 1000 nm) and ability to measure deeply buried layers and interfaces (due to a low absorption cross section); (iii) they can offer high contrast of different interaction cross sections of different atoms; and (iv) they can provide information about many different parameters, such as elemental composition, crystallographic structure, orientation, magnetization, thickness, density roughness, etc.

The advancement of the analytical methods based on grazing incidence X-ray reflectivity are reviewed periodically.\(^{69-72,74}\)
describe the advancement in grazing incidence X-ray diffraction.

density of the walls, the radius of the pores, and subsequently electron density of the films, the wall thickness, the electron critical angle of the substrate allows for obtaining the average critical wave vector value reported along the line is the average critical wave vector of the film. The modifications induced by the rinsing procedure are obvious both on the electron density profiles and on the average critical wave vector (from Fig. 4 in Ref. 81, reproduced with permission).

There were also several published reviews on grazing incidence X-ray scattering and on TXRF and glancing incidence X-ray standing wave techniques. References 37, 38 and 80 describe the advancement in grazing incidence X-ray diffraction.

2 Scientific Cases

2.1 Pores, particles, segregated element and other nanostructures

In many cases, complex nanostructures are embedded in the nano-layers, such as pores, channels, particles, dots, lines, etc. Measuring and analyzing such structures is very challenging, and one cannot directly apply the methods developed for analysis of nano-layers and interfaces, so customized measurement techniques are needed.

Two-dimensional hexagonal silica thin films templated by a triblock copolymer were investigated by grazing incident small angle X-ray scattering and X-ray reflectivity before and after removing the surfactant from the silica matrix \(^{41}\) (see, Fig. 1). Analysis of the X-ray reflectivity curves above and below the critical angle X-ray scattering were used \(^{87}\) to study the influence of annealing at 230°C on Si nanowire was reported. \(^{85}\) The method allows obtaining the concentration and distribution of chemical elements in three-dimensions in the radial direction of the nanowires. Surface structures and morphology of embedded Co nanostructures on Au substrate were studied by scanning tunneling microscopy. \(^{86}\) It was shown that the structure and morphology of the samples change significantly after post-annealing at 230°C. Small angle neutron scattering and small angle X-ray scattering were used \(^{87}\) to study the influence of doxorubicin on the surface structure of the solid lipid nanoparticles. Four techniques (atomic-force microscopy, X-ray diffraction, X-ray reflectometry, and neutron reflectometry) were applied \(^{88}\) to determine the depth density distribution of Au nanoparticles on functionalized silicon planar substrate. Doping with heavy water was used to observe isotope difference in layers by the neutron reflectometry experiment. Quantitative determination of interface information about nano structures by synchrotron radiation small-angle X-ray scattering was presented. \(^{89}\)

2.2 Solid-liquid and liquid-liquid interfaces

Liquid/solid and liquid/liquid interfaces are of high interest in developing new technologies and products. There are many types of different simple and complex fluids (such as pure water, organic liquids, liquid crystals, liquid metals, electrified liquid-liquid interfaces, interfacial monolayers of amphiphiles, nanoparticles, polymers, and biomolecules), which are needed and used in the modern world. The ability to understand the molecular ordering, the structures, and physical and chemical properties at liquid interfaces is of great interest, so current methods for investigating liquid interfaces are being improved and new methods developed. Measurements of different types of samples (bulk liquids, thin wetting films, buried liquid-liquid and liquid-solid interfaces, etc.) is required. The testing methods should allow for experimental investigations into the basic physical and chemical properties of liquid surfaces and interfaces, which would benefit the research in many fields, such as physics, chemistry, biology and materials science. Liquids have many interesting properties that differentiate them from solids, such as the fact that liquid surfaces cannot be tilted, and that capillary wave fluctuations at liquid surfaces can generate significant roughness. Liquids also play a critical role in the transport across ionic membranes and creation of ultrathin ionomer films confined by surfaces effects, electrochemical activity, and proton transport.

Liquid interfaces can be curved, so X-ray reflectivity from
non-planar surfaces has to be considered. Model and computer modeling of X-ray reflectivity from spherical samples were discussed. General model for calculating X-ray and neutron reflectivity from curved surfaces was also discussed. The proposed method has become practical due to the availability of high quality 1D or 2D detectors.

Historical and theoretical review and recent developments of X-ray and neutron reflectivity of thin films at liquid interfaces and buried liquid/liquid interfaces were discussed. A detailed description of the apparatus and techniques based on synchrotron X-ray sources and methods (including X-ray reflectivity and diffuse scattering), together with theoretical approaches to data analysis, were presented in a book. Synchrotron based X-ray methods allow for experimental investigations into the basic physical and chemical properties of liquid surfaces and interfaces, including examination of surfaces of bulk liquids, thin wetting films and buried liquid-liquid interfaces, complex fluids, ultra-pure water, organic liquids, liquid crystals, liquid metals, electrified liquid-liquid interfaces, and interfacial monolayers of amphiphiles, nanoparticles, polymers and biomolecules. A chapter in another book presents an overview of several liquid surface X-ray scattering techniques based on high-brilliance synchrotron radiation sources and their applications in interfacial chemistry and biology. X-ray reflectivity theory for the determination of the density profile of a liquid inside a nanometer-scale X-ray interferometer-confinement has been presented. A method for an increase in the electron density contrast between the deposited layers and the surrounding water by decoration of layer-by-layer structures with heavy metal ions, which allows high-contrast X-ray reflectivity measurements at the solid/water interface, was presented. The approach was applied to study the interaction of DNA molecules with multilayers, and the results were independently verified with null-ellipsometry. A high-pressure cell for in situ X-ray reflectivity measurements of liquid/solid interfaces in the pressure regime of protein unfolding hydrostatic pressures up to 500 MPa was presented.

Atomistic molecular dynamics simulations in combination with high-resolution X-ray reflectivity measurements were used for understanding the molecular-level behavior of ionic liquids in electrochemical systems such as liquid-solid interfaces. Surface sum-frequency generation spectroscopy and X-ray reflectivity were used to study the surface of ionic liquids. The combined use of sum-frequency spectra with X-ray reflectivity data suggests that the molecules forming the topmost layer are on average polar-oriented with their butyl chains toward the gas/liquid interface, while the imidazolium cores/anions are in contact with the bulk liquid. X-ray reflectivity study of the interaction of an imidazolium-based ionic liquid with a soft supported lipid membrane was reported. The liquid ionic liquid alters the pressure-area isotherm of the monolayer formed at an air-water interface by the lipid, and the in-plane elasticity of the lipid layer is reduced, which leads to a considerable decrease in bilayer thickness and a corresponding increase in electron density. The presence of ionic multilayers at the free surface of an ionic liquid, extending into the bulk from the surface to the depth of 6 nm, has been probed by X-ray reflectivity measurements. The analysis using model fittings revealed that at least four layers are formed with the interlayer distance of 1.6 nm. The effect of water on the surface structure of ionic liquid was investigated using X-ray reflectometry. It was determined that a significant amount of water is adsorbed at the surface, with the first layer from the gas (nitrogen)-liquid phase boundary mainly occupied by a mixture of cations and water. Beyond the cation and water layer, the scattering length density increases towards the bulk value, indicating the decrease of water and cations, and/or the increase of anions. The structure at air interface and water interface of a hydrophobic ionic liquid (IL) was studied using X-ray reflectometry. Multilayering of ions has been found at the IL/air interface, with the topmost ionic layer having lower density than the IL bulk. For the IL/water interface, X-ray reflectivity data depends on the phase-boundary potential across the IL/water interface.

A combined high-energy X-ray reflectivity and molecular dynamics simulation study of the water depletion at a per fluorinated hydrophobic interface with a spatial resolution on the molecular scale was presented. Interfacial depletion of less than a monolayer of water, due to surface chemistry and molecular geometry of a hydrophobic coating, was observed. Results of a synchrotron X-ray reflectivity study of bulk liquid-crystal surfaces that are coated by thin wetting films of an immiscible liquid were reported. The surface structure of the liquid phase of the Au$_2$Ge$_5$ eutectic alloy was measured using resonant and non-resonant X-ray reflectivity and grazing incidence X-ray diffraction. It was found that the Gibbs adsorption enhancement of Ge concentration at the surface is minimal, despite the significant differences in the surface tension of liquid Ge and Au. X-ray reflectivity measurements of the liquid Bi and liquid Sn surfaces were reported. It was observed that both Sn and Bi exhibit a weak broad peak with smaller wave-vector transfers, which corresponds to an enhanced electron density in the near-surface region. X-ray reflectivity studies of dielectric and metal liquids were reported. Oscillatory surface-density profiles layers were reported in several metallic liquids and one dielectric liquid, in the temperature range from 130 to 285 K, which corresponds to the liquid-gas critical temperature. A comparison of the grazing incidence X-ray reflectivity and X-ray defuse (off-specular) scattering methods for studying surface monolayers assembled on a liquid sub-phase surfactant films were presented. While both methods provide the same results for electron density profiles and monolayer thickness, the density profiles obtained by X-ray off-specular (diffuse) scattering are systematically sharper than those obtained with X-ray reflectivity. Three synchrotron-based X-ray characterizing methods (grazing incidence X-ray diffraction, X-ray reflectivity and total reflection X-ray fluorescence) were reported to monitor Gibbs or Langmuir monolayer structural changes at the soft air/liquid interface.

