

Metal Films as Mass Standard Samples in the Nano-Gram Range

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Attestation of magnetron sputtered films as mass standards is presented. Homogeneous, long-lived metal films were measured by different methods for comparison. The accuracy of the order 1 ng was found to be provided by application of the metal film standards for element analysis by X-ray fluorescent method.

Keywords: Thin Films, Nano-Standards, Magnetron Sputtering, X-ray Reflectometry, X-ray Fluorescent Method.

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1. INTRODUCTION

Modern nano-technologies deal with extra-small element contents, thus determining requirements to the measurement methods. Using X-