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A simple solution to systematic errors in density determination by X-ray reflectivity: The XRR-density evaluation (XRR-DE) method

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Abstract

X-ray reflectivity (XRR) is a non-destructive, accurate and fast technique for evaluating film density. Indeed, sample-goniometer alignment is a critical experimental factor and the overriding error source in XRR density determination. With commercial single-wavelength X-ray reflectometers, alignment is difficult to control and strongly depends on the operator. In the present work, the contribution of misalignment on density evaluation error is discussed, and a novel procedure (named XRR-density evaluation or XRR-DE method) to minimize the problem will be presented. The method allows to overcome the alignment step through the extrapolation of the correct density value from appropriate non-specular XRR data sets. This procedure is operator independent and suitable for commercial single-wavelength X-ray reflectometers. To test the XRR-DE method, single crystals of TiO_2 and $SrTiO_3$ were used. In both cases the determined densities differed from the nominal ones less than 5.5%. Thus, the XRR-DE method can be successfully applied to evaluate the density of thin films for which only optical reflectivity is today used. The advantage is that this method can be considered thickness independent.

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1. Introduction

Surface and structure analysis are fundamental for understanding thin films properties and assess future technological applications. In particular, density is a property critical for both mechanical and functional performances of the films but still challenging to investigate. Density is often indirectly determined by making separate measurements of thickness and mass per unit area. Mass per unit area can be determined by Rutherford backscattering or forward-recoil spectrometry, X-ray fluorescence, and neutron activation analysis. Methods for thickness evaluation include medium-energy ion scattering spectrometry, neutron reflectometry and ellipsometry [1]. The common direct techniques for density determination are (single-wavelength) X-ray reflectivity (XRR), which is considered most accurate and fast [2], and neutron interferometry [3].

To date, XRR is a non-destructive technique widely employed to study surfaces and interfaces of crystalline as well as amorphous thin layers at atomic resolution [4–7]. In this paper, we will focus on XRR density evaluation measurements, discussing the possibility to obtain reliable values by a dedicated procedure.

In a typical XRR experiment, sample-goniometer misalignment, which reflects in scanning the sample in non-specular (also referred as off-specular) condition, is the most significant limiting factor in accurately determining the density [8]. The (systematic) error is due to the fact that non-specular data are treated as specular. A smart solution to this problem is to employ an energy-dispersive detector and to exploit the whole energy spectrum of the X-ray source for extrapolating with a proper analysis method the true density (at infinite wavelength) [8]. The flip side to this is that an energy-dispersive detector is a non-standard, expensive equipment and may not be available for entry-level commercial reflectometers.

In the present paper the incidence of misalignment on the error related to the evaluated density will be addressed. Then, a method that allows to overcome misalignment difficulties and

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is suitable for conventional single-wavelength reflectometers will be presented and discussed. Hereafter, it will be referred as the XRR-density evaluation (XRR-DE) method.

2. Effects of misalignment on density evaluation

In the X-ray energy region, the refractive index of a solid medium is lower than the refractive index of the air. Thus, at proper incidence angles, an X-ray beam travelling in the air is totally externally reflected by the medium.

A typical XRR radial scan is performed in specular condition (Fig. 2a and Ref. [9]) and the XRR curve is obtained by plotting the scattered X-ray intensity against the angle of incidence, θ (see for example the top curve reported in Fig. 3). Due to total external reflection, at low incidence angles the scattered intensity is in first approximation constant and determines a plateau. The plateau ends with a shoulder due to the fact that the X-ray beam is no longer totally reflected off the medium surface.

The incidence angle beyond which total reflection is cut off is referred as the critical angle of total external reflection, θ_c. In the X-ray region, θ_c is generally in the range of tenths of degree [7] and is directly related to the mass density, ρ, by the following equation [10]:

$$\frac{\theta_c^2}{\rho} = \frac{r_e \lambda^2 Z N_A}{\pi A} = B, \qquad (1)$$

where r_e is the classical electron radius (2.82×10^{-15} m), λ the X-ray wavelength, Z the atomic number, N_A the Avogadro's number, and A the mass number. Thus, B is constant for a given material and irradiating beam. θ_c is the experimental parameter used for determining ρ by XRR. ρ is directly calculated from Eq. (1) after that θ_c has been evaluated from the XRR curve. This step is not straightforward, but in most cases, θ_c can be reliably matched to the angle at which the intensity is half of the plateau value [9]. This will also be the evaluation way adopted in this work.

