Soft x-ray resonant magnetic reflectivity studies for in- and out-of-plane magnetization profile in ultra thin films

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Abstract. The possibility to investigate complex magnetic profiles throughout an ultrathin magnetic film or an interface by soft x-ray resonant magnetic reflectivity is presented. The determination of in- and out-of-plane magnetic profile is shown to be possible with a subnanometer resolution by measuring the reflectivity over a wide angular range. The technique is applied to a granular magnetic multilayer and to a perpendicular exchange bias coupled system.

1. Introduction

The investigation of magnetism in reduced dimension systems attracts a considerable interest. Motivated by the development of new materials in spintronics, a detailed understanding of the organization of magnetic moments at surfaces, interfaces and in heterostructures is mandatory. When magnetic properties in an embedded ultra thin film are changing at the unit cell level, most of the conventional or advanced methods [1] are limited either by the lack of in-depth spatial resolution or by surface limited sensitivity. In this paper, we examine the capability of the Soft X-ray Resonant Magnetic Reflectivity (SXRMR) in specular geometry over a wide angular range to probe the distribution of in- and out-of-plane magnetic profile components in an ultra thin film. In particular, only a few techniques allow one to probe the perpendicular magnetization distribution in thin films. In specific cases, nuclear resonant scattering can be sensitive to the out-of-plane magnetization distribution, and lateral resolution may be achieved with imaging techniques as, for example, spin polarized scanning tunneling microscopy or magnetic force microscopy but none provide in-depth spatial resolution with chemical selectivity.

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2. Soft X-ray resonant magnetic reflectivity

The x-ray resonant magnetic reflectivity exploits the magnetization sensitivity of the atomic scattering factor (ASF) at an absorption edge [2-4], which may be expressed on the basis of the two polarization states chosen either parallel or perpendicular to the scattering plane [5]:

\[ f = f_c \begin{pmatrix} 1 & 0 \\ 0 & \cos(2\theta) \end{pmatrix} - i f_m \begin{pmatrix} 0 & m_y \cos(\theta) + m_z \sin(\theta) \\ -m_y \cos(\theta) + m_z \sin(\theta) & m_x \sin(2\theta) \end{pmatrix} \]  

(1)

The first term of (1) is the Thomson and resonant charge scattering with \( f_c = f_0 + f'(E) + i f''(E) \) where \( E \) is the incident photon energy. The second term is the resonant magnetic scattering where \( f_m = m'(E) + i m''(E) \) [3]. The second terms in brackets shows the dependence on the scattering angle \( \theta \) of the transverse \( (m_y, m_z) \), longitudinal \( (m_x) \), polar \( (m_p) \) components of the magnetic moment. In order to analyze the x-ray reflectivity data, it is usually convenient to consider the change of the refractive index or of the dielectric tensor at an interface and the propagation through a continuous layer. These complex quantities are related to the x-ray atomic scattering factor for the forward scattering \( (q=0) \) [4].

X-ray resonant magnetic reflectivity has been mainly used in the hard x-ray range for investigating the magnetism of rare-earths [6], 5d transition metal [7] and 5f actinides [8] in superlattices. In order to probe the magnetism of 3d levels of transition metals, it is necessary to conduct experiments in the soft x-ray range (200 to 2000 eV) in the vicinity of their \( L_{2,3} \) edges \( (2p \rightarrow 3d \) transition). These transitions exhibit sharp and strong resonances [9]. They provide a high charge and magnetic contrast up to large incident scattering angles (up to 85 degree). We point out that such capability is essential to probe the \( m_e \) component.

The SXMR experiments have been conducted on the SIM beamline of the Swiss Light Source at the Paul Scherrer Institut using circularly polarized light and the RESOXS endstation [11]. In order to probe the in-plane magnetization, the measurements are performed in the longitudinal geometry using an electromagnet for sample magnetization. At each incidence angle \( \theta \) the reflectivity \( I(+) \) and \( I(-) \) are obtained by reversing an applied magnetic field \( (\mu_0 H \text{ up to } 0.2\text{T}) \) while keeping the x-ray helicity unchanged. In order to probe the out-of-plane magnetization, the measurements are performed in the polar geometry where the sample is magnetized by a permanent perpendicular magnet \( \mu_0 H=0.4\text{T} \) brought to the sample surface followed by data collection in remanence. In this case, \( I(+) \) and \( I(-) \) are obtained by reversing the x-ray helicity.

