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Characterization of subnanometric layers by grazing incidence X-ray reflectometry

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ABSTRACT

We present a method to characterize subnanometric layers based on grazing incidence X-ray reflectometry. For this purpose, we propose to use a "Fabry–Pérot" type multilayer structure in order to improve the sensitivity of the measurement to the layer thickness. For our study, this structure consists of a thin layer of scandium inserted between two periodic chromium (Cr)/scandium (Sc) multilayers. We describe the principle and estimate the sensitivity of the method by simulation. Experiments were performed on two optimized Fabry–Pérot structures with 0.6 and 1.2 nm Sc layer thicknesses using a laboratory grazing incidence reflectometer at 8.048 keV (Cu Kα radiation). Fitting of experimental data allows determining the Sc layer thickness. Finally, the structural parameters used in the fit were confirmed by measurements at 3 keV on the hard X-ray branch of the synchrotron SOLEIL Metrology and Tests beamline.

1. Introduction

Nanometric thin films and multilayers are used in a variety of technological and scientific areas including optical coating, magnetic recording, microelectronic and photovoltaic industry. Multilayer interferential mirrors (MLMs) are actually key components for several applications in the X-ray and Extreme Ultra-Violet (EUV) spectral ranges: EUV photolithography, solar corona imaging, plasma diagnostic, etc. Obviously, a precise characterization of layer thicknesses is required in order to achieve good performances. In many cases, the thinnest controllable layer represents a limiting factor. Normal incidence multilayer mirrors have a limit towards short wavelengths in the water window domain (wavelengths between 2.2 nm and 4.4 nm), when the thickness of each layer becomes less than 1 nm [1,2]. In the EUV domain, barrier layers with subnanometric thicknesses are frequently used to limit interdiffusion and/or smooth the interfaces [3–6]. Subnanometric layers are also required to design EUV normal incidence broadband coatings [7,8], chirped mirrors for attosecond pulses [9–13] or grazing incidence mirrors for X-ray diagnostics [14–17] or hard X-ray telescopes [18,19].

Grazing incidence X-ray reflectometry (GIXR) proved to be a relevant technique to determine nanometric layer thicknesses in a periodic coating [20,21]. However, the precision obtained from periodic structures is a limit to subnanometric characterization. Usually, one needs to extrapolate the calibration laws (for example, deposited thickness versus deposition time) towards very small thicknesses. Moreover, this extrapolation requires hypothesis on the initial growth stage and interface formation. Thus, to overcome these limitations, we propose to use a specific multilayer structure in which the subnanometric layer to calibrate is inserted between two similar periodic multilayers. Such structure can be seen as a "Fabry–Pérot" (FP) type multilayer, similar to FP etalon that has been extensively studied in the past [22,23]. However, in our case the layer in between both periodic multilayers is much thinner than the multilayer period while in FP etalon, this layer is thicker than the period. The method proposed in this paper allows a direct access to the subnanometric layer thickness and will lead to a better understanding of the physical phenomena occurring at interfaces and thus an improvement of MLM fabrication and performances for the related applications. For the present study, we used a scandium layer between two chromium (Cr)/scandium (Sc) periodic multilayers. This example is particularly interesting for the development of an X-ray broadband diagnostic [17] in which the high reflectivity in the 2–4 keV energy range is achieved by the use of a Cr/Sc aperiodic MLMs (90 non-periodic Cr/Sc layers, with thicknesses ranging from 0.6 to 10 nm). A precise control of each layer thickness in such coating is essential to achieve the required performances. In the first part, we will estimate from simulations the sensitivity of calibration expected from FP structures and compare it to the classical calibration method using periodic multilayers. In the second part, we will present the experimental results obtained using FP stacks to calibrate thin Sc layers.

