Surface structure

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Surface physics is a thrust area of research in almost all technologically developed countries not only because it has enabled us to probe basic physical and chemical interactions existing in various two-dimensional (2D) systems, surface physics has also opened up exciting opportunities to study surfaces and interfaces of materials which are technologically important. To understand the nature of surfaces and interfaces, it is important to study its structure in atomic length scale. Two new techniques having atomic resolution, developed recently, to study surface structure, namely grazing incidence X-ray scattering and scanning probe microscopy (SPM), has changed our level of understanding. We shall discuss the merit of these two complementary techniques, which we are setting up in Saha Institute of Nuclear Physics (SINP). This facility will be first of its kind in our country.

CONDENSED matter interacts with environment consisting of vacuum/gas/vapour and with other condensed systems mostly through surfaces and interfaces respectively. As a result, to understand the fundamental properties of materials and to tailor these properties for specific purpose, we need to study surfaces and interfaces of condensed systems in details. Apart from generating considerable basic research activity, the surface physics determines the growth of many technological areas. These application areas include semiconductor electronics, optics, sensors, polymer coating-lubrication, electrochemistry, catalysis, corrosion, surfactants and biological membranes. Moreover ever increasing miniaturization of technologically important materials has increased the importance of surface physics considerably. We shall discuss here few such areas and shall refer interfaces as surfaces, which are buried.

The spectacular progress in surface physics during the last 10 years is due primarily to the development of new experimental and theoretical techniques capable of probing surfaces of materials in atomic length scale. Traditionally characterization of surfaces used to be done in ultra high vacuum using nearly perfect single crystal faces that remain free of contamination for the duration of the experiment. Although this approach of studying surfaces in ideal condition is pursued actively, more emphasis is now given to the studies of surfaces which are exposed to realistic environment, for obvious technological reasons. Moreover this exposure of surfaces to ambient condition generates interesting physical and chemical interactions for basic research. To understand the nature of these interactions, it is important to study surface structure in atomic length scale. Amongst the various techniques developed recently to study surface structure, two techniques namely grazing incidence X-ray scattering and scanning probe microscopy (SPM), has changed our level of understanding in surface physics. Averaged structural information of the interfaces over large surface area from grazing incidence X-ray measurements along with local information of structures in real space obtained from SPM techniques are generating fascinating knowledge about the molecular interactions in 2D systems.

In SINP we are setting up a laboratory for studying surfaces using both these complementary techniques. This will be the first such facility in our country.

Grazing incidence X-ray techniques are unique because these are nondestructive and can probe even buried interfaces. Three different measurement techniques are used and each of them gives us different information regarding surface structure. These grazing incidence techniques are specular reflectivity, surface crystallography and diffuse scattering. As surface is a 2D system, one obtains in reciprocal space rods of intensities, known as the crystal truncation rods (CTR), corresponding to a surface structure instead of spots obtained for 3D structures. Once the intensities of these rods are measured, methods of analysis in surface crystallography[1] are similar to those of conventional crystallography.

In X-ray specular reflectivity experiments a well-collimated monochromatized incident beam strikes the surface at an angle α and the scattered intensity is recorded using a detector placed after a tight slit in the plane of incidence also at an angle β ($\simeq \alpha$). Thus, the scattering vector q is perpendicular to the surface. The experiment, which measures the intensity as a function of the grazing angle starting from about 2 mrad, provides information about the mean electron density along the normal z (refer Figure 1). The measurements of reflectivity curve require a very high accuracy in incident angle and precision movements (around 10^{-3} degree) of sample and detector.

The electron density profile is directly related to the refractive index[2] profile along z by