Grazing-incidence X-ray diffraction measurements were carried out to investigate the surface structure of neat ionic liquid. A broad Debye-Scherrer ring was observed in the diffraction patterns, indicating that the molecules near the surface are randomly orientated, similar to those in the bulk liquid. X-ray photoelectron spectroscopy investigation of how electronic properties of buried semiconductor/ionic liquid interfaces may influence the charging effects was carried-out. Reflection-absorption infrared spectroscopy was applied to study films of ionic liquid and compared to amorphous and crystalline solid films from the same material. The bound state of water in (polyethylene glycol)-H$_2$O systems was studied by using high frequency spectroscopy. Depending on the mixing ratio, both weakly bound water, cold crystallization and free water states were observed. The progress in the studies of buried solid/liquid and solid/solid polymer interfaces using sum frequency generation vibrational spectroscopy was reviewed. Different polymers exhibit varied surface restructuring behavior in water, indicating the importance of probing polymer/water interfaces in situ. Molecular interactions at polymer/liquid
interfaces dictate interfacial polymer structures.

The recent progress exploiting neutron reflectivity for structural and compositional investigations of the solid–liquid interface was outlined. The key areas of development were identified as the increased range of accessible substrates, such as metals and minerals; the investigation of novel liquid phases; the strong accent at different applications, for example electrochemistry (e.g., batteries), corrosion, polymers; and increasing application at extreme conditions. The advances in kinetic and dynamic studies at the air/water interface using specular neutron reflectometry were reviewed. The advancement in instrumentation allows for time-resolved measurement investigations in soft matter, biophysics, environment and health, and to study processes such as oxidation of monolayers targeted from the gas phase, adsorption of various types of molecules from solution, compression/expansion cycles of a Langmuir trough, etc. Measurements and analysis of neutron reflectivity data from a buried oil–water interface was presented and it was found that the hexadecane–water interface is “rougher” than what was expected from the capillary wave theory. Water uptake and swelling in a thin Nafion film on SiO2 native oxide layer on a Si wafer was studied as a function of relative humidity and of temperature by neutron reflectometry. Water penetration into thin sulfonated polyphenylene ionomer films was investigated by neutron reflectometry as a function of time, ionic strength, and film thickness. A non-uniform distribution of water molecules was observed with a high concentration at the air-polymer interface. An excess of water was also found at the polymer-silicon interface. A modeling approach for the treatment of specular neutron reflectometry data of surfactant and phospholipid monolayers at the air/water interface was proposed. Neutron reflectometry was used to measure the shear response of an adsorbed anionic surfactant at the alumina-water interface. The water distribution and the hygro-expansion of three different sulfonated fluoropolymers, varying in the composition and length of sulfonic group terminating side chains, were examined by neutron reflectometry, ellipsometry, and quartz crystal microbalance.

2.3 Bio-chemical and polymer interfaces

Organic, polymer, and biological nanostructures and nanolayers are very important. Due to the delicate character of these materials, they have to be measured without being changed. X-ray and neutron methods are often used for investigating thin films made of organic and biological materials or polymers. There are many processes at buried bio-chemical and organic layers and interfaces that influences their properties and that are of interest to physicists, chemists and biologists, such as adsorption of proteins to surfaces, interactions among proteins, interactions between solution and substrate, etc. Most of these processes at interfaces depend on the uppermost atomic layer, and are defined by surface chemistry, surface morphology, surface electrochemical interactions, and surface compositions and roughness. Important applications of bio-chemical and organic nanolayers and structures are organic light-emitting diodes, antimicrobial coating, bio-sensing, biological membranes, surface immobilizers, controlling enzyme orientation on surfaces and interfaces, controlling chemical activity at interfaces, controlling and optimizing orientation of molecules and structures and surfaces, controlling biochemical reactions as surfaces, etc.

Characterization of Langmuir–Blodgett organoclay films using X-ray reflectivity and atomic force microscopy was discussed. In situ high energy X-ray reflectivity technique was applied to study the interfacial structure of protein adsorbates and protein adsorption kinetics, and more specifically the adsorption of lysozyme at the hydrophilic silica–water interface. The structure of adsorbed lysozyme layers was measured for various aqueous solution conditions, and the effect of solution pH and lysozyme concentration on the interfacial structure was determined. In situ X-ray reflectivity with a maximum momentum transfer of at least 5.2 nm⁻¹ was employed to study the adsorption of a variety of proteins on hydrophilic (silicon oxide) and hydrophobic (octadecyltrichlorosilane self-assembled monolayers) surfaces. Time evolution at time-scans in 5 min intervals was observed, allowing for some time-resolved information about the evolution of the protein film structure. In situ X-ray reflectivity was used for studying the influence of functionalized silicon surfaces on the structure of protein adsorbates. As far as the strength of the van der Waals forces affects the final layer density and hence the adsorbed amount of proteins, it was determined that van der Waals forces mainly influence surface processes, which govern the structure formation of the protein adsorbates, such as surface diffusion and spreading. X-ray reflectivity was used to investigate the structures of vertically oriented multilayers composed of two saturated phospholipids and deposited on silicon as a function of composition. The phase stability was investigated at various annealing temperatures under humid conditions. The results indicated that the lipid spacing of the mixed phospholipid multilayers varied systematically and that no macroscopic phase separation occurred during the annealing process under both dry and humid conditions.

The structural configuration of molecules assembled at organic/inorganic interfaces within electronic materials strongly influences the functional electronic and vibrational properties relevant to applications ranging from energy storage to photovoltaics. It is known that some kind of an organic monolayer assembled on an oxide surface, exhibits structural and electronic reconfiguration under ultraviolet illumination. The mechanism of the structural changes corresponding to reversible photoisomerization has been clarified by X-ray reflectivity and atomic force microscopy. The reconfiguration of these monolayers provides additional means to control excitation and charge transfer processes that are important in applications in catalysis, molecular electronics, and solar energy conversion (see, Fig. 2).

Thermoresponsive smart polymers, which change their physiochemical properties in response to temperature, have attracted a great deal of attention recently because of their biomedical applications such as drug delivery, smart bioactive surfaces, temperature-sensitive membranes, and mammalian cell release surfaces. Methylcellulose belongs to this class of thermoresponsive polymers and exhibits a thermo-reversible switching at ~70°C in water, which is known as the lower critical solution temperature (LCST). At the LCST, while a volume phase separation occurs wherein the polymer chains change from a random coil state to a globular state in solution, in the case of thin film form, surface and interfaces are changed depending on the temperature. Systematic analysis has been done for methylcellulose thin films by the use of X-ray reflectivity and atomic force microscopy, particularly in view of stability, thermal cycling, hydrophobic switching, and swelling.

Grazing incidence resonant soft X-ray scattering method was utilized for investigating morphology of blended multicomponent thin polymer films used in organic photovoltaics. The investigation reveals that films without solvent additive tend to show only vertical phase separation, while films prepared with solvent additive also have phase separated laterally. Electrochemical impedance spectroscopy was used to obtain...
information about ongoing polymer degradation and electrochemical interactions at interfaces. Parameters influencing the interfacial bonding properties between carboxylic polymers and Zn surfaces include surface pretreatment, chemical composition, morphology, roughness, and semiconductor properties. Sum frequency generation vibrational spectroscopy and ATR-FTIR were used for determination of conformation and orientation of immobilized peptides and proteins at buried interfaces. Surface immobilized peptides/proteins have important applications such as antimicrobial coating and biosensing. Structures of chemically immobilized peptides are determined by immobilization sites, chemical environments, and substrate surfaces. In addition, controlling enzyme orientation by engineering the surface immobilization site demonstrated that structures can be well-correlated to measured chemical activity. The use of vibrationally resonant sum-frequency generation spectroscopy to investigate the structure of surfaces and interfaces was presented. Some limitations of vibrationally resonant sum-frequency generation spectroscopy were discussed, such as the fact that not all vibrational modes observed in linear spectroscopic techniques (IR and Raman) are necessarily present in the vibrationally resonant spectrum, and that the technique does not only probe the surface, but is also sensitive to molecules in any environment with broken symmetry. These results demonstrate that great care must be taken in assigning vibrationally resonant sum-frequency spectra.

In addition to the review article on neutron methods for investigation of organic and biological material thin films, some other recent advances in neutron reflectivity studies of biological membranes were published. Some insights about the future developments in the technology and methodology of the neutron reflectivity method were also suggested. A review of the use of neutron reflectivity as a probe of organic thin films, concentrating on its application to study buried interfaces in thin polymer films, was presented. The temperature dependence of the conformation of a layer of very high molecular weight polymer chains chemically grafted to a silicon interface and coated by a chemically different polymer matrix was studied. At high temperatures the layer abruptly changes from an extended conformation to one with a sharp interface with the matrix layer. X-ray synchrotron radiation and neutron reflectivity study was reported for investigation of solid-supported lipid membranes prepared by spin coating. Results indicate that DNA contributes to the order in the lipoplexes layers. Neutron reflectometry was used to determine the existence of a relatively thick, continuous phase of water stemming from within an antifouling mono-ethylene glycol silane ad-layer prepared on oxidized silicon wafers. In contrast, this physically distinct (from bulk) interphase is much thinner and only interfacial in nature for the less effective ad-layer lacking internal ether oxygen atoms. Neutron reflectometry and hard X-ray photoelectron spectroscopy were used to study the composition of the active layer of a benchmark functional organic solar cell. Thermal annealing was performed in several steps and NR and HAXPES were recorded for every temperature, and the evolution of the composition of the active layer as a function of temperature was established.