Below, we derive the relation that allows to estimate the error induced in the evaluated density by an incorrect measurement of the critical angle (θ'_c). Assuming that θ'_c differs from the true critical angle (θ_c), of a systematic error ($\delta\theta_c$), (i.e. $\theta'_c = \theta_c \pm \delta\theta_c$), Eq. (1) leads to a calculated mass density (ρ'), different from the true value (ρ). By matching the equations written from Eq. (1) for θ_c and θ'_c, it follows that:

$$\frac{\theta_c^2}{\rho} = \frac{(\theta_c \pm \delta\theta_c)^2}{\rho'}, \qquad (2)$$

which can be used for expressing the absolute variation coefficient of the mass density, $|\Delta\rho|/\rho$, as a function of θ_c and $\delta\theta_c$:

$$\frac{|\Delta\rho|}{\rho} = \frac{|\rho' - \rho|}{\rho} = \left| \left(1 \pm \frac{\delta\theta_c}{\theta_c}\right)^2 - 1 \right|. \qquad (3)$$

The two functions given by Eq. (3) are plotted in Fig. 1. The plot indicates that systematic errors of 10% in the determination of θ_c reflect in systematic errors of at least 20% in the calculated mass density. In particular, considering some typical values of

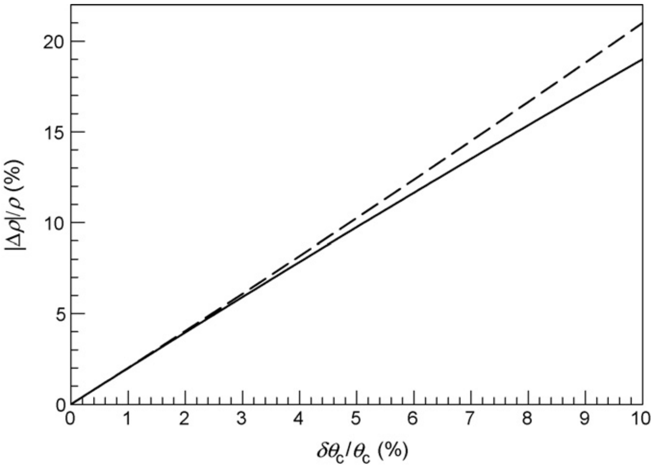

Fig. 1. Plots of the two functions given by Eq. (3).

θ_c for Cu Kα radiation, an error of $\delta\theta_c = 0.01°$ produces an error in the calculated mass density that varies from about 5% for $\theta_c = 0.4°$, to about 20% for $\theta_c = 0.1°$.

The most common source of a systematic error in angle measurements is sample-goniometer misalignment (i.e. a tilting of the sample reflecting surface with respect to the goniometer center plane, see also Fig. 2b and next section). In particular, a misalignment of $\delta\theta_c$ reflects in an error of evaluation of the critical angle of about $\delta\theta_c$. The above calculations indicate that a misalignment of few hundredths of degree may reflect into a relative error in the density higher than 20%. These figures explain how much misalignment affects density evaluation by XRR and why it is not trivial to eliminate.

3. The XRR-density evaluation (XRR-DE) method

As shown in the previous section, alignment is a compulsory and crucial factor for density evaluation. Indeed, with commercial single-wavelength reflectometers, alignment needs a solid expertise to be achieved. It will be presented here a novel reliable procedure, that allows to overcome the alignment step. It is based on the extrapolation of the correct θ_c from a set of XRR curves collected with random alignment.

In reflectometers basic geometry the goniometer centre plane is parallel to a reference plane, which coincides with the physical surface on which the sample is loaded. Misalignment arises from the difficulty in resting the sample with its reflecting (upper) surface parallel to the goniometer reference plane, and in turn to the goniometer centre plane, with a precision higher than hundredths of degree. In order to align the goniometer centre plane to the sample reflecting surface, it is possible to reset the reflectometer basic geometry and to tilt the goniometer centre plane of a proper offset angle (α) (Fig. 2a). Searching for the correct α is the key operation of alignment.

The searching method relies on the fact that the measured scattered X-ray intensity in a misaligned geometry (off-specular scan, Fig. 2b) is lower than the measured scattered X-ray intensity in aligned geometry (specular scan, Fig. 2a), which is the maximum achievable. This happens because in the

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