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2. Principle

2.1. Thickness characterization with periodic multilayers

The simplest way to calibrate the Sc film thickness in multilayer environment is to deposit a periodic multilayer with the desired thickness of Sc and to analyze this multilayer with X-ray reflectometry (XRR) under grazing incidence. It is well known that the multilayer period d (i.e., the bilayer thickness) can be deduced with a good precision from the Bragg peak positions. However, in order to obtain a precise value of each layer thickness, one needs to measure a sufficient number of Bragg orders with significant intensity modulations (the ideal case being to achieve complete extinction). Unfortunately, in the case of subnanometric layers, this approach encounters practical issues that limit the precision in the determination of the layer thicknesses. On one hand, in order to obtain significant Bragg peak modulations, one has to choose a similar thickness for both materials (Cr and Sc in our case). In this case, the period thickness becomes very small (typically less than 2 nm) and the number of measurable Bragg peaks is very limited (due to the finite dynamic of GIXR detection, typically less than 10^{-7}). On the other hand, in order to obtain several Bragg peaks on GIXR measurements, one has to choose the Cr thickness significantly larger than the Sc thickness. In this case, the modulation of Bragg peak intensities will be very limited. Consequently, a compromise has to be found between the number of measurable Bragg peaks and the modulation of Bragg peak intensities. This is illustrated by the following example. We chose to compare the theoretical reflectivity at photon energy $E = 8.048$ keV versus grazing incidence angle of three Sc/Cr multilayers with different Sc thicknesses (d_{Sc}) in the subnanometric range: 0.5 nm, 0.7 nm and 0.9 nm. The three multilayers consist of 20 periods on a silica substrate. The Cr thickness (d_{Cr}) is fixed so that the multilayer period d ($=d_{Cr} + d_{Sc}$) is kept constant at 5 nm: $d_{Cr} = 4.5$ nm, 4.3 nm and 4.1 nm respectively for $d_{Sc} = 0.5$ nm, 0.7 nm and 0.9 nm. The roughness is fixed at 0.35 nm at all interfaces and at the surface. The results of numerical simulations using IMD software [24] are presented in Fig. 1a. The three spectra look very similar. The positions of Bragg peaks do not vary and the modulation of their intensities is very slight. The only differences appear in the Kiessig fringe modulation between Bragg peaks but those are not usable due to instrumental noise. In Fig. 1b, we plot the evolution of the 2nd order Bragg peak intensity as a function of the Sc thickness. One can think of using the Bragg peak intensity to determine the Sc thickness. However, the absolute intensity is obtained after normalization of the spectrum, which induces uncertainties on this value. Moreover, the Bragg peak intensity depends on other parameters, such as the interfacial roughness. We plot in Fig. 1c the 2nd order Bragg peak intensity according to the roughness at Sc-on-Cr interfaces in the case $d_{Sc} = 0.5$ nm. As plotted in this figure, a ± 0.1 nm uncertainty on the roughness value corresponds to a variation of the 2nd Bragg peak intensity from 5.5×10^{-3} to 8.2×10^{-3}. By reporting these values in Fig. 1b, we deduced an uncertainty on the Sc thickness of about ± 0.06 nm. Although, this result depends on the Sc thickness under study and the Bragg order used for calculation, we chose for demonstration purposes the most favorable case (2nd Bragg order reflectivity with $d_{Sc} = 0.5$ nm) for analysis of the periodic Sc/Cr multilayer.