2-4 Semiconductor and electronic interfaces

Semiconductor and electronic devices are becoming more and more complex, with increased density of 3D structures with dimensions smaller than 5 nm, and required dimension tolerances of better than 10%. These requirements for measuring near atomic scale dimensions generate a need for optimizing current inspection techniques and developing new inspection techniques. Some of the challenges in testing complex semiconductor and electronic devices are the need for performing measurements of physically inaccessible structures (such as buried layers and interfaces, or small confined volumes), evaluating nanoscale roughness stacks of multiple layers, etc. There are a number of parameters that could influence the
performance of the semiconductor devices, such as composition, critical dimensions (size and shape), surface and interfacial physical and dielectric properties, film thickness/dimensions variation, defects and defect density, strain. Deep understanding of the physics of the measurement, material properties at nanoscale, and possible sources of error related to instrumentation, sampling, and data analysis, are required in order to address the challenges posed by the modern semiconductor industry. In addition, the use of new materials, such as organic semiconductors, also requires development of new measurement techniques. Especially important is the use of organic self-assembled monolayers, which can be used in such devices as organic light emitting diodes, organic photovoltaics, organic thin film transistors, and non-volatile memory. Self-assembled monolayers have several advantages in comparison to classical thin film deposition techniques, such as surface selectivity, controllable thickness at angstrom scale, and controllable functionality via the chemical structure of such molecules and their orientation on the surface.

Advances in nano-electronics in the past decade and the effect of the miniaturization of the electronic devices on the characterization and metrology techniques are discussed in a currently published book, together with the recent developments in several inspection methods. The major shift from 2D to 3D characterization of nanoscale structures was identified as one of the technology trends in the semiconductor industry. Another major trend is the need for new measurement capabilities for the new materials used in the semiconductor industry, and the need for on-line process control for the epitaxial growth of films, nanowires, and other nanosized device. Implementation of various X-ray techniques for the characterization of advanced semiconductor devices was discussed. The advantages and disadvantages of XRD (for measuring strain), XRR (for measuring thickness), and XPS (for determining composition) were presented, and the application of hybrid techniques was suggested. The metrology for the next generation of semiconductor devices was also presented, and the state-of-the-art dimensional metrology methods for integrated circuits were reviewed. Critical dimension small angle X-ray scattering was identified as potentially powerful emerging measurement technology. This technique can be used to determine important parameters of nano-structures such as sidewall angle, linewidth, and pitch. Modern experimental methods for investigation of organic macromolecular semiconductor systems, such as X-ray reflectivity, grazing-incidence X-ray scattering, and X-ray standing waves, were reviewed. These methods allow for the collection of information necessary for improvement of the operating efficiency of elements of organic electronic devices, such as thin-film transistors, light-emitting diodes and photovoltaic cells. The growth of the interfacial SiO₂ layer between HfO₂ films and Si substrate was studied using a synchrotron X-ray reflectivity setup. The effects of the thermal annealing and oxygen partial pressure were observed and evaluated. Continuous in situ X-ray reflectivity measurements were used to investigate the growth process of an InGaN epilayer, and the surface roughening of the epilayer as a function of growth time was calculated. X-ray reflectivity was used to investigate the growth by radio-frequency sputtering technique of an amorphous indium gallium zinc oxide active layer of thin film transistors. Study of self-assembled organic monolayers by X-ray reflectivity was reported. The XRR technique provides information about surface-normal electron density profile and thickness of the self-assembled monolayers, and allows for the determination of molecular tilt angles and packing densities. Organic semiconductor films on quartz substrate were studied by slow positron beam, X-ray reflectivity, grazing incidence X-ray diffraction, and atomic force microscopy measurements. Parameters such as depth profiles and structural inhomogeneity in as-deposited film in comparison to annealed films at high temperature were determined. An overview of soft X-rays techniques, such as microscopy, reflectivity and scattering, that have been developed in recent years, was presented. The utility of these techniques for providing insight into the complex structure of organic semiconductor thin films was discussed, and their ability of offering high chemical specificity, sensitivity to molecular orientation and order, and high spatial resolution, were highlighted. The sensitivity of polarized soft X-ray beams to the orientation of bonds in organic materials makes them a unique probe of molecular orientation. The application of quantitative resonant soft X-ray reflectivity for analyzing organic semiconductor single crystal was presented. This allows for assessment of anisotropic optical constants and electronic properties of organic crystal. Simultaneous in situ real-time measurements of X-ray reflectivity and differential reflectance spectroscopy were conducted in order to study the growth of organic semiconductor thin film from sub-monolayer to bilayer. This combined measurement enables the study of the relationship between structural and optical properties of organic semiconductor thin films. The study of the growth and the post-growth dewetting process of organic semiconductor using real-time X-ray reflectivity measurements was reported. Post-growth AFM measurements confirm the conclusions from the X-ray data and show the morphology of the dewetted film. Identification of an organic semiconductor super-lattice structure via resonant and non-resonant X-ray scattering was presented. The use of grazing incidence X-ray scattering techniques for characterization of ion-induced nano-patterns on semiconductor surfaces was presented. The corresponding theory and data evaluation are described in the distorted wave Born approximation. Such in situ measurements are especially suited to study the early stages of pattern formation, which in some cases reveal a transition from dot to ripple formation. Grazing incidence X-ray fluorescence (GIXRF) is useful to study periodic structures on silicon and silica surfaces. The fitting of grazing incidence X-ray fluorescence and X-ray reflectivity data was used to improve profiling of ultra-shallow depth distributions. This combined analysis reduces the uncertainties of the individual techniques, allowing for the determination of depth profile of the implanted elements with drastically increased confidence level. While XRR is sensitive to the electronic density profile, GIXRF is sensitive to the atomic density (i.e., the elemental depth profile). Similarly, simultaneous parameter optimization of X-ray and neutron reflectivity data using genetic algorithms, was presented. Combination of X-ray and neutron reflectivity is well suited for obtaining physical parameters of nanostructured thin films and superlattices, because neutrons provide a different contrast between the elements than X-rays and are also sensitive to the magnetization depth profile in thin films and superlattices. A depth-sensitive polarized neutron reflectometry method was used to provide details of the composition and magnetization profiles of Cu doped ZnO films, and it was confirmed that the presence of the copper at Zn sites induces ferromagnetism at room temperature. Glancing incidence X-ray fluorescence in combination with near-edge X-ray absorption fine structure measurements were applied for investigations on buried ZnO/Si interfaces for silicon solar cells. The Si/ZnO layer system was studied in its as-deposited and its annealed state. Diffusion of contaminants from the ZnO into the Si was observed after...
annealing. Photoemission spectroscopy based on hard and soft X-rays was used to extract information about depth-resolved electronic and chemical structure, band alignment at the interface, the momentum-resolved electronic dispersions of buried electron systems, and oxygen vacancies. Soft and hard X-ray standing-wave angle-resolved photoemission method was reported for measurement of depth-resolved composition and electronic structure of buried layers and interfaces in a LaNiO₃/SrTiO₃ superlattice. The current state and future perspectives in angle-resolved soft and hard X-ray photoemission are as follows: (i) use of higher photon energies will permit better probing of bulk electronic structure and buried layers and interfaces; (ii) there is a need for more accurate modeling of angle-resolved photoemission; (iii) using the tunability of the standing-wave excitation could provide much enhanced depth sensitivity; and (iv) here is a need to apply photoelectron holography to time-resolved studies of molecular reactions and dissociation. Some specific application examples were also discussed, including solid/gas and solid/liquid interfaces, magnetic semiconductor, multilayer structures of complex metal oxides, thin water solution on a metal oxide surface, and halogen-substituted benzene molecules. Hard X-ray photoemission with angular resolution and standing-wave excitation was employed for studying element-specific bulk atomic structures (including dopant site occupations) and composition and chemical states of buried layers and interfaces. High resolution X-ray photoemission spectroscopy was utilized to study the intermixed SiOₓ/ZnS interfaces of ultrathin films and chemical state of S at metal-oxide to metal-sulfide transition region. Photoluminescence and deep level transient spectroscopy were used for evaluation of SiGe layers on insulator and for studying defect generation and transformation during the temperature ramp-up process. Another method, which is widely used for measuring buried layers and interfaces in the semiconductor and electronics industry, is the photoelectron spectroscopy. Non-destructive analysis of concentration of chemical components at buried interfaces on Ge-based CMOS by means of hard X-ray photoelectron spectroscopy and low angle X-ray reflectivity was presented. The magnitude of the shifts the Si interlayer prevents the Ge oxidation. Probing the ionic structure of the InGaN caused by Ba adsorption were found to originate predominantly from the local interaction of the Ga, In, and Ba atoms, that results in effect of the suppression of the two intrinsic surface states and appearance of a new induced state. Positron annihilation spectroscopy is also useful to study defect depth profile in organic semiconductor multilayers and characterize the buried interfaces and layers. It was revealed that the presence of defects at the interfaces vary with the layer thickness.

