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Determination of Thickness and Density of Ultra Thin Iron Films by Grazing Angle Incidence X-ray Fluorescence

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An efficient and accurate method to characterize the physical thickness of ultra thin iron films is presented. Fe thin films were grown directly on n-Si(111) substrates by unbalanced magnetron system. X-ray fluorescence system was applied to measure coating thickness and perform material analysis. The composition and density of the films were characterized by measuring critical angle of reflection using X-ray fluorescence. It is shown that XRF analysis allows determination of thickness of samples potentially important for future technological interest.
Keywords: ultra thin films, iron, X-ray fluorescence, critical angle.

INTRODUCTION

In recent years there has been growing interest in the application of grazing incidence X-ray technique for the study of the structure and morphology of buried layers and interfaces in thin films. Grazing incidence X-ray diffraction (XRD) is a valuable analytical tool for the characterization of thin epitaxial films. X-ray reflectivity has been demonstrated to be very powerful technique in studying the structure of the buried interface and surface morphology [1]. Properties of ultra-thin films deviate from those of the corresponding bulk material already because of the mere reduction of dimensionality and, related to that, the reduction of symmetry. This applies to all types of collective phenomena as geometrical structure, electronic properties and magnetism [2, 3]. Also, the alternating combination of different films material stacked perpendicular to the surface can lead to completely new physical phenomena as the giant magnetoresistance (GMR), i. e. the enhanced sensitivity of the electrical resistivity to external magnetic fields.

An absolute and highly accurate method for thickness determination is X-ray reflectrometry (XRR). In this technique the reflectance of the sample is measured as a function of grazing incidence angle of X-rays. Due to interference effects of radiation reflected from the layer surface and radiation reflected from the layer/substrate interface, oscillations occur on the reflectance curve, which can be fitted by recursive application of Fresnel equations [3, 4]. While the oscillation amplitude at fixed photon energy depends on the density and roughness, the oscillation period is mainly determined by the layer thickness [5 – 7]. As the angle is increased beyond critical angle (Θ_C) the reflectivity drops dramatically and it is virtually equal to zero for $\Theta > 3\Theta_C$. The rate of decrease is determined by the microroughness of the sample, being proportional to Θ^{-4} for a perfectly smooth sample and decreasing even faster for a rougher sample. The much brighter synchrotron radiation provides an improvement of at least 2 orders of magnitude in the minimum detection limit. It is well known that the angular dependence of reflected intensity of X-rays from thin films shows the oscillation known as the Kiessig fringes, which provide information on the layers. The oscillation intervals ($\Theta \cdot 2q$), which come from the interference of X-rays at a thin film, can be approximated as [1]:

$$\Theta \cdot 2q = \lambda / t, \quad (1)$$

where λ is the X-ray wavelength, t is a layer thickness, and Θ is the glancing angle of an X-ray.

According to the equation, the interference interval increases with the decrease of layer thickness. This relation indicates that the measurement of wide area of Θ is required to evaluate precisely a thin film. Since the intensity of reflected X-ray quickly decreases as $1/\Theta^4$, a high-flux X-ray is required to obtain data at high α angles.

In the customary X-ray fluorescence analysis, incident X-rays illuminate the sample at a high angle, enhancing a highly scattered X-ray background, so that there is no sensitivity to the excited X-ray fluorescence analysis. Incident X-rays illuminate the sample at a high angle, enhancing a highly scattered X-ray background, so that there is no sensitivity to the excited X-ray fluorescence coming from the elements just below the sample surface. A model for calculation of the X-ray fluorescence from the bulk materials and thin films at grazing incidence was reported in [6]. The dependence of the penetration depth on the incident angle was shown. The intensity of grazing incidence X-ray fluorescence (GIXRF) signal depended on the concentration of atom *a* in the layer, the photoabsorption coefficient, absorption jump, fluorescence yield and emission rate. For thin films GIXRF intensity depended also on the irradiated volume, i. e. on the X-ray beam incidence angle Θ for layer.

In this paper we present developed grazing incidence X-ray fluorescence (GIXRF) technique based on an angle dispersive (αD) fluorescence equipment with low-brilliance radiation X-rays at DRON-3M. The technique has been successfully applied to the evaluation of the stratified structure of giant magnetoresistance (GMR) ferromagnetic layers. Because of the good energy resolution and high-count rate of the detector, high quality data in dependence of fluorescence intensities on the angle of incidence for the composition elements were obtained.