We turn next to the quantitative analysis of SXMR aiming at the determination of the magnetic profile along the growth axis. A crucial issue is the knowledge of the resonant terms in the atomic scattering factor. The charge \( f'(E) \) and magnetic \( m''(E) \) imaginary parts are obtained from x-ray absorption and XMCD spectra, respectively. Ideally, these parameters have to be obtained from the sample under investigation. Alternatively, they can be derived from a reference system provided the XMCD and SXMR measurements are collected with a similar energy resolution. \( f'(E) \) and \( m''(E) \) are calculated by using the Kramers-Kronig relation. Another important issue is the determination of the structural parameters. In the first step of the analysis, the geometrical film structure is derived by fitting the average signal \( [I(+) + I(-)]/2 \) measured at energies far and near the resonance. The magnetic profile is derived from the refinement of the magnetic asymmetry while keeping the structural parameters constant. The magnetic film is subdivided into slices and the magnetization vector of each slice can be described by an amplitude term and two angles to take into account arbitrary orientations. The magnetic amplitude of each slice is refined by varying a weighting factor \( w_m \) applied to \( m'(E) \) and \( m''(E) \). The magnetic moment amplitude is estimated from the value of \( w_m \) and from sum rules applied to the XMCD data [12]. The simulations are performed using a recursive calculation involving the reflection and transmission coefficients at each interface for magneto-optics [13].
3. Applications of soft x-ray resonant magnetic reflectivity

In this section, we discuss two specific applications of soft x-ray resonant magnetic reflectivity to the study of in- and out-of-plane magnetic profile.

3.1. FePt/C granular multilayer

Nano-particles are attracting considerable attention due to their potential in the field of ultrahigh density magnetic recording media [14]. To achieve high storage densities beyond 1 Tbit in², assemblies of ferromagnetic monodomain particles with uniform and small size below 10 nm are required. However, as the magnetic bit size is further reduced to the superparamagnetic limit, the magnetization of the particles is easily perturbed by thermal agitation. In order to overcome superparamagnetism, recent studies have been focused on CoPt and FePt nanoparticle arrays owing mainly to the existence of chemically ordered phases with large magnetocrystalline anisotropy constant above 10⁷ erg cm⁻³ [15]. Additional requirements for future magnetic recording media are that the nanoparticles have to be magnetically isolated but also chemically and mechanically stable. Therefore, much research has been done on granular thin films consisting of CoPt and FePt nanoparticles embedded in various nonmagnetic matrices [16]. Among the prospective materials, C/FePt granular thin films have attracted great interest because carbon not only impedes the growth of the nanoparticles, but also provides protection against outside degradations and reduces interparticle exchange interactions [17].

In this contribution, we describe the SXRMR technique applied to a C/FePt multilayer where the FePt granular layer is analyzed as a continuous film. The motivation is to probe the possibility of a core/shell magnetic structure. A change of the magnetization at the surface of the particles could be detected as a change along the z-axis at the interface between the FePt and C layers stronger than the modification at the core of the layer. The discussion is limited to the as-prepared sample. The investigation of the change under annealing will be published elsewhere [18].