2.5 Magnetic and spintronic interfaces

Multilayered structures with artificial complex oxide heterostructures have useful properties and functionalities at the interfaces, such as symmetry breaking, electronic reconstruction, magnetic modulation, magnetic coupling, and interface induced magnetization. Studying such complex oxide interfaces is particularly challenging and very important for understanding the fundamental mechanism and interaction across the interfaces, and for determining their technological applications. The study of such magnetic structures, spintronic systems, and the magnetism at interfaces requires tools with interface specificity. Both neutron and X-ray reflectivity methods are well suited for testing magnetic properties of nano-structures and buried layers and interfaces. A good review of these methods was presented in a recently published book. Standing-wave photoemission techniques were reviewed. These are powerful and versatile non-destructive techniques for probing element-specific electronic, magnetic, and structural properties of buried layers and interfaces with sub-nanometer depth resolution. One of the promising new directions is to combine several X-ray techniques, such as magnetic circular dichroism, total reflection and X-ray waveguide effects, hard X-ray photoemission spectroscopy, angle-resolved photoemission, and photoemission microscopy, in order to widen the scope of the performed measurements. Soft X-ray magnetic circular dichroism was applied to investigate magnetic interlayer coupling between Fe over-layers and Ni substrate. Antiferromagnetic coupling has been revealed with direct evidence of opposite magnetic circular dichroism signal of Fe to Ni in the absorption spectra. The antiferromagnetic coupling energy is estimated to be in order of a hundred μeV at the interface. X-ray magnetic circular dichroism of a RuOₓ/CrO₂ bilayer can be strongly influenced by non-magnetic cover layers. X-ray absorption spectroscopy and X-ray scattering were utilized to determine the oxidation reactions at the buried MgO/Fe interface as a result of the deposition of MgO. The transformation of the interfacial oxide from a more Fe₂O₃-like phase to a more FeO-like phase was observed as a result of the annealing process. X-ray resonant magnetic scattering was used to investigate the induced magnetic moments in the electronic states of interface atomic layers in a Fe/V superlattice (see, Fig. 3). This method takes advantage of the enhanced depth sensitivity to the magnetic profile over a certain resonant energy bandwidth in the vicinity of the Bragg angles. It was observed that the induced V moments decay more rapidly when measured by X-ray magnetic scattering than in standard X-ray magnetic circular dichroism. The electric field induced modifications of magnetic anisotropy in CoFeB/MgO systems were studied using X-ray resonant magnetic scattering and magnetooptical Kerr effect. X-ray resonant magnetic scattering measurements reveal that the small in-plane magnetic component of the remnant state of CoFeB/MgO systems with weak magnetic anisotropy changes depending on the applied voltage leading to modification of the magnetic anisotropy at the CoFeB/MgO interface. Conversion electron Mössbauer spectroscopy (CEMS), X-ray diffraction (XRD), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and X-ray reflectivity (XRR) were employed to study Fe/Se₃Te interface. The 30 nm Sb₆Te₃ layer was formed by MOCVD (metal organic chemical vapor deposition), while the 54Fe(10 nm)/57Fe(1 nm) bilayer was deposited by PLD (pulsed laser deposition). CEMS and XRD showed the polycrystalline nature of both the Fe and Sb₂Te₃ layers, while ToF-SIMS and XRR confirmed the partial elemental inter-diffusion between the Fe and Sb₂Te₃ layers. The role of interface structure and the magnetoresistance in Fe/Au multilayers were studied by
functionalized silicon was studied by neutron reflectometry. 188

nanoparticles from highly stable magnetic fluids on crystalline
reflectometry.  The adsorption of surfactant coated magnetic
Hurst parameter, as obtained from X-ray and neutron
magnetization, large in-plane correlation length, and higher
magnetoresistance was associated with interfaces with larger
were obtained from diffuse X-ray reflectivity.  Large
reflectometry,187 and details of the interface fractal morphology
specular X-ray reflectometry and polarized neutron
reflectometry,187 and details of the interface fractal morphology
were obtained from diffuse X-ray reflectivity.  Large
magnetoresistance was associated with interfaces with larger
magnetization, large in-plane correlation length, and higher
Hurst parameter, as obtained from X-ray and neutron
reflectometry. The adsorption of surfactant coated magnetic
nanoparticles from highly stable magnetic fluids on crystalline
functionalized silicon was studied by neutron reflectometry.188

Only one well-defined adsorption layer of nanoparticles was
detected for both types of magnetic fluids studied: (i) based on
nanomagnetite dispersed and stabilized in non-polar organic
solvent (deuterated benzene), and (ii) strongly polar solvent
(heavy water). Despite the presence of an aggregate fraction in
the water-based system, the width of the adsorption layer is
consistent with the size of separated particles, thus showing the
preferable adsorption of non-aggregated particles. A method for
investigation of weakly magnetic films placed inside a tri-layer
planar waveguide, based on the use of polarized neutrons
tunneled into waveguide through the surface, channel along the
layers, and are emitted from the end face as a narrow and
slightly divergent microbeam, was described.189  Polarization
analysis permits the detection of very small magnetization in the
order of a few 10 Gauss. Polarized neutron reflectometry was
used to determine the temperature dependence of the
magnetization of thin AuFe films with 3% Fe concentration in
the temperature range from 295 to 2 K.190  Brillouin-type
behavior was observed from 295 K down to 50 K, and a constant
magnetization of about 0.9 µB per Fe atom below 30 K.

A review of recent experiments in the use of polarized neutron
reflectometry for studying the process of magnetization at the
interfaces of complex oxide heterostructures was presented.191
Polarized neutron reflectometry (PNR) was also discussed in
several other publications. PNR was used to study the
superlattice 40 [(6 nm)ErFe2/(6 nm)DyFe2].192  This structure
consists of two hard magnetic materials and was grown by
molecular beam epitaxy. When the cryomagnetic field was
aligned along the [1 −1 0] direction, the net magnetization
reverses through the [2 2 1] direction during the process of
magnetization reversal, with the magnetization of the DyFe2
reversed over a smaller range of applied fields. The magnetization
reversal of a CoPt/Permalloy/Ta/Permalloy heterostructure was
studied with PNR,197 and quantitative depth resolved information
of the magnetization reversal processes for a multilayer of
mesoscopic thickness was obtained. Polarized neutron reflectivity
measurements were used to determine the temperature dependence
of the magnetization of thin AuFe films in the thickness range
between 1 and 50 nm and in a temperature range from 200 to 2 K.194  The magnetization of the 1-nm-thick film could be
described with a Brillouin function below 50 K proving that
ultrathin AuFe layers below 1 nm do not show spin glass
behavior anymore but are paramagnetic. Design of tunable
hearthless neutron spin rotators, based on remnant magnetization
of FeCoV film, was presented.195  Such devices allow for the
characterization of the depth-dependent vector magnetization in
the films. Spin-echo resolved grazing incidence scattering setup
for the neutron interrogation of buried nanostructures was
reported.196  This setup allows one to achieve a very high in-plane
momentum resolution without collimation of the incident
neutron beam in the corresponding direction, and can be used as
an alternative or complementary method to conventional grazing
incidence neutron scattering experiments. Grazing incidence
small angle neutron scattering was used to perform surface
diffraction on magnetic nanostructures in thin films.197  A grazing
incidence neutron spin-echo spectroscopy method was reviewed.198  This method can be used for observing the
thermally driven dynamics of macromolecules close to rigid
interfaces, and to retrieve information about the dynamics of the
scattering depth in the range of 10 - 100 nm. Depth-resolved
studies of layered magnetic nanostructures using 57Fe probe
layers and Mössbauer spectroscopy was presented.199  The
potential offered by the application of isotope-selective
measurements for the study of Fe-based layered magnetic
nanostructures was illustrated, and the depth-dependent spin
structures and interfacial interdiffusion in exchange-biased
ferromagnetic/antiferromagnetic bilayer systems were
demonstrated. Spin polarized low energy electron microscopy
was applied to investigate the quantum size effect in electron
reflectivity from Fe thin films grown on a W(110) surface
precovered with a two monolayer Cu film.200  Evidence was
obtained to show that the buried interface that defines the thin
film quantum well boundary is located one layer above the
W(110) surface. These results suggest that the Cu layer in
direct contact with the substrate remains largely intact, but the
weakly-bound second Cu layer mixes or segregates freely.

2-6 Self-organizing and complicated interfaces

Nanometer-scale structures can be realized through bottom-up
strategies, by exploiting buried networks of dislocations and the
process of self-organizing. By using ultra-high vacuum molecular
beam epitaxy and appropriate growth steps, it is possible to
grow self-organized nano-structured films and structures with

Fig. 3 Example of X-ray analysis of magnetic superlattices. X-ray
reflectivity and diffraction of the Fe(6ML)/V(7ML) superlattice
measured with conventional θ–2θ Cu Kα radiation (λ = 0.154 nm)
X-ray source. (a) Low-angle X-ray reflectivity data with the main X-ray
diffraction (XRD) peaks indicated. (b) High-angle XRD where the
main superlattice 002 peak indicated by “0” is surrounded by satellites
denoted ±1 and ±2 (from Fig. 1 in Ref. 184, reproduced with
permission).
Si-rich silicon nitride thin film were reported. The samples on GaAs (100) substrate, grown by molecular beam epitaxy (see characterization of self-assembled InAs quantum dot stacks on interfaces, and film thickness. The growth systems are very important, their properties have to be studied, surfactant behavior, and biologically relevant monolayers and transitions in quasi-2D systems, chemical self-assembly, liquids, and in this case the important research areas are phase tunable sizes. Surface monolayers can also be self-assembled liquids, and in this case the important research areas are phase transitions in quasi-2D systems, chemical self-assembly, surfactant behavior, and biologically relevant monolayers and membranes. In general, self-organizing nano-materials and systems are very important, their properties have to be studied, and methods for their growth have to be optimized. The growth mode depends on the surface morphology, chemical interactions as interfaces, and film thickness.