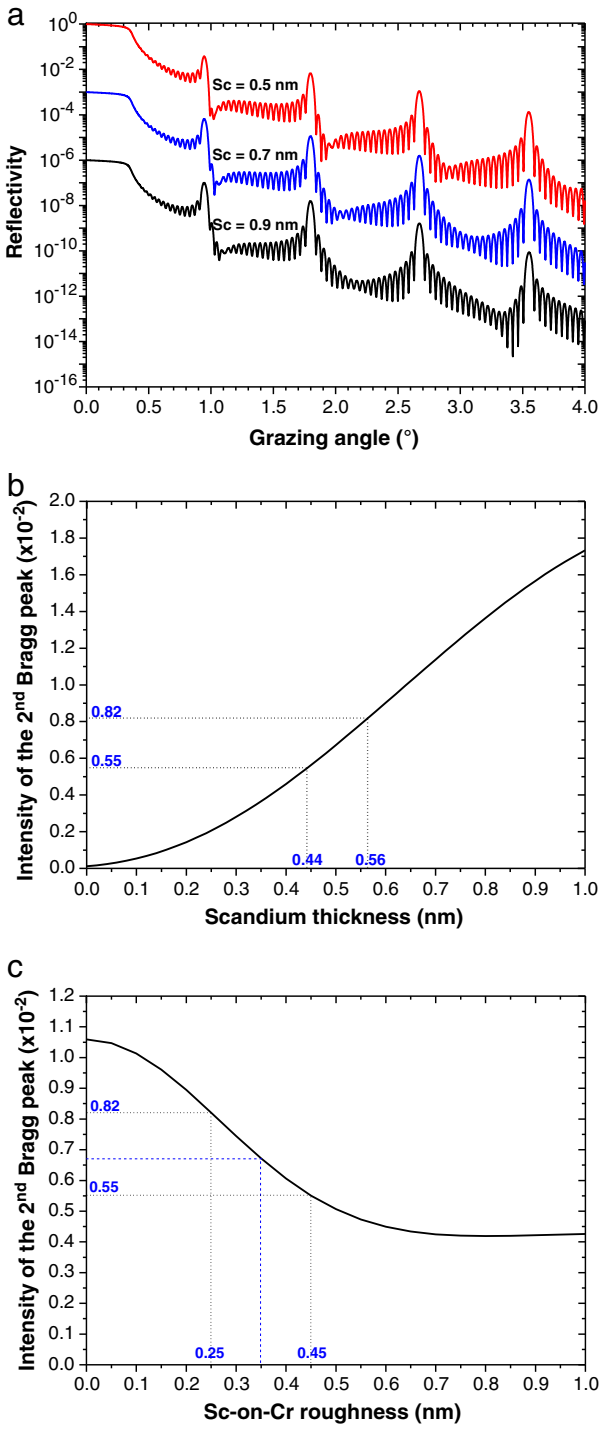

Fig. 1. Results of numerical simulations at energy $E = 8.048$ keV: (a) Periodic multilayer reflectivity versus grazing incidence angle for 20 Sc/Cr periods. In red: $d_{Sc} = 0.5$ nm; in blue: $d_{Sc} = 0.7$ nm; in black: $d_{Sc} = 0.9$ nm. For clarity, each curve is offset by a factor of 1000 from the previous curve. (b) Intensity of the 2nd order Bragg peak versus Sc thickness with the roughness fixed at 0.35 nm. (c) Intensity of the 2nd order Bragg peak versus the roughness at Sc-on-Cr interfaces in the case $d_{Sc} = 0.5$ nm.

2.2. Thickness characterization with "Fabry–Pérot" stack

In order to be less sensitive to parameter uncertainties and to the error on absolute intensity measurements, we propose to use the multilayer structure shown in Fig. 2. This structure, that we will call "Fabry–Pérot" (FP) stack, consists of a superposition of two periodic multilayers, ML1 and ML2, with the layer to calibrate (LC) in between. The number of periods in ML1 (resp. ML2) is N1 (resp.N2). In ML1 and ML2, the thicknesses of Cr and Sc layers (d_{Cr} and d_{Sc}, respectively) are chosen identically. If the scandium LC thickness d_{LC} is equal to d_{Sc} of the multilayers, we will obtain Bragg peaks corresponding to a periodic multilayer stack. When d_{LC} is zero, the wave reflected from both multilayers ML1 and ML2 will have opposite phase leading to extinction in the center of the Bragg peaks. This extinction is very sensitive to small variation of d_{LC} because its value determines the phase of the wave reflected from ML2 with respect to ML1. As an example, we compare