$$n(z) = 1 - \delta(z) + i\beta(z), \qquad (1)$$

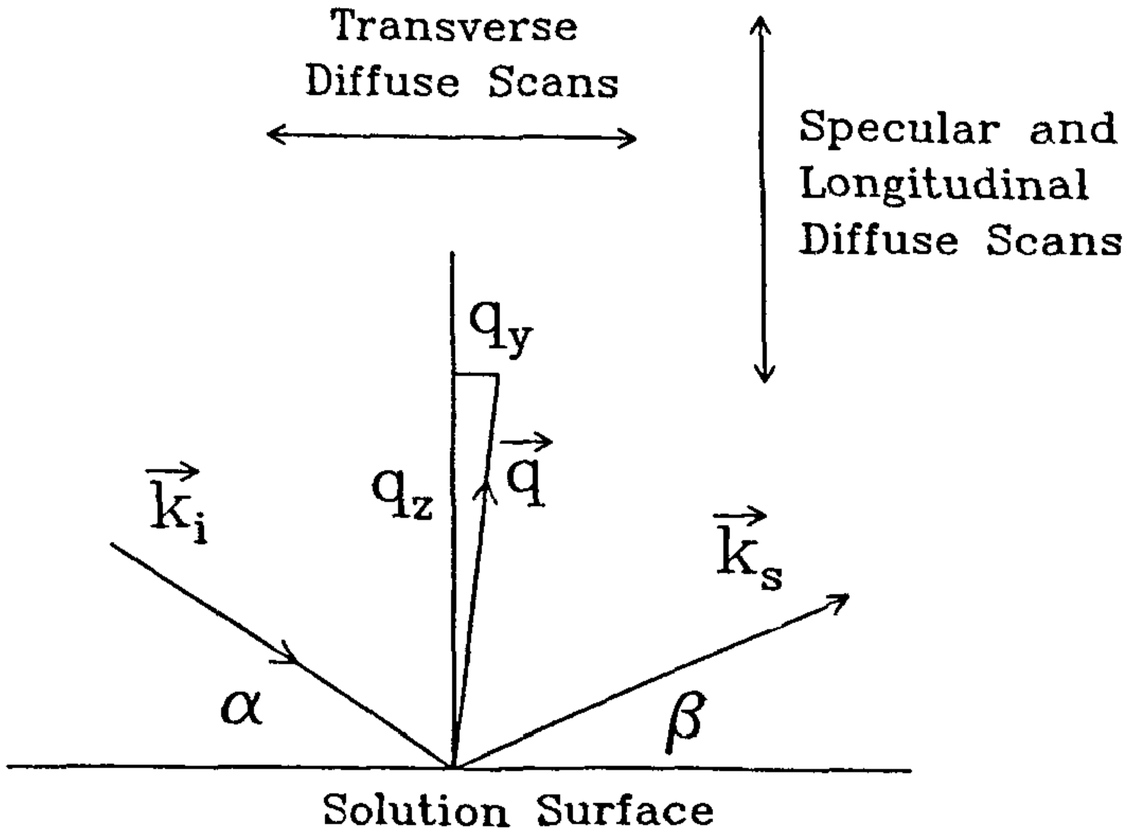

Figure 1. Schematic reciprocal-space diagram for scattering experiments. The scans indicated are transverse (i.e. q_y scans for constant q_z) or longitudinal (i.e. q_z scans for constant q_y). Specular scans correspond to $q_y = 0$.

where

$$\delta(z) - i\beta(z) = (r_0 \lambda^2/2\pi) \sum_i N_i(z) f_i(z). \qquad (2)$$

In the above equations f_i is the complex atomic scattering factor, λ the wavelength, r_0 the classical electron radius and N_i the atomic density. If the absorption is neglected, $n(z)$ can be written as $n(z) = 1 - \delta(z)$ with $\delta(z) = (r_0 \lambda^2/2\pi)\ \rho_e(z)$, where $\rho_e(z)$ is the electron density along the z-axis.

One can calculate reflectivity as a function scattering vector q rigorously[2] by treating the electron density profile along z of a thin film as a succession of homogeneous laminae characterized by its thickness and refractive index. For many applications it is sufficient to take into account the part of the experimental reflectivity curve that corresponds to incident angles sufficiently greater than α_c. In this case one enters the range of application of kinematic theory and the first Born approximation can be used[3]. It has been shown recently that one can also calculate the portion of the reflectivity curve near critical angle α_c by using Distorted Wave Born Approximation—this approach has enabled us to develop a new technique called anomalous reflectivity[4]. X-ray reflectivity measurement and proper data analysis[5] yield an independent determination of interfacial roughnesses, thicknesses and densities of different sublayers of a thin film (that is the projection of the electron density of the film along the normal of the surface).

To have a better understanding of the correlations in an interface and between interfaces, we need a technique which is sensitive to in-plane structure; grazing incidence X-ray diffuse scattering directly provide us this information. The diffuse scattering intensities at different points in the reciprocal space are measured by suitably changing incident and unequal scattered angles that X-ray make with sample surface (this is off-specular measurements) (refer Figure 1).

