X-ray Reflectometry, Grazing Incidence Small Angle X-Ray Scattering, Small Angle Scattering.

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1. Introduction

Nowadays, because of the tremendous development of the use of nanostructures in microelectronicc or in magnetic storage media for examples, there is an increasing need of morphological characterization of deposited layers, multilayers and nanoobjects like quantum dots or supported islands. Among the available techniques, the use of X-ray scattering in the grazing incidence geometry presents several advantages over the microscopy techniques:

- an averaged statistical information over all the sample;
- the technique can be applied in any kind of environments ranging from ultra-high vacuum to gas atmospheres;
- kinetic studies can be undertaken as function of temperature, pressure, etc...;
- using the variable probed depth with the incidence angle, X-rays offer the opportunity to characterize buried particles or interfaces.

X-ray reflectometry (XRR), Grazing Incidence Small Angle X-Ray Scattering (GISAXS) and Small Angle Scattering (SAS) are not directly used to characterize the magnetism; they are rather devoted to investigating the morphology (sizes, shape, repartition, roughness, interdiffusion…) of the samples, which are often very intimately connected to their magnetic properties. The characteristic length-scale probed by these techniques varies from a few tenth of nm to micrometers.

During this course, emphasis will be put on XRR and GISAXS, since they are techniques of choice to characterize magnetic thin films and islands deposited on substrates. Many examples will be given, in particular by using these techniques *in situ*, during the growth of the nano-structure. The use of these techniques to characterize the magnetism by magnetic scattering will be briefly presented at the end. It uses the enhancement of the magnetic scattering cross section with respect to Thomson (electron) scattering near absorption edges.

2. Introduction to X-ray scattering

In a first approximation, and away from the adsorption edges of the elements, electromagnetic waves in the X-ray range (wavelength λ between 1 nm and 0.01 nm) are scattered by the electrons of the atoms. The scattered amplitude as a function of momentum transfer $\mathbf{q}=\mathbf{k_f}-\mathbf{k_i}$ ($\mathbf{k_f}$ and $\mathbf{k_i}$ exit and incident wavevectors) or of the scattering angle 2θ ($q=4\pi\sin(\theta)/\lambda$) is directly the Fourier transform of the electron density in real space. It has been known for more than one century that scattering by crystals yields very sharp peaks whose position and intensity allow determining the symmetry of the crystal and the content of the unit cell. For a typical wavelength of 0.1 nm, these peaks correspond to large scattering angles, which thus yield information on the atomic ordering at the atomic scale: this is the classical domain of X-ray diffraction.

When the matter is structured at a larger scale, typically in the nanometer range, the corresponding variations of the electron density yield X-ray scattering at small momentum transfer (or small scattering angles), which can thus be measured to probe the sample morphology. This is the domain of the techniques presented below.

However, in general, the X-ray beam is incoherent over the sampled volume, so that only the average intensity is measured: the knowledge of the phase (which would allow recovering the electron density by an inverse Fourier transform) is lacking. Hence, analysis of X-ray scattering is in general not unambiguous, and requires appropriate background, which is presented below.

3. X-Ray Reflectivity

An X-ray reflectivity measurement consists in measuring the intensity scattered perpendicular to the surface as a function the incident angle θ, and for an exit angle equal to the incident angle. Because the refractive index of matter n is slightly less than one: $n = 1 - \frac{\lambda^2}{2\pi} r_e \rho_{el}$ (where ρ_{el} is the electron density, of the order 10^{30} m^{-3}, and $r_e = e^2/(4\pi\varepsilon_0 mc^2) = 2.818\ 10^{-15}$ m is the classical electron radius) the reflectivity is equal to one below a critical angle θ_c (the beam is completely externally reflected), and next falls quickly as θ^{-4} with increasing the scattering angle (Fresnel reflectivity $R_F(\theta) = |r|^2 = \frac{\Delta n^2}{4\theta^4}$) for a perfectly flat surface.

We will show that X-ray reflectivity can be used to characterize:

-the roughness of a surface: for a rough surface, the reflectivity falls faster than for a flat one ($R(q) = R_F(q)\exp(-q^2\sigma^2)$);

-the thickness of a layer of material deposited on a surface. This yields the so called Kissieg fringes, whose period is inversely proportional to the layer thickness.