The structural properties of the granular multilayer were characterized by several techniques [16, 17]. The x-ray reflectivity has been carried out far from Fe resonances (E=8051 eV and 740 eV) as well as at the Fe L₃ absorption edge (E=706.4 eV). The scans were recorded at room temperature with unpolarized light (8051 eV) and circularly polarized light (740 and 706.4 eV). Figure 1 displays the experimental intensities for two opposite directions of an applied magnetic field at 706.4 eV. The refinement of all the reflectivity data leads to the following structure C(57±5Å)/[FePt(12.8±0.2Å)/C(42.4±0.2Å)]₁₀/SiO₂(27±3Å)/Si(001) with a period Λ=55.2±0.1Å with and roughnesses σᵥ/C=4.5 Å, σᵥ/FePt=2.5 Å, σᵥ/C=2.9 Å (σᵥ/SiO₂ has been set to 2 Å and has no influence on the fit). The peaks in between the main Bragg peaks (BP) are not related to third
harmonic photons. They are observable in the soft and hard x-ray range. Although it is possible to reproduce nicely these peaks by considering a superstructure ($\Lambda' = 3\Lambda$) with three different thicknesses of the C layer ($\pm0.5\AA$), which is highly unlikely, they are ascribed to complex scattering process between particles, not taken into account in the analysis. In the refinement, all the FePt and C layers in the multilayer stack were assumed to be identical except for the very top C layer, which was found to be thicker. It turned out to be very important to reproduce the magnetic asymmetry in the 0-0.1 A\(^{-1}\) range (see hereafter in Fig. 3). The best agreements impose to reduce the effective density of the FePt layers which is a granular layer. Indeed, a layer with the composition (FePt)\(_x\)C\(_{1-x}\) should be taken into account. However, because of the strong contrast between the FePt and the carbon layers, there is a large uncertainty on the \(x\) parameter as determined from x-ray reflectometry. Also, using three slices to describe the FePt layers, it was not possible to evidence a change of the density along the growth axis inside the FePt layers and the concentration is found to be the same within 2\%. Finally, the analysis indicates an increase of the density of the C layer in agreement with the presence of isolated Fe and Pt atoms in the C layers [17].

The magnetic reflectivity scans \(I(+)\) and \(I(-)\) were collected by reversing a 0.2T applied magnetic field both with respect to the incident photon energies at different angular position and with respect to the x-ray incidence angle at 706.4 eV. The analysis of the reflectivity and of the difference across the Fe \(L_{2,3}\) edges, measured at 6 deg (Fig. 2), allows the determination of the averaged magnetization of Fe atoms inside the FePt layers [12]. The difference can be adjusted by reducing \(w_m\) to 0.73$\pm$0.03 which yield a magnetic moment of 1.58$\pm$0.06 $\mu$B.

**Figure 3.** Experimental asymmetry measured at 706.4 eV along with three different models. The difference are also displayed on a linear scale for 4\textsuperscript{th}, 5\textsuperscript{th} and 6\textsuperscript{th} BP.

The magnetic profile across the FePt layer is determined from the analysis of the angular dependence of the asymmetry $|I(+) - I(-)|/|I(+) + I(-)|$ or of the difference at the Bragg peaks (BP) position. We started from a uniform Fe magnetization profile inside the FePt layers (Fig. 3). The agreement between the experiment and the calculation is valid up to the 4\textsuperscript{th} BP and strongly deviates above. Then, the FePt layers have been divided in three identically thick sublayers. The green curve in Fig. 3 shows also that a symmetric reduction of the magnetization from the interfaces, while keeping the averaged value equal to 0.73, does not improve the agreement. In particular, it is difficult to reproduce the area where the asymmetry converges to zero. The best result is obtained with \(w_m\) values
from the bottom to the top equal to 0.8/0.82/0.6. It indicates that the profile is mostly constant inside the FePt layers except close to the top surfaces with a 25% reduction of the magnetization.

We point out that XRMR is indeed sensitive to the product concentration time magnetization [6]. Therefore, our result may indicate alternatively that the Fe concentration varies at the top of the layer either due to inhomogeneity or to the shape of the particles (reduction of the diameter during growth). However, this concentration change was not evidenced using x-ray reflectivity refinement. Hence, the change in magnetization is tentatively ascribed to a variation of the disorder inside the particle from the bottom to the top, not detectable by hard x-ray diffraction [17] or by x-ray reflectivity. We encounter here a limitation inherent to the approach, showing that the details of the structure must be known in order to draw firm conclusions about the structure of the magnetization. However, SXMRM turned out to be the only technique to detect such a small change on a subnanometer scale.