Under the assumption of a gaussian height distribution for surface roughness, diffuse scattering cross section from a single rough surface may be written by extending the Born approximation as[6]

$$\frac{A\,|k_0^2(1-n^2)|^2}{16\pi^2}\ \frac{\exp(-q_x^2\sigma^2)}{q_z^2}\ |T(\alpha)|^2\ |T(\beta)|^2 \times$$

$$\iint dx\,dy\,[\exp(q_z^2\,C(x,y)) - 1]\ \exp(i(q_x x + q_y y)), \qquad (3)$$

where

$$C(x, y) = \langle Z(0, 0)\,Z(x, y)\rangle \qquad (4)$$

is the height–height correlation function at lateral separation (x, y) along the mean surface, A is the total surface area, k_0 the incident wave vector, n the refractive index, σ the RMS surface roughness, $T(\alpha)$ and $T(\beta)$ are the Fresnel transmission coefficient for a smooth surface at grazing incidence and scattered angles α and β respectively. This equation can also be generalized in the case of a multilayer system by considering correlation between interfaces[7] in the film.

On the other hand, scanning probe microscopy (SPM) techniques[8,9] [such as scanning tunnelling microscopy (STM) and atomic force microscopy (AFM)] show surface in near atomic detail, revealing the surface order, steps and adsorbed molecules. The possibility of seeing atoms has always had a romantic attraction for scientists and these techniques appeared promising for the elucidation of surface structure at the atomic level. As the name suggests, the STM operates by the mechanism of tunnelling. Electrons tunnel from a small metallic tip held above the surface into the surface if the tip is biased negatively with respect to the surface or vice versa if the bias is changed. The vertical resolution is achieved by the exponential dependence of the tunnelling current on the tip-to-surface separation. A typical variation in current is an order of magnitude for every angstrom of separation. An image in the lateral direction is achieved by scanning the tip across the surface. AFM appears to be more general use since it no longer necessitates conducting tip and samples as STM does. In AFM the probing tip is attached to a cantilever which is deflected in response to the forces between the probing tip and the sample. These techniques have already demonstrated the capabilities of probing organic films, such as LB films, adsorbed DNA and polymer films, in atomic resolution. Recently complementarity of AFM and diffuse scattering study have been

demonstrated[10] in observing an interesting dewetting phenomena of ultra-thin polymer films.

Most active application areas of surface physics can be grouped in four broad categories such as (i) solid surfaces and overlayers, (ii) artificially structured multilayers or superlattices, (iii) liquid surfaces, and (iv) organic thin films. We shall briefly discuss these systems and application of the above mentioned two new techniques here.

Top surface of semiconductor or metal surfaces are sometime coated with different materials to modify the surface properties. These overlayers are sometime epitaxial in nature. It is also possible to have overlayers of same bulk materials by modifying the top surface by means of chemical, electrochemical and other processes. These well-characterized single crystal surfaces of various materials and overlayers are being studied by many active research group[1,11].

Artificially structured multilayers are class of new materials with intentionally produced spatial variations in composition. The overwhelming majority of research in this area concerns semiconductor materials, especially Group III-V materials such as gallium arsenide. This research activity has applications in the areas of high speed devices and in optical communications. This activity has also given us exciting fundamental knowledge regarding low-dimensional systems. A superlattice consists of a periodic double layer sequence of two different materials grown generally by molecular beam epitaxy (MBE), or metal organic chemical vapour deposition (MOCVD) techniques. Although bulk properties of the constituent materials are well known, the superlattices have new properties because their composition can be controlled and varied on length scale as short as 5–10 Å. Many semiconductor superlattice structures have been produced and their complexity is increasing. The correct choice of materials permits the spatial variation of the band structure (generally perpendicular to the film surface). A recent experimental advance, namely strained-layer epitaxy has enabled us to tailor the band-gap almost at will and the production of such artificially structured materials may be called 'band-gap engineering'[12]. Grazing incidence X-ray scattering techniques will play a major role[6,7] in the development of these materials. These studies will provide accurate knowledge of the actual composition, interfacial roughness and in-plane correlations in and between interfaces of superlattice structures, defect generation at interfaces, role of buffer layers and intermixing at interfaces. All these informations are vital for the further progress of this field. In Figures 2 and 3, we have shown typical results[7] of analysis of specular reflectivity and diffuse scattering data obtained from a GaAs/AlAs multilayer system.