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2. EXPERIMENTAL TECHNIQUES

Deposition experiments were carried out in a vacuum chamber with a base pressure of 2×10^{-5} Pa equipped with a DC facing magnetron system [8 – 10]. Fe films were deposited on Si (111) substrate at pressure 10^{-2} Pa. The voltage and discharge current were measured with the digital multimeters. The deposition rate was monitored by a quartz crystal monitor [8]. In order to evaluate a considerable porosity of sputtered Fe, thickness was determined by both GIXRF a an by XRR. We also applied scanning electron microscopy (SEM) for observations of surface morphology and crystalline structure of the Fe/Si(111) thin films.

Sputtered iron layers were deposited by varying layer thickness systematically. The processing of results was facilitated by a personal computer (PC). The equipment and PC were accommodated by a special electronic scheme [9].

Grazing incidence (with an incidence angle typically less than 10 degrees) limits the penetration depth, so the significant part of beam interacting with material originate from the uppermost part of the sample. The thin films have to be randomly oriented, as oriented thin film might have no reflections from the grazing incidence. To achieve right measurement conditions, the line source and X-ray mirror used there allowed to make the beam uniform.

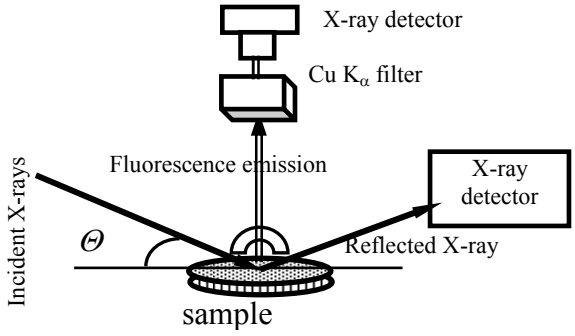

Fig. 1. Schematic drawing of grazing incident X-ray fluorescence configuration. Fluorescence emission from the sample is detected by the wavelength disperssive spectrometer

The X-ray fluorescence equipment (Fig. 1) was constructed employing an universal diffractometer DRON-3M radiation wavelength mode. For fast analysis and high reliability, we installed the energy-dispersive detector. We used a monochromatic Cu K_α line at Fe fluorescence excitation source for the XRF measurements. The wavelength of Cu K_α is at the absorption edge of iron (producing intense fluorescence flux) and contributes to the improvement of minimum detection limit, so that it enables measurements of very thin films. Figure 2 shows the attenuation length characteristics for the used Fe filter.

X-ray fluorescence calibration data is displayed in this plot of the measured X-ray intensity as a function of thickness. We also incorporated a four-axis sample stage applied in the monocrystal analysis used in the goniometer GUR-8. The parallel-optics equipment consists of a combination of Soller slits and planar crystal monochromator in addition to either an NaI scintillation counter or flow-type proportional counter.

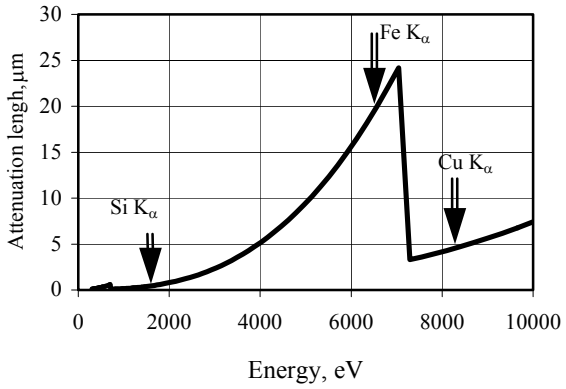

Fig. 2. X-ray attenuation length vs. X-ray energy plot [9]

The used Fe filter increases Si K_α fluorescence intensity ratio by 10 times to diffusion scattering intensity of the incident beam.

3. EXPERIMENTAL RESULTS

3.1. X-ray Fluorescence measurements

The experimental X-ray reflectivity curves recorded at the different films thickness and for the uncovered Si (111) substrate are plotted in Fig. 3. The intensity of the reflected beam by the Fe bulk plate substrate shows a classical evolution of the reflected intensity versus the incidence angle. The X-ray fluorescence intensity increases as the exit angle increases just as in the case of the bulk materials. For the films thickness less than attenuation length, the X-ray fluorescence intensity is proportional to the thickness given by the fine beam spot. In the analysed Fe film thickness ranges from 5 nm to 900 nm, the K_α Fe GIXRF intensity varies linearly with the Fe film thickness measured using XRR [3].