X-ray and neutron reflectometry were used for structural characterization of self-assembled InAs quantum dot stacks on GaAs (100) substrate, grown by molecular beam epitaxy (see Fig. 4). The macroscopic density profile of uncapped InAs layer was extracted and showed a three-dimensional pyramidal structure of maximum height of 5 nm. The interface roughness of the capping layers was found to be smaller than 0.5 nm, showing the high quality of the epitaxial surfaces. Soft X-ray reflectivity measurements near the Si-L\textsubscript{2,3} absorption edge for Si-rich silicon nitride thin film were reported. The samples were prepared Hg-sensitized photochemical vapor deposition. The combined study of soft X-ray reflectivity and optical density obtained from the reflectivity fitting at various photon energies provide a qualitative estimation of the film composition and its growth. The precise analysis of optical index profile derived over extended energy region gives additional compositional details of the film. Interfacial structures of the basal surface of muscovite mica in fulvic acid solutions were investigated using \textit{in situ} X-ray reflectivity. Molecular-scale variations in the thickness and internal structure of the fulvic acid film were observed and quantified as a function of pH and reaction time. The presence of the near-surface peak is attributed to condensation of FA molecules during sorption. The growth of self-organized nano-structured CoO islands on Fe(001) substrates was studied by X-ray photoemission spectroscopy, Auger electron spectroscopy, and scanning tunneling microscopy measurements. When CoO is grown at 470 K by reactive deposition on the Co(001)-p(1 × 1)O surface of a 5 ML thick Co layer grown onto Fe(001), the growth proceeds without inducing Fe cation migration and oxidation, at variance with the growth of CoO directly on Fe(001). In such conditions, furthermore, it has been found that a misfit dislocation network develops in the very early stages of CoO growth. Grazing incidence X-ray scattering measurements and synchrotron X-ray diffraction were used to study orientation of polymer thin films. Both in-plane and out-of-plane geometries have been combined in order to obtain complementary structural information. Hard X-ray photoelectron spectroscopy was used to investigate electronic properties and to perform compositional analysis of structures and interfaces buried below several layers of a heterogeneous sample. This technique is used to study depth resolved electronic properties of nanocrystals, internal structures of multilayer superlattices, and buried interfaces. Synchrotron radiation-based X-ray photoelectron spectroscopy and near-edge extended absorption fine structure measurements were performed to examine azide-terminated self-assembled monolayer of ethynylterpyridine on gold.

The hetero-interface between graphene grown by ambient pressure chemical vapor deposition on strontium titanate SrTiO\textsubscript{3} was analyzed by Raman spectroscopy and X-ray photoelectron spectroscopy. The combined measurements allowed for determining the valence band offset and conduction band offset at the interface.

### 2.7 Catalytic interfaces

Most of the catalyst devices are prepared on metallic surfaces, so the properties of catalyst/metal interfaces are very important and are studied intensively in order to improve the selectivity and conversion rates of the catalytic processes. The catalytic reaction depends on both the electronic structure and the geometric arrangement of the surface, so both the chemistry and morphology of the buried catalytic layers and interfaces have to be studied.

The electronic structure and the surface composition of ultrathin films of In on Pd(111) catalysts were characterized by X-ray photoelectron spectroscopy, while the atomic surface structure was determined by a combination of low energy electron diffraction and X-ray photoelectron diffraction. The samples were ultra-thin In films of 1 to 5 mono-atomic layers, deposited at room temperature, and then annealed at 500 K. Results indicate the diffusion of In atoms into the outermost layers of the Pd(111) single-crystal, and formation of bidimensional In islands, with some bare patches on the substrate. Grazing-incidence X-ray fluorescence combined with a near-edge X-ray absorption fine-structure investigation was carried out to study speciation of deeply buried TiO\textsubscript{2} nanolayers. Both the chemical speciation and the layer composition were determined, which is difficult to achieve with nondestructive methods based on electron emission due to restricted information depth of these methods. Neutron reflectometry measurements of deuterium absorption in thin films of Al-containing Mg alloys capped with a Ta/Pd, Ni/Pd and Ti/Pd-catalyst bilayer was carried out. The absorption mechanism observed was found to involve spillover of atomic deuterium from the catalyst layer to the Mg alloy phase, followed by the deuteration of the Mg alloy. Complete deuteration...
of the Mg alloy occurs in a pressure range between 0.01 and 0.05 MPa, dependent on the type of bilayer catalyst. Neutron reflectometry was used to study the hydrogen desorption kinetics in Ta/Pd bilayer catalyst.\textsuperscript{212} Full hydrogen desorption occurred at 100°C with a noticeable desorption even at room temperature. The Ta/Pd bilayer remained intact both after hydrogen absorption and following the hydrogen desorption. Additionally, X-ray diffraction analysis was used to determine the crystal structure of the as-synthesized, sorbed and desorbed film. Stability of the multilayered thin-film catalytic structure Si/Ta/Mg/Fe/Ta/Pd after deuterium absorption and desorption and after annealing at 250°C were investigated with neutron reflectometry and analytical transmission electron microscopy.\textsuperscript{213} Such nanolayered composites based on Fe and Mg are important hydrogen storage materials. The neutron reflectometry provides evidence that interdiffusion is significant at 250°C, but with the film general structure still in place. Electron microscopy observations indicate that annealing at 250°C leads to phase transformation to form Mg$_2$Pd$_3$ at the upper sections of the Mg layer.

2.8 Electrochemical interfaces

Thin-film based electrochemical systems are very important and are used in many modern technological devices. Several important electrochemical processes take place at buried interfaces, such as formation of chemical bonds, adsorption/desorption, electron transfer, solvation/desolvation, etc. These processes need to be understood, which involves obtaining information about changes in the surface composition, changes in electronic structures of the interfaces, and corresponding atomic and molecular arrangement and orientation. This requires the development of efficient methods and techniques for in-situ analysis and observation of interfacial processes and reaction mechanism, specifically tailored to electrochemical nano-systems.

Historical and current progress in X-ray absorption fine structure and surface X-ray scattering as tools for in situ studies on electro-catalytic reactions was reviewed.\textsuperscript{214} Electrochemical cell for neutron reflectivity measurements of solid/liquid interfaces was presented.\textsuperscript{215} The cell allows for performing neutron reflectivity measurements in vertical geometry, which offers higher degrees of freedom in controlling and measuring the sample environments. Planar electrochemical interfaces of metal/liquid lithium ion electrolyte were studied with specular neutron reflectometry (see Fig. 5). The structure of the lithium enriched layers formed on the working electrode was analyzed in terms of the scattering length density depth profiles obtained from the modelling of the reflectivity curves. A principal change in the interface profile evolution was observed when a non-electroactive additive is present in the electrolyte. The lithiation/delithiation processes were investigated over four cycles using neutron reflectometry in combination with electrochemical impedance spectroscopy.\textsuperscript{217} Successive growth of the lithiated zone was observed, and the loss of Coulombic efficiency could be directly correlated to a decrease in electronic structure.

X-ray reflectivity measurements were employed to evaluate the importance of O$_2$ pulse duration during the encapsulation process of organic light emitting diodes with ultra-thin inorganic atomic layer.\textsuperscript{218} X-ray reflectivity and vibrational sum frequency spectroscopy were used to probe the structure of the ethylammonium nitrate/air interface. X-ray reflectivity reveals that the interface is structured and consists of alternating nonpolar and charged layers that extend 3.1 nm into the bulk.\textsuperscript{219} Vibrational sum frequency spectroscopy reveals that interfacial cations have their ethyl moieties oriented toward air. X-ray photoelectron spectroscopy was used to study interface layer formation between LiPON and metallic lithium, and the ion transfer resistances and interface reactions between the electrodes and the electrolyte.\textsuperscript{221} Hard X-ray photoelectron spectroscopy was applied to examine the electronic structure of various functional materials, and to measure bulk-sensitive and buried interface electronic structures.\textsuperscript{222} Hard X-ray photoelectron spectroscopy was also used to identify chemical interactions involving zinc and aluminum, and elemental redistribution at the buried silicon/aluminum-doped zinc oxide thin-film solar cell interface.\textsuperscript{223} An increase of zinc- and aluminum-related signals after solid-phase crystallization of the deposited amorphous silicon thin films was observed. The effect of aqueous electrolyte on the polymer/metal oxide interface was monitored with spectro-electrochemical setup of Fourier transform infrared spectroscopy in the Kretschmann geometry, and with odd random phase multisine setup of Fourier transform infrared spectroscopy in the Kretschmann geometry, and with odd random phase multisine spectro-electrochemical impedance spectroscopy.\textsuperscript{224} The interfacial interactions of ultrathin polyacrylic acid film on an aluminum oxide surface were identified as carboxylate ionic bonds and
changes induced by the effect of water diffusion at the interface were monitored in situ. Initial increase in ionic bonding is observed, followed by replacement of interfacial interactions by water molecules, leading to macroscopic delamination.

2.9 Adhesive interfaces

An understanding of the molecular-level mechanisms of the adhesion process between different materials is important for creation of adhesive interfaces and materials. Especially important are adsorption processes at buried interfaces, where it is difficult to study the physical and chemical phenomena that take place. Again, methods allowing both chemical state analysis and morphology determination are needed.

In situ observation using hard X-ray photoelectron spectroscopy was applied for chemical state analysis of buried polymer/metal adhesive interfaces. The larger probing depth of this technique allows determination of the chemical state of the buried interface without exposing the interface. It was demonstrated that copper sulfides formed at the buried rubber/brass interface are distinguished from S-containing species in the rubber overlayer. Total internal reflection Raman spectroscopy was applied to probe sulfate ion behavior at the buried hematite/solution interface. This technique is very suitable for studying inorganic anion adsorption at buried interfaces. The obtained data suggest that inner-sphere sulfate adsorption proceeds in a bidentate fashion at the hematite surface. Sum frequency generation vibrational spectroscopy and X-ray photoelectron spectroscopy were used to probe the buried interface between polyethylene-terephthalate and 3-glycidoxypropyl-trimethoxy-silane (γ-GPS), and to describe the role of interfacial structures to polymer adhesion. It was shown that the fluorinated silane segregate to the polymer interface. The use of colored picosecond acoustics for characterization of complex stacks of thin films was reported. The technique is a unique combination of optics and acoustics that implements an acoustic pulse-echo technique at the nanoscale using a tunable ultrafast laser. Very high frequency acoustic waves (up to several hundreds of GHz) are emitted and detected using ultra-short laser pulses, allowing for thin-film thickness and thin-film elasticity measurement via the acoustic time-of-flight detection. Acoustic mapping/imaging of the sample surface can reveal in non-destructive manner the presence of weak points at the buried interface.