The interfacial profile along the surface normal

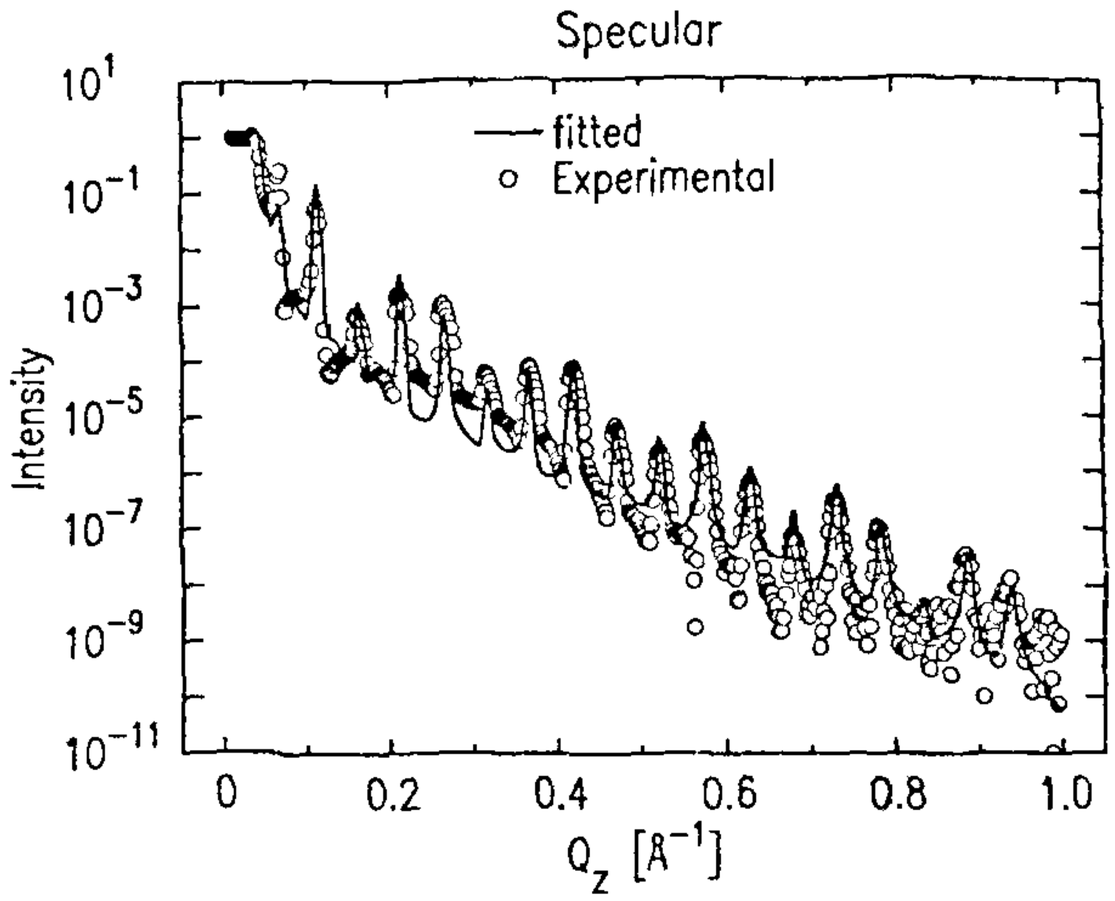

Figure 2. Measured and fitted specular data obtained from a GaAs/AlAs multilayer system. From fitting the following parameters are obtained, periodicity of the multilayer equal to 120 8 Å, ratio of GaAs thickness with the total bilayer thickness (120.8 Å) equal to 0 68 and interfacial roughness of 2.1 Å.

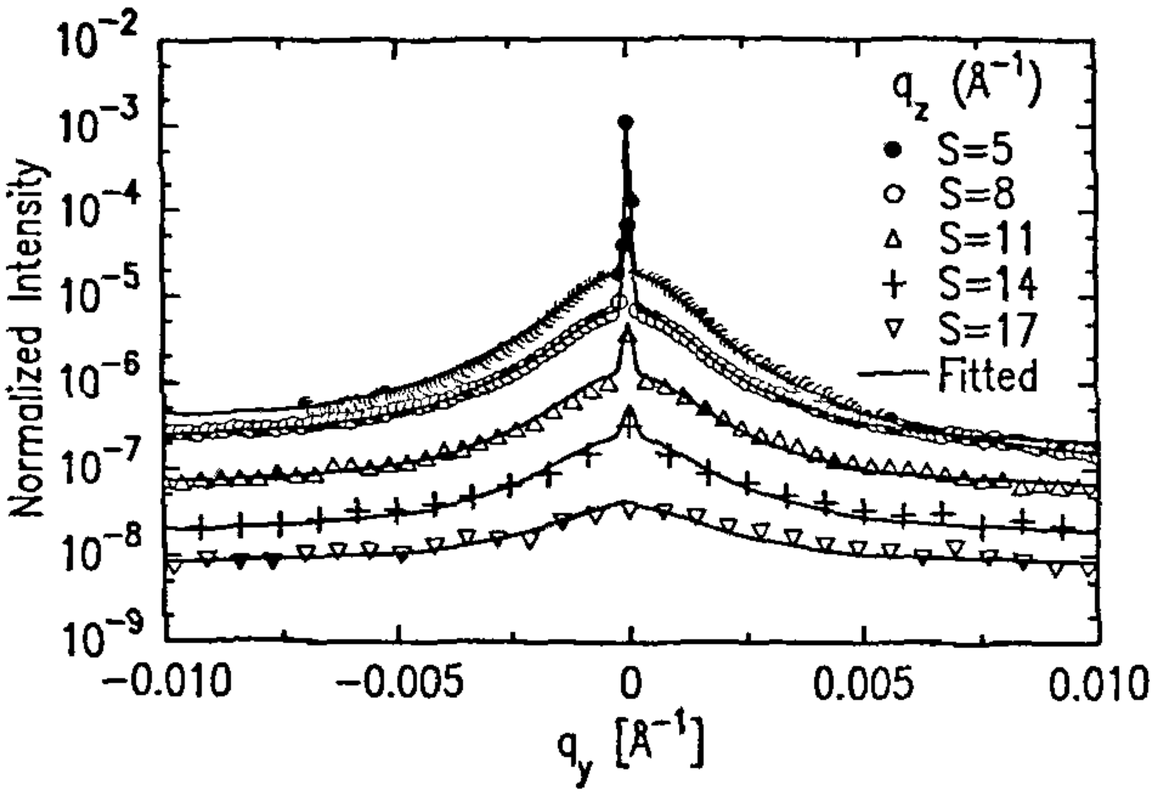

Figure 3. Measured and fitted transverse scans of some peaks (numbers indicated) of the same multilayer. The fitting was done using formalism indicated in equation (3) and lateral correlation and exponent were found to be 1200 Å and 0 64 respectively.

between a pure liquid and its vapour is characterized by a combination of an intrinsic profile which describes the molecular distribution of an otherwise flat interface and thermally-induced capillary fluctuations which roughen the interface. The interplay between these aspects of the interfacial profile has generated considerable theoretical interest, but experimental information has been meagre. It is believed that grazing incidence X-ray scattering will play a major role in this subject in near future. Although it is not clear that there is an unambiguous way to separate these two interfacial features

at liquid/vapour interface, thermally-induced roughening increases the average width of the interfacial profile. Currently, very little is known about the structure of more complex fluids such as microemulsions, surfactants, micellar systems, liquid crystals, langmuir films in the immediate vicinity of fluid/air or fluid/solid interface. It has been shown[13] that capillary wave fluctuations lead to a remarkable long-range algebraic decay of density correlations at liquid/vapour interfaces of simple liquids. This in turn produces power law tails in the grazing incidence X-ray diffuse scattering. Much more interesting results can be obtained if such studies are performed on complex fluids.

Ultra-thin organic films are simple and well defined chemical systems which involve the basic physical interactions existing in more complex structures, for example biological membranes. Moreover, ultra-thin ordered organic films with a thickness of a few nanometers to about a tenth of a micrometer show considerable technological potential as a novel class of materials. Langmuir–Blodgett (LB) technique for depositing thin organic films has recently been the subject of a renewed interest since it allows the construction of various systems, having both fundamental and technological interests. In the most common deposition mode (Y type) amphiphilic molecules (i.e. molecules with hydrophilic head and aliphatic tail) stack in tail-to-tail configuration. The orientation of the first layer strongly depends on the treatment of the substrate. Despite the potential, the applications of LB films have been slow to materialize due to lack of nondestructive characterization techniques and resultant feed back to the basic chemical process involved in their deposition. It is recognized now that X-ray reflectivity will play key roles in this area. From reflectivity measurements the spacing between adjacent layers in a multilayer LB film can be determined along with the density of the phases and the planarity of the layers, which sheds important light on the manner in which the films are formed[4].

Investigation of both free-standing[14] and deposited polymer films[10] using both X-ray techniques and SPM is an active area of research. The interface between two polymer phases is an area of much theoretical and technological importance. X-ray reflectivity experiments of deposited polymer films will provide us powerful means to determine the thickness of the equilibrium interface between two unlike polymers. Using diffuse scattering measurements we should be able to sort out the contributions of capillary-type fluctuations and of chain interpenetration at the interface. These results will also have important technological implications in the areas of polymer adhesion and composites.

In conclusion, we can state that local structural information in real space obtained from SPM techniques along with averaged information in reciprocal space over large surface area from grazing incidence X-ray measurements will provide us fascinating knowledge regarding the molecular interactions in surface/interfaces of condensed systems.

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