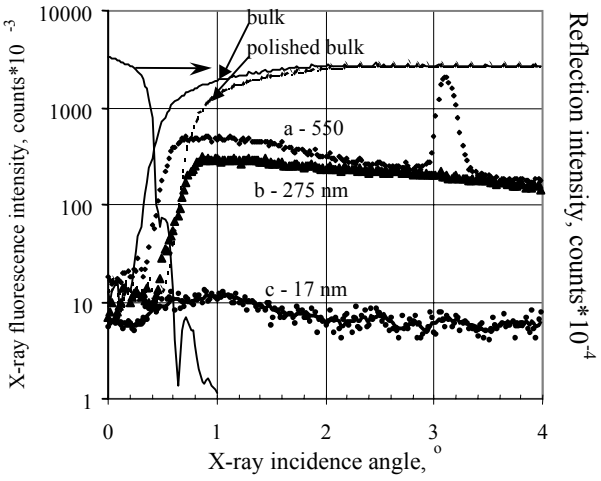

Fig. 3. Dependence of the Fe K_α GIXRF intensity for various Fe coatings thickness on the grazing angle: a – thickness 550 nm, b – 275 nm, c – 17 nm and "bulk" presents the iron plate

According to the experimental results [9, 10], the critical angle of the Fe samples is 0.386 degrees. According to our results the measured critical angle ($\Theta_C = 0.3° – 0.45°$) corresponds to the total reflection, and it is in good

agreement with the theoretical value (theoretical is $\Theta_C = 0.386°$). Acording to XRR results the roughness is about 0.6 nm. X-ray fluorescence measurements and XRR data of Fe films (thickness 17 nm) are shown in Fig. 4. The measured X-ray intensity as a function of glancing angle is displayed in a logarithmic scale. The reflection curve of the Fe layer exhibits a critical angle about 0.32°. Kiessig fringes are at 0.54° and 0.74° angular positions. The thickness of films is calculated from the positions of Kiesing fringes. This fact is used as a calibration standard, because of XRR measurements provide absolute values [3].

Figure 4 displays the fluorescence calibration data. The measured X-ray intensity as a function of Fe films thickness is shown in this plot.

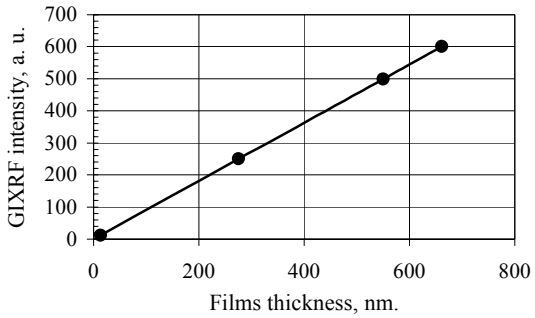

Fig. 4. The calibration plot of X-ray intensity of Fe films versus thickness

Grazing incidence X-ray fluorescence was employed for the phase analysis of thin films as well. The GIXRF experiment was carried out at varied incidence angle of 0°÷6°, with the step of 0.04°, and the scan speed was 1/60 °/s.

The electronic density of the Si substrate is smaller than the one of the Fe layer, so in this angular domain, the refracted X-ray beam propagated into the substrate in total reflection on the coating surface [3]. The results of Fe film thickness measurement by weight, XRR and scanning GIXRF stay within the accuracy of these methods.

3.2. Density measurements

The critical angle for X-ray total reflection and film density has a simple relationship shown in equation (2) [13]. The critical angle is proportional to the wavelength of the radiation λ and to the square root of the surface density ρ:

$$\Theta_C = \lambda\sqrt{\rho}\ . \qquad (2)$$

The Θ_C is typically between 0.25° and 0.75°. The reflectivity drops dramatically as the angle is increased beyond Θ_C and is virtually 0 for $\Theta > 3\Theta_C$. The rate of decrease is determined by the microroughness of the sample, being proportional to Θ^{-4} for a perfectly smooth sample and decreasing even faster for a rougher sample.

Very smooth surface is a necessary for XRR measurements. For the GIXRF measurements maximum intensity films are insensible to the surface roughness. Contrary, determinations of the Θ_C like in XRR method is very sensitive to roughness. Two measurement curves are shown for the bulk samples Fe (density 7870 kg/m^3). In Fig. 3 the polished surface sample has $\Theta_C = 0.39$ degrees and rough surface of the bulk Fe sample has a critical angle of 0.25 degrees. According to the density measurements one can conclude that the analysed sample have of very smooth surface.

CONCLUSIONS

It was shown that the developed X-ray fluorescence method can be applied for both ideally smooth as well as rough thin Fe films. In the case of Fe films this method can be applied for the range of the film thicknesses from 10 nm to 700 nm. Like in the case of X-ray reflectometry, the method enables measuring the film density with the accuracy influenced by the surface roughness.

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