-the roughness or interdiffusion at the interface between the layer and the substrate, as well as the layer roughness;

-a stacking of several layers of different materials deposited on a substrate: thickness and roughness or interdiffusion.

4. Small Angle Scattering

Small angle X-ray Scattering does not specifically applies to surfaces, but rather to any material with in-homogeneities of the electron density at the nanometre scale. For isotropic systems, the corresponding scattering are classically used to estimate the average size of these in-homogeneities, as well as the differences in electron density they imply, their surface over volume ratio and their fractal dimension. More specifically, the intensity is the Fourier transform of the autocorrelation function of the electron density. This function expresses the correlation between densities measured at any two points separated by a given distance, average over the total irradiated volume. Two extreme limits might be considered: the Porods's limit allows deducing the surface area per unit volume $\Sigma=S/V$ as being proportional to the limite of $q^4I(q)$ when q tends to infinity. This laws is valid at all distance for which the interface is seen as sharp. If the $q^4I(q)$ does not tend to a constant at large q, the volumes of different electron density are likely to be fractal. Their fractal dimension D can be determined by looking at the large q limit ($I(q) \sim q^{-(6-D)}$). In case when the sample can be described as an assembly of particles surrounded by a homogeneous medium, and in case it is not too dense, *i.e.* particles can be viewed as sufficiently isolated from each other, a typical "Gyration" radius of the average particle can be deduced by looking in the so-called Guinier range, i.e. at the small-q limit, where the intensity can be approximated by: $I(q)=I_0\exp(-q^2R_g^2/3)$.

When the assembly of particles becomes denser, the scattering intensity reflects both the geometry of the particles and their spatial correlations. For identical, randomly oriented and centrosymmetric particles, the scattered intensity can be written as $I(q)=F(q)S(q)$, where $F(q)$ is the form factor of the particle and $S(q)$ the structure factor of the assembly. $F(q)$ is the Fourier transform of the average particle shape, while $P(q)$ is the Fourier transform of the particle-particle correlation function, and thus characterizes the particle ordering.

5. Grazing Incidence Small Angle X-Ray Scattering

The GISAXS technique is derived from classical small-angle scattering but applied to surface or interface problems. The principle of GISAXS is to send a monochromatic beam of X-rays with a low divergence on the sample surface under grazing incidence. This geometry ensures the surface sensitivity and the probed depth can be adjusted by varying the incidence angle. Any kind of roughness on the surface or any kind of electronic contrast variation in the subsurface region leads to beam scattering in an out-specular direction. In particular, this is the case for islands or dots on a substrate or for buried particles or aggregates. With respect to SAS, the main new features is that, when the incident beam is very grazing, it is totally reflected, and multiple scattering events have to be taken into account under the Distorted Wave Born Approximation. Some emphasis will be put on the quantitative analysis of the data. We will show how various kinds of simple geometric shapes can be considered with a full account of size and shape distributions in the Decoupling Approximation (DA) or in the Local Monodisperse Approximation (LMA). Both, disordered systems of particles defined by their particle-particle pair correlation function and bidimensional crystal or paracrystal will be considered.

Many examples of characterization of nanostructures by GISAXS will be given, with an emphasis on in situ measurements during growth.

6. Grazing Incidence Wide Angle X-Ray Scattering (GIXS)

GIXS, also called GIXD or GID (Grazing Incidence X-ray Diffraction) is a complementary technique that allows characterizing the structure at the atomic scale of the nano-structures: their lattice parameter, domain sizes, composition, epitaxial relashionships with the substrate, possible strain relaxation, coherent or incoherent (plastic), the interfacial structure and so on.
The technique is in principle similar to standard x-ray scattering (or diffraction), except that the incident beam is kept grazing with respect to the surface in order to minimize the unwanted scattering from the bulk. This technique allows exploring the whole reciprocal space of nanostructures, which will be emphasized. Several examples will be shown in diverse systems such as semi-conductor or magnetic quantum dots.

7. Magnetic resonant X-ray scattering

Very few examples will be given at the end of the emerging technique of Soft X-ray Magnetic Scattering (SOXMAS) that yield information which is complementary to magnetic force microscopy since it allows probing the sample magnetisation in depth.

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