2.10 Multilayers and other interfaces

This section summarizes the advancements in the use of surface and interface techniques for analysis of buried layers and interfaces, which were not covered by previous sections.

Table top mapping ellipsometry, X-ray reflectometry, and optical reflectometry, were used for measuring Al₂O₃ films with thickness in the range of 1–50 nm. The amount of surface contamination was estimated together with thicknesses of the interface layer, surface nano-roughness by in situ reflectometry measurement during removal by UV radiation. The use of X-ray reflectivity and X-ray fluorescence spectrometry for measuring the thickness of the thin layer of polycrystalline TiO₂ was demonstrated, for the thickness range from 5 to 300 nm. The role of the interface and interface roughness on the precision of thin film thickness measurement was discussed. Investigation of Zr/Cf interfaces in an Al/ZrCf/Cf/W waveguide-like structure by soft X-ray reflectivity technique was carried out. Structural parameters of the stack, together with density, thickness and roughness of the layers, were determined through fitting the data. Back-side specular X-ray reflectivity and back-side off-specular X-ray measurements were utilized to measure interface roughness of deeply buried layers. Front side reflectivity measurements provide information only within a thickness range of approximately 80 nm, because most photons are totally reflected from this region. In contrast, specular and off-specular measurements from the back side provide quantitative information on the buildup of roughness at the interfaces as well as the lateral and vertical correlation lengths of the roughness. Soft X-ray reflectivity and X-ray photoelectron spectroscopy (XPS) techniques were used to perform a depth resolved compositional analysis of aluminum oxide thin film and to estimate the optical index profile. XPS techniques do not have enough penetration capability to analyze the interface (the thickness of the aluminum oxide thin film was 24 nm), so only X-ray reflectivity measurements could provide information about this region. The results suggests that the film region is comprised of Al₂O₃ and Al₂O₃₆ phases, while the interface region is comprised of SiO₂ and Al₂O₃₆ mixture. A new model for interpretation of X-ray reflectivity data was proposed, based on canonical functions. It allows for better interpretation of experimental data from low contrast multilayer systems. X-ray diffraction, grazing incidence X-ray diffraction, and X-ray reflectometry techniques were applied for analysis of Ti and TiO₂ nanolayers with thickness of up to 75 nm deposited on silicon, quartz and BK7-glass substrates. The aim of the studies was to investigate the crystal structure and morphology of the nanolayers with respect to dependence on the substrate type. In addition, the nanolayer thickness and roughness together with substrate roughness were estimated for all samples. The largest roughness was observed for the BK7-glass substrate. The interface of Ti/Al/Ti structure was studied by X-ray diffraction and synchrotron diffraction. Synchrotron diffraction revealed the presence of residuals of Al phase in the structure in addition to the Ti and Al/Ti phases. Thermal diffusion characteristics in naturally grown ultra-nanoscale superlattice structures were studied using high resolution X-ray diffraction. Variations in the diffusion coefficient as a function of time at different temperatures was obtained, and it was determined that the diffusion coefficient was highly nonlinear across the interface with time. The activation enthalpy values for interdiffusion were also estimated, and it was demonstrated that the interdiffusivity increases with temperature only in the range from 500 to 625 °C. The carbon diffusion barrier at the interface of Mo/Si multilayers was investigated by grazing incidence X-ray reflectivity and grazing incidence extended X-ray absorption fine structure. An improvement in reflectivity of multilayers with carbon diffusion barrier layer was observed. The study confirms the reduction of diffusion of Mo and Si layer into each other when the carbon buffer layers are present at the interfaces, thus reducing the chance of formation of MoSi₂. X-ray photoelectron spectroscopy study of the first atomic layers of TiN nanofilms grown by ion beam assisted deposition on crystalline silicon was presented. The expected hydrogen passivation effect by the Si-H formation bond limiting the Si-O bonds was quantitatively evaluated and correlated with the retention of H and O at the substrate surface. It was also reported that cleaning procedure plays an important role in the bond formation at the interface since minute amounts of oxygen jeopardize the bulk properties. The variable energy excitation capability of a synchrotron X-ray source was used to create high kinetic energy electrons with energies up to 15 keV, which enables hard X-ray photoelectron spectroscopy to access interfaces buried by several tens of nanometers. The proposed method is well suited to study chemical diffusion inside a compound where the density contrast is extremely low and X-ray reflectivity technique cannot be applied. Three ion-probing techniques (Rutherford backscattering spectroscopy,
secondary ion mass spectroscopy, and glow-discharge optical emission spectroscopy) were used to perform depth profiling and elemental analysis of complex layer systems and to examine their interface width. Ultra-thin chromium layers of 2.5 nm, buried at different depths in titanium matrices, were resolved and evaluated. Four techniques (X-ray diffraction, X-ray reflectivity, neutron reflectivity, and atomic force microscopy) were applied to study the structure and interface morphology of an electrodeposited Cu/Ni film. The crystalline structure of the film was determined by X-ray diffraction, while the depth profile of density was obtained from specular X-ray and neutron reflectivity measurements. Atomic force microscopy of the air-film interface shows that the surface is covered by globular islands of different sizes. Absorption kinetics in nanoscale magnesium based hydrogen storage multilayers was investigated with a combination of neutron reflectometry, X-ray diffraction, and atomic force microscopy. The effect of chromium and vanadium alloying on the hydrogenation of a magnesium thin film was studied by neutron reflectometry. Immediate formation of a blocking MgD layer is observed in pure Mg, while in the alloyed film deuteration is rapid and almost completely homogeneous. Hydrogen absorption and desorption properties of thin Pd-covered Mg, Al alloy films was measured as a function of temperature and alloy composition using neutron reflectometry. Electrochemical behavior of Ni in an alkaline heavy water electrolyte was studied using cyclic voltammetry and polarized neutron reflectometry. Delays in the hydrogen and oxygen evolution reactions on Ni electrodes and slower kinetics of the reactions in heavy water compared to light water were observed.

3 Emerging Analytical Techniques, Instruments and Applications

3.1 Imaging of inhomogeneous and patterned buried layers and interfaces

When designing some functions in thin film systems, one of the key concepts is the structure of the constituent layers and interfaces. In an actual system, the layers and interfaces are often inhomogeneous in different scales, from hundreds of microns to several nanometers, causing differences in properties, despite very similar average structures. In this case, the choice of the observation point is critical to clarify the problem. Another critical aspect is the identification of these points by surveying the entire inhomogeneous thin film system. Therefore, so far, there has been strong demand for nondestructive visualization of inhomogeneous buried layers and interfaces in thin films.

X-ray reflectivity imaging is a unique extension of conventional X-ray reflectometry, which just gives average depth-profiling of the electron density of layered thin films. The reflectivity imaging is able to provide a full picture of the inhomogeneity. To obtain such images, one would not always have to insist on the XY scanning of a sample with a tiny X-ray beam. Just by employing a 1D or 2D position sensitive detector to record the profile of the X-ray reflection (rather than integrated X-ray reflection intensity), one can collect a series of such profiles at a set of different in-plane angles. Similar to computer tomography, it is possible to obtain the specimen’s two-dimensional (2D) X-ray reflectivity distribution as one image (see, Fig. 6). The special resolution is mainly limited by the angular dispersion of the primary X-rays and also by the pixel size of the detector. Typical spatial resolution is around 10–20 microns. To obtain further better resolution, the use of some kind of imaging optics (such as imaging mirrors and/or zone plates), will be necessary. The measurement can be done not only with synchrotron X-rays, but also with a low power (15 W) laboratory X-ray source.

A similar idea has been introduced for neutron reflectivity. Unlike X-rays, in neutron scattering (including neutron reflectivity), the experiments always need to assume some homogeneous and large-size samples, that might not meet well with the demands in modern materials sciences and engineering. No doubt it is important to find some good solutions about the lack of imaging capability in neutron scattering. The above discussed reflectivity imaging technique using a fairly wide beam is suitable for neutron experiments, as the primary neutrons are used in perfectly the same condition (optics, slits, the final beam size, etc.), as conventional neutron reflectometry. The essential addition is the in-plane rotation of the sample and the measurement of the intensity profile of the reflected neutron beam. If any high-resolution neutron detectors are available, the neutron reflectivity imaging measurements can be easily done. Even without the use of 1D/2D position sensitive detectors, the measurements are still achievable if a Hadamard coded mask is employed to measure the reflection projection in front of the point detector, such as 3He detector. In this case, the spatial resolution is limited by the angular divergence of the primary neutron beam and the slot size of the mask. The mask needs to scan with a step of the slot size. When the time-of-flight (ToF) mode is used for the neutron experiment, one can obtain many images as a function of ToF, i.e., the wavevector transfer. Such series of images can be displayed as a video. This indicates that the neutron reflectivity profiles of local points can be retrieved from the video images. It is possible to measure the neutron reflectivity profile at some specific points in the sample, without the use of any small beam.