3.2. Out-of-plane exchange bias system

The depth dependence of the out-of-plane magnetization across the AF/FM interface of the ultra-thin [NiO(3ML)/CoO(3ML)]3/PtCo/Pt(111) bilayer with perpendicular exchange bias has been investigated by SXMRM [19]. The measurements were carried out in remanence at $T = 340$ K, right above $T_B$ and below $T_N$, where the FM layer (1 ML of Co below 1ML of Pt) has a strong perpendicular magnetic anisotropy (PMA) and where the interfacial magnetic coupling with the AF layer constrains the reversal process, as indicated by the increased $H_C$.

Angle dependent reflected intensities were collected at 776.9 and 778.5 eV (Fig. 4) close to the Co $L_3$ edge. At both energies, a separation of the curves with right and left polarized light is observed. The magnetic asymmetries are close to zero at small angles and exhibit larger amplitude at high angles (Fig. 5), as expected for an out-of-plane magnetization component. The interference in the angle dependence of $R$ indicates the Co magnetization extends beyond the ultra thin FM Pt-Co layer inside the oxide layer. A further indication of the net magnetization in the AF oxide layers came from measurements at the Ni $L_3$ edge, which showed a small net magnetic moment on Ni atoms, either due to an extended polarization through the first 3 ML CoO layer or by contact with the PtCo interface due to discontinuity of this layer. Both situations indicate that the Co atoms in the oxide layer, at least close to the interface, are magnetically polarized.

The structural parameters of the film were derived from the refinement of the average reflectivity [19] and found in good agreement with other structural data from SXRD and AFM [20]. The magnetic profile comes from the analysis of the $R$ at both energies. A model assuming that Co atoms in the oxide may be magnetically ordered up to the first CoO/NiO interface works well. The refinement of the magnetic structure was performed by dividing the first CoO layer in three slices and by adjusting their thicknesses as well as the magnetic moments carried by the Co atoms. The results indicate the
out-of-plane magnetization is distributed beyond the 3.6 Å Pt-Co layer and extends over 10 Å in the oxide layer. The coupling to the FM Co spins is parallel in a 3Å thick slice, roughly the first CoO monolayer. Then, it is antiparallel in a 7 Å thick one, with similar amplitude. The last slice that completes the CoO layer is found to be 2 Å thick and has no net magnetization. Considering models with no net magnetization in the oxide layer, completely parallel or antiparallel magnetic slices and more extended magnetization with reduced magnetic amplitude do not fit the interference effect observed experimentally.

This result can be understood as follows: the Co atoms in the first CoO slice, right on top of the Pt-Co layer, have a mixed electronic character in between metallic and oxidized state. Their net induced magnetizations are likely to be dominated by the proximity of the Pt-Co layer and are ferromagnetically coupled to it. For the next CoO slice, the Co atoms are fully oxidized and the net magnetization is antiferromagnetically coupled to the first one. The net magnetization found equal to zero in the third slice means that beyond the second oxide layer the AF material break into domains that are not biased by the field cooling processes.

4. Conclusion
It is well established that combining spectroscopy and scattering brings magnetic spatial selectivity. SXRMR has been measured from ultrathin films over the maximum accessible angular range (or $q$ range) with high signal to noise ratio. In depth in- and out-of-plane magnetic profiles have been obtained with sub-nanometer resolution. The sensitivity to magnetic configurations with an antiparallel component has been shown. Because of its sensitivity to the magnetization distribution, SXRMR is a technique of choice either to determine the magnetic profile inside thin films or to distinguish between different proposed magnetic models. This approach can be used to probe the extension of interfacial magnetic properties, in a “non-magnetic” or spacer layer, on each side of two layers with different magnetic phase. It should be also very useful to probe magnetic layers exhibiting both in- and out-of-plane magnetic components like systems exhibiting spin reorientation transition.

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