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X-ray characterization of thin films

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X-ray scattering techniques play inportant role in obtaining information on the structure and morphology of thin film materials. Clearly, the understanding of thin films` structural features, in relation to their properties, is the basic requirement for one to design and produce functional thin film. X-ray characterization techniques have several important advantages in comparison to the microscopy techniques (which provide complementary information, however): (i) they are non-destructive for the sample, (ii) measurements are averaged over all the thin film volume, (iii) the probing depth can be varied, (iv) experiments can be applied in any kind of environments ranging from ultra-high vacuum to gas atmospheres.

The family of X-ray diffraction techniques measures coherent Bragg peaks at wide angles, revealing atomic order and crystalline structure in the sample [1]. Structural ordering at larger scale (in the 10^0-10^2 nanometer range) yield X-ray scattering at small exit angles (<5°). Comparing to the conventional X-ray experiments on bulky material, when having sample in the form of thin film it is important to ensure small (or grazing) angle (<1°) between incoming X-ray beam and the sample surface. This will enhance the sensitivity of X-ray experiment to thin film volume. The scattered (or diffracted) intensity is measured behind the sample and can be, generally, classified in three categories, as is shown schematically in Fig.1.

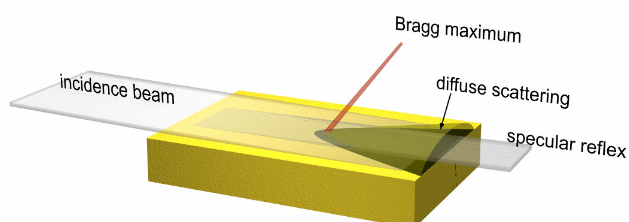

Figure 1. Schematic of grazing incidence X-ray experiments relating three categories of measured scattering.

The corresponding techniques are termed Grazing Incidence; GIXRD - for Diffraction, and GISAXS - for a derivation of conventional Small Angle X-ray Scattering technique [2]. Specially, by measuring only specularly reflected intensity as a function of incidence angle the technique is sensitive to the electron density profile along surface normal (laterally averaged). The technique is termed X-ray reflectivity (XRR). Here we will present, in more details a few examples of GISAXS and XRR measurements.

GISAXS

GISAXS is powerful method for characterization of particles in thin film matrix: their size distribution, average shapes and orientation, and spatial arrangement [3]. The technique is also convenient to determine parameters of roughness between layers. GISAXS measurement is carried out at a fixed and small incidence angle and the scattered intensity is measured using a 2D detector, Fig.2. This gives the possibility to measure anisotropy of the scattering which is extremely useful in getting information about the way nanoparticles are distributed in thin films and multilayers or on top of the substrate surface. The angle of incidence is directly related to the penetration depth in the sample. By varying this angle, it is possible to analyze either the top surface of the sample (nanoislands) if this angle is smaller than the critical angle of total reflection, or thicker portion of the film (buried nanoparticles) for angles greater than the critical. Since the specular plane is usually blocked by an attenuator to avoid the saturation of the detector, only diffuse scattering corresponding to small enough lateral correlation lengths, typically in the range 2–40 nm, can be recorded. This is controlled by setting sample to detector distance in the range 50-300 cm.

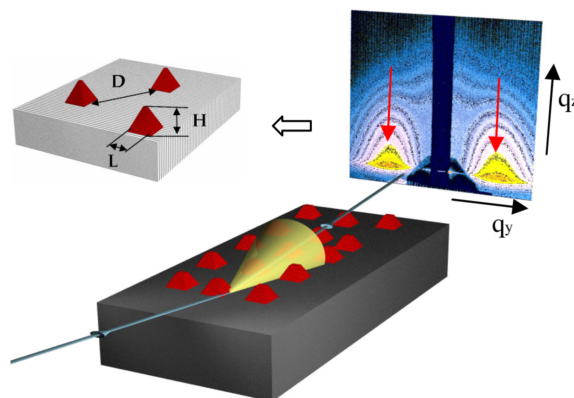

Figure 2. Schematic drawing of the experimental GISAXS set-up. The sample shown has an isolated nanoparticles grown on top of the substrate. The corresponding scattering exhibits side maxima (red arrows) indicating ordering of nanoparticles in the surface plane. Morphological parameters of nanoparticles like vertical (H) and lateral (L) sizes and their mean separation (D) can be deduced from GISAXS pattern.

The analysis of the 2D GISAXS pattern is qualitatively straightforward since one records an almost undistorted image of reciprocal space at low angle with the q_z direction perpendicular to the film surface and the q_y direction parallel to the film. When thin film contains heterogeneities which are spatially ordered at the nanometer scale, the pattern will exhibit Bragg maxima in scattered intensity typical of partially ordered or amorphous nanostructure. In Fig. 2, the q_y positions of side maxima (marked by red arrows) are inversely proportional to the mean separation of nanoislands D. However, since the coherent scattering term (due to correlation of nanoparticles` positions), is convoluted with the incoherent one (revealing form factor and size distribution of nanoparticles), one needs appropriate model [3] in order to separate these two contributions and get correct structural and morphological parameters of the thin film.