Method for non-destructive imaging of buried electronic interfaces using a decelerated scanning electron beam was described. Low-bias scanning tunneling microscopy was applied for imaging of buried MgO/Ag interfaces. It was demonstrated that the interface features’ contrast is completely determined by the atoms on the surface of MgO. A method for high-resolution analytical transmission electron microscopy characterization of corrosion and cracking at buried interfaces was described. Performed analyses of the oxide films and impurities in the narrow intergranular penetrations and crack tips with widths of up to 10 nm confirm the importance of the grain boundary characteristics and water chemistry, and can be used to identify the local electrochemistry promoting degradation in complex environments. Nondestructive imaging of buried interfaces by scanning photoemission microscopy is described. This imaging method is based on the highly sensitive extinction for characterizing the contacts formed on wide-gap materials. High resolution transmission electron microscopy was applied for studying organic photovoltaics based on nano-structures in the semiconductor layers and in the donor-acceptor interface. The donor-acceptor interface morphology was further studied using scanning transmission electron microscopy in combination with energy dispersive X-ray spectroscopy. Spatially resolved ballistic electron emission spectroscopy was applied for imaging buried organic islands and pentacene film.

Application of synchrotron-based photoemission electron microscopy for chemical and magnetic imaging of surfaces, interfaces, thin films and buried layers, was discussed. The tunability and polarizability of the synchrotron X-ray source allows for spectroscopic investigations with a lateral resolution of a few tens of nanometres. Spin-polarized low-energy electron microscopy for imaging magnetic microstructures at surfaces
and in thin films was described. The method can be used to investigate spin re-orientation transition phenomena, to determine magnetic domain configurations in low-dimensional structures, and for in-situ and real-time determination of micromagnetic configurations and structure-property relationships. Energy-filtered X-ray photoelectron emission microscopy was used to analyze the spatial distribution of the silicon sub-oxide structure at the SiO$_2$/Si interface as a function of underlying doping pattern. Sub-oxide binding energy and intensity distributions over the full field of view were obtained with a spatial resolution of 120 nm. Hard X-ray photoemission spectroscopy with high lateral resolution was proposed. By using energy-filtered photoemission microscope and hard X-ray excitation of up to 6.5 keV photons, the authors were able to obtain X-ray photoemission spectra from regions less than 500 nm in diameter. Spectroscopic photoemission and low energy electron microscopy were applied for investigation of surfaces, interfaces, buried layers and nanoscale objects like nanoparticles and nanowires. The combination of photoemission electron microscopy with low energy electron microscopy allows for a complementary chemical and structural analysis, and was applied for studying the growth mechanism and doping profile of nanowires, growth and intercalation of graphene, droplet dynamics on surfaces, surface chemistry, and control of nanostructure fabrication. High-spatial resolution cathode-luminescence spectroscopy for imaging and characterization of nanometer-sized v-defects in InGaN single quantum well films was reported.

Three-dimensional terahertz imaging for non-destructive characterization and determination of spatial and statistical distribution of coating thickness was studied. The terahertz signal can penetrate up to 3 mm into organic materials, and can be used to investigate interfaces in multilayered structures. Microwave imaging of dielectrics buried under a rough surface, based on a nonlinear tomographic approach and contrast-source nonlinear inversion method, was reported. High-resolution high-frequency acoustic microscopy for characterization of buried interfaces was reported. Nanoscale imaging of buried structures via scanning near-field ultrasound holography was proposed. The phase and amplitude of the scattered ultrasound wave by perturbations is recorded holographically with the help of the surface acoustic standing wave, which provides nanoscale-resolution images of the internal substructure of diverse materials, and was applied to imaging buried nano-structures and to performing subsurface metrology in microelectronic structures. A high frequency micro acoustic imaging method is capable of detecting buried defects through layers that are not perfectly flat.

Three-dimensional coherent X-ray surface scattering imaging near total external reflection is discussed. The method is based on enhanced X-ray surface scattering and interference near total external reflection, and allows for reconstruction of non-periodic surface patterns in three dimensions with nanometer resolution in the direction normal to the substrate. Quantitative chemically specific coherent diffractive imaging
using extreme ultraviolet was demonstrated for characterization of oxidation and diffusion reactions at buried interfaces with nanometer precision.\(^1\) Short wavelength (29 nm) high harmonic extreme ultraviolet light can penetrate aluminum layers, yielding high-contrast images of the buried structures such as copper nanostructures inlaid in SiO\(_2\) and coated with 100 nm of aluminum.

Application of kinoform lenses for the X-ray reflectivity characterization of thin layered materials was demonstrated.\(^2\) The kinoform lens can focus an X-ray beam to a 50 \(\times\) 2 \(\mu\)m focal spot, which allows for the measurement of the X-ray reflectivity of thin layered materials in sample scanning mode with micron-scale spatial resolution. A new experimental set-up developed for both soft X-ray spectroscopy and holography imaging was reported.\(^3\) The setup for spectroscopy analysis allows for the quantification of the magnetic moments, while the holography experiments give a direct view of magnetic structures. Structural characterization of epitaxial thin film with atomic-layer-resolved interface by surface X-ray diffraction was presented.\(^4\) Phase-sensitive specular neutron reflectometry for imaging the nanometer-scale composition depth profile of thin-film materials was presented.\(^5\)

The X-ray standing-wave imaging\(^6\) is a newly proposed extension of X-ray standing wave technique, which can give very accurate depth/height position of specific impurity elements by the use of slight motion of the X-ray standing wave near the Bragg angle. While the X-ray standing wave technique has an atomic-scale resolution, in the direction perpendicular to the reflection plane, so far, it has had no spatial resolution parallel to the reflection plane. On the other hand, in X-ray standing wave analysis, the probing area is determined by the illumination area of the incident X-rays, which is frequently larger than a few square millimeters. As impurities would not be likely have regular depth distribution for every point in the whole probing area, the conventional X-ray standing wave technique gives an average. For this reason, it is significant to combine the existing X-ray standing wave technique with an in-plane imaging capability. As the area of nanolayers and interfaces is frequently a few square centimeters to square millimeters, an imaging resolution at the submillimeter level to micron level is already sufficient to see the inhomogeneity of the entire sample. In the X-ray standing wave imaging, multi-element XRF images are collected at all angle positions near the Bragg angle. To sort out the huge-size experimental datasets, the use of a feature map is proposed to clarify the distribution of specific elements in the depth direction.

### 3-2 Real time analysis of changes in buried layers and interfaces

Generally, in natural phenomena, one can find more unstable and changing systems than stable and unchanging ones. The functional materials are often designed to respond to any external input, such that electric current flows when it is exposed to some light. Some of these functions are related to the interface structures in layered thin films. The operando measurement is important to clarify the mechanism of the function, by understanding the structural change in real time.\(^7\)

The multi-channel X-ray reflectometer can be applied to precise and reproducible determination of the thermal expansion coefficients of thin films and the glass transition temperature.\(^8\) The advantage of this method is that the whole reflectivity profile is obtained without angular scan. This means that all angular points are recorded simultaneously, and therefore one can discuss the changes with confidence. The mechanism of uni-axial negative thermal expansion has been discussed in detail, based on the set of X-ray reflectivity data taken by this scheme\(^9\) (see, Fig. 7). The same method has been applied to the study of the hydrophobic-hydrophilic switching phenomena observed in the poly-c-(N-isopropylacrylamide) ultrathin film.\(^10\)

Design of a high-pressure high-temperature sample chamber for \textit{in situ} high-energy X-ray studies of thin film and crystal growth at deeply buried interfaces in a harsh environment was described.\(^11\) The temperature can be controlled from 20 to 700°C, and pressure from 0.1 to 5 MPa. The formation of GaN layer at 1073 K and 5 MPAs of N\(_2\) was presented as a performance test. Time-resolved surface X-ray diffraction using synchrotron radiation was applied to study the structural dynamics of electrochemical interface.\(^12\) Kinetic processes of the atomic interdiffusion across the interface in thin platinum-nickel bilayer across the temperatures ranging from 230 to 300°C was investigated by \textit{in-situ} X-ray reflectivity.\(^13\) It was determined that the interdiffusion is dominated by Ni atoms with an associated activation energy of 0.87 eV. \textit{In-situ} liquid cells and soft X-ray absorption spectroscopy were used to investigate...
solid/liquid interfaces between electrode and electrolyte. This in-situ/operando method provides both element and chemical interfacial information, and allows for measuring the deposition of solute species on electrode surface, morphological and chemical changes of electrode surface, and potential-dependent orientations of interfacial solvent molecules. The evolution of lattice deformations in the InGaAs structure grown by molecular beam epitaxy was presented. The real-time structural analysis of the interfaces was performed by in situ synchrotron X-ray reciprocal space mapping. The experiments confirmed that the introduction of a thin InAs layer effectively improved the crystal quality during the initial growth of InGaAs. In situ synchrotron X-ray scattering techniques were deployed to observe the nucleation and early stage solidification behavior when liquid is in contact with a specific crystal plane of a solid substrate. The diffraction data reveal the orientation relationship between the substrate and the nucleus, in particular the interface plane, and its influence on the required undercooling for nucleation. Measurement of structural changes in functional thin films during the application of external electrical field was reported.

In-situ X-ray diffraction was used to determine the polarization and structural changes in sol-gel lead zirconate titanate (PZT) thin film as a function of external electric field. The evolution of two different effects (cell extension and switching between a- and c-tetragonal domains) was successfully separated. X-ray absorption fine structure measurements were used for in situ observation of electrochemically driven deposition of palladium nanoparticles at a liquid/liquid interface. A novel glass/plastic hybrid electrochemical cell was used to enable control of the potential applied to the liquid/liquid interface. It was found that the introduction of citric acid results in the formation of spherical nanoparticles at the interface. Grazing incidence X-ray reflectivity and grazing incidence X-ray diffraction were utilized for measurement of thermally induced interface changes in W/B4C multilayers as a function of annealing temperature.

5 References

1. “Surface and Thin Film Analysis: A Compendium of Principles, Instrumentation, and Applications”, ed. G. Friedbacher and H. Bubert, 2nd ed., 2011, John Wiley & Sons.
2. T. Imae, “Nanolayer Research: Methodology and Technology for Green Chemistry”, 2017, Elsevier.
3. J. González-Cobos and A. de Lucas-Conseguera, Catalysts, 2016, 6, 15.
4. "Methods of Surface Analysis", ed. A. W. Czanderna, 2012, Elsevier.
5. S. Hofmann, “Auger- and X-ray Photoelectron Spectroscopy in Materials Science: A User-Oriented Guide”, 2012, Springer.
6. H. Arai and T. Fujikawa, Anal. Sci., 2010, 26, 147.
7. Y. Yano, M. Naskano, and D. Takakura, Anal. Sci., 1997, 13(Supplement), 355.
8. J. Kawai, Anal. Sci., 1997, 13, 797.
9. J. Pavluch, L. Zimmer, K. Masek, T. Skála, F. Sutara, V. Nehasil, I. Piš, and Y. Polyak, Anal. Sci., 2010, 26, 209.
10. K. Kimura, K. Nakajima, T. Conard, W. Vandervorst, A. Bergmaier, and G. Dollinger, Anal. Sci., 2010, 26, 223.
11. J. Rubio-Zuazo and G. Castro, Surf. Interface Anal., 2008, 40, 1438.
12. K. Rokosz and T. Hryniewicz, World Scientific News, 2016, 37, 232.
13. M. Brown, M. Faubel, and B. Winter, Annu. Rep. Prog. Chem. Sect. C, 2009, 105, 174.
14. A. Jablonski, Anal. Sci., 2010, 26, 155.
15. C. S. Fadley, J. Electron Spectrosc. Relat. Phenom., 2010, 178-179, 2.
16. Y. Fukuda, Anal. Sci., 2010, 26, 187.
17. M. Kobata, I. Piš, H. Iwai, H. Yamazui, H. Takahashi, M. Suzuki, H. Matsuda, H. Daimon, and K. Kobayashi, Anal. Sci., 2010, 26, 227.
18. A. Ueda, D. Kato, N. Sekioka, S. Hirono, and O. Niwa, Anal. Sci., 2009, 25, 645.
19. R. Xie, Y. Song, L. Wan, H. Yuan, P. Li, X. Xiao, L. Liu, S. Ye, S. Lei, and L. Wang, Anal. Sci., 2011, 27, 129.
20. Z. Wang, M. Saito, S. Tsukimoto, and Y. Ikehara, Journal of the Ceramic Society of Japan, 2011, 119, 783.
21. D. Homeniuk, M. Malac, and M. Hayashida, Ultramicroscopy, 2018, 194, 64.
22. D. P. Woodruff, “Low Energy Electron Diffraction”, in “Reference Module in Materials Science and Materials Engineering”, 2016, Elsevier.
250. I. Jiang and K. Sakurai, Rev. Sci. Instrum., 2016, 87, 093709.
251. I. Jiang, K. Hirano, and K. Sakurai, J. Appl. Cryst., 2017, 50, 712.
252. K. Sakurai and I. Jiang, J. Surf. Sci. Soc. Jpn., 2017, 38, 448 (in Japanese).
253. K. Sakurai, M. Mizusawa, J. Jiang, and T. Ito, Phys. B, 2018, 551, 426.
254. K. Sakurai, J. Jiang, M. Mizusawa, T. Ito, K. Akutsu, and N. Miyata, Sci. Rep., 2019, 9, 571.
255. A. Hirohata, Y. Yamamoto, B. Murphy, and A. Vick, Nat. Commun., 2016, 7, 12701.
256. A. Malashevich, E. I. Altman, and S. Ismail-Beigi, arXiv:1407.5645, 2014.
257. S. M. Bruemmer and L. E. Thomas, Surf. Interface Anal., 2001, 31, 571.
258. K. Shiojima, S. Yamamoto, Y. Kihara, and T. Mishima, Appl. Physics Express, 2015, 8, 046502.
259. J. B. Gilchrist, T. H. Basey-Fisher, S. C’E. Chang, F. Scheltnens, D. W. McComb, and S. Heutz, Adv. Funct. Mater., 2014, 24, 6473.
260. K. Goh, A. Bannani, and C. Troadec, Nanotechnology, 2008, 19, 445718.
261. A. Locatelli and E. Bauer, J. Phys.: Condens. Matter, 2008, 20, 093002.
262. N. Rougemaille and A. Schmid, Eur. Phys. J. Appl. Phys., 2010, 50, 20101.
263. F. de la Peña, N. Barrett, L. F. Zagone11, M. Walls, and O. Renault, J. Electron Spectrosc. Relat. Phenom., 2012, 185, 1429.
264. C. Wiemann, M. Patt, S. Cramm, M. Escher, M. Merkel, A. Gloskovskii, S. Thiess, W. Drube, and C. M. Schneider, Appl. Phys. Lett., 2012, 100, 223106.
265. A. A. Zakharov, A. Mikkelsen, and J. N. Andersen, J. Electron Spectrosc. Relat. Phenom., 2012, 185, 417.
266. M. Yoshikawa, M. Murakami, H. Ishida, and H. Harima, J. Surf. Sci. Soc. Jpn., 2010, 31, 571.
267. C. L. Koch-Dandolo, T. Tiltenborg, K. Fukunaga, J. Skou-Hansen, and P. U. Jepsen, Appl. Opt., 2015, 54, 5123.
268. J. A. Zeitzer, Y. Shen, C. Baker, P. F. Taday, M. Pepper, and T. Rades, J. Pharm. Sci., 2007, 96, 330.
269. T. U. Gurbuz, B. Aslaynurek, E. P. Karabulut, and I. Akduman, IEEE Transactions on Geoscience and Remote Sensing, 2014, 52, 3013.
270. S. Ramanathan, Proceedings of 2006 Electronic Components and Technology Conference, 2006, 1865.
271. S. Ramanathan and D. Cahill, J. Mater. Res., 2006, 21, 1204.
272. G. Shekhawat and V. Dravid, Science, 2005, 310, 89.
273. T. Sun, Z. Jiang, J. Strzalka, L. Ocola, and J. Wang, Nat. Photon., 2012, 6, 586.
274. E. R. Shanblatt, C. L. Porter, D. F. Gardner, G. F. Mancini, R. M. Karl Jr., M. D. Tankalsvala, C. S. Bevis, V. H. Vartanian, H. C. Kapteryn, D. E. Adams, and M. M. Murnane, Nano Lett., 2016, 16, 5444.
275. M. K. Tiwari, L. Alianelli, I. P. Dolbnya, and K. J. S. Sawhney, J. Synchrotron Radiat., 2010, 17, 237.
276. J. Camarero, E. Jiménez, J. Vogel, C. Tieg, P. Perna, A. Bollero, F. Yakhou-Harris, C. Arm, B. Rodmacq, E. Gautier, A. Saffret, B. Delau, G. Gauduin, B. Dieny, and R. Miranda, J. Appl. Phys., 2011, 109, 07D357.
277. T. Shirasawa, M. Ohyama, W. Voegeli, and T. Takahashi, Phys. Rev. B, 2011, 84, 075411.
278. B. J. Kirby, P. A. Kienzle, B. B. Maramville, N. F. Berk, J. Krycka, F. Heinrich, and C. F. Majkrzak, Curr. Opin. Coll. Int. Sci., 2012, 17, 44.
279. W. Zhao and K. Sakurai, Phys. Rev. Mater., 2019, 3, 023802.
280. K. Sakurai, M. Mizusawa, and M. Ishii, Trans. Mater. Res. Soc. Jpn., 2007, 32, 181.
281. M. Mizusawa and K. Sakurai, IOP Conference Series: Materials Science and Engineering, 2011, 24, 012013.
282. Y. Liu and K. Sakurai, Langmuir, 2018, 34, 11727.
283. Y. Liu and K. Sakurai, Polym. J., 2019, 51, 1073.
284. Y. Liu and K. Sakurai, Chem. Lett., 2017, 46, 495.
285. Y. Liu and K. Sakurai, ACS Omega, 2019, 4, 12194.
286. A. E. F. de Jong, V. Vonk, V. Honkimäki, B. Gorges, H. Vitoux, and E. Vlieg, J. Cryst. Growth, 2015, 420, 84.
287. M. Nakamura, Current Opinion in Electrochemistry, 2019, 14, 200.
288. V. Tran, S. Ha, H. Oh, S. Kim, I. Cho, J. Chung, B. Mun, O. Seo, and D. Noh, Thin Solid Films, 2019, 689, 137518.
289. Y. Ye, C. Wu, L. Zhang, Y. Liu, P. Glans-Suzuki, and J. Guo, J. Electron Spectrosc. Relat. Phenom., 2017, 221, 2.
290. T. Sasaki and K. Takahasi, J. Cryst. Growth, 2019, 512, 33.
291. A. J. Brown, H. B. Dong, P. B. Howes, and C. L. Nicklin, Scr. Mater., 2014, 77, 60.
292. B. Allouche, I. Gueye, G. Le Rhun, P. Gergaud, and N. Renault, Curr. Opin. Coll. Int. Sci., 2015, 20, 012013.
293. S. G. Booth, S. Chang, A. Uehara, C. La Fontaine, G. Cibin, S. L. M. Schroeder, and R. A. W. Dryfe, Electrochim. Acta, 2017, 235, 251.
294. P. N. Rao, S. K. Rai, A. K. Sinha, M. N. Singh, and G. S. Lodha, Thin Solid Films, 2015, 589, 268.