XRR

XRR spectra display only specularly reflected intensity (q_y=0) for the range of incidence angles α_i (usually from zero to couple degrees), see Fig. 3. Experimentally, XRR measurements are much less demanding than GISAXS since specular reflection is several orders of magnitude stronger than the weak diffuse scattering; the incoming beam need to be collimated only in one direction (perpendicular to the surface plane). Because the refractive index of matter is slightly less than one, the reflectivity is equal to 1 below a critical angle α_c (the beam is completely externally reflected), and next falls quickly as α^{-4} with increasing the scattering angle for a perfectly flat surface. Critical angle is linked with the electron density of the totally reflected material so, density of the surface layer can be determined from XRR profile.

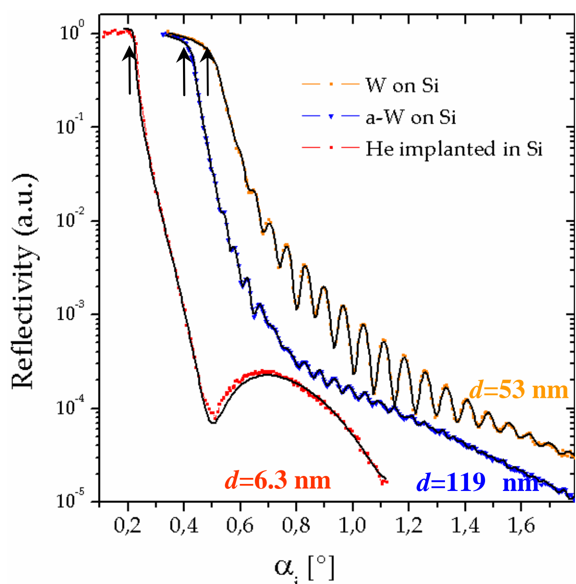

Figure 3. X-ray reflectivity data of the three thin films with different thicknesses. Solid lines passing through the data are the best fit curves which yield thickness (indicated on the figure), density and roughness of the film and the substrate. Black arrows indicate the position of α_C.

For a rough surface, the reflectivity falls faster than for a flat one. The oscillations in intensity over several orders of magnitude, visible on the reflectivity spectra shown on Fig. 3, are the result of constructive interference between the reflected waves at the interfaces air-film and film-substrate and their period gives the thickness of the film *d*. Moreover, XRR can yield the roughness or interdiffusion at the interfaces of the layers.

Besides for the single phase layers, some parameters can be obtained directly (and quickly) also from the refelctivity for periodic multilayer. The reflectivity curve of a periodic multilayer exhibits a typical shape in which one can find Bragg peaks separated by Kiessig fringes [4], see Fig. 4. The angular positions of Bragg peaks are related with the periodicity of the multilayer *P* via Bragg equation and the period of the Kiessig fringes gives the total thickness of the film *d*.

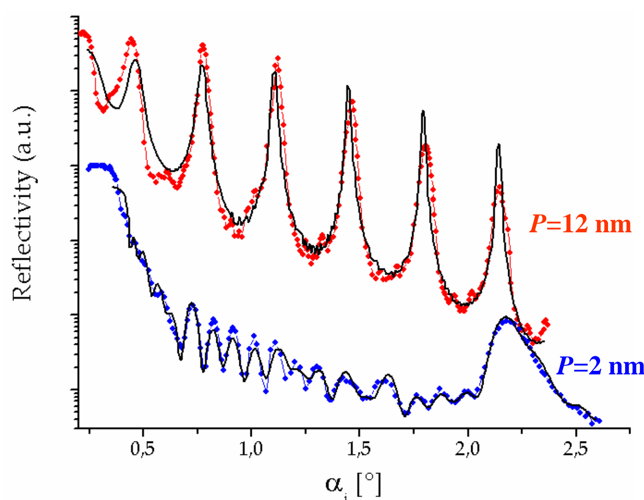

Figure 4. XRR data of the two W/C periodic multilayers with different thickness of C layers (thickness of W layers is 1 nm in both samples). Intensity of the reflectivity peaks depends on the quality of the periodic structure: roughness between layers and thickness variation of the W and C layers.

For other, more complex types of layered systems it is necessary to fit the model [5] to the data in order to extract structural parameters. Model curves, shown on Figs. 3 and 4, gives refinement of layers thicknesses and densities and will give us interface roughnesses. In principle, reflectivity measures density profile of the thin film along surface normal, and depends mainly on variations of composition regardless of the crystalline (or amorphous) features within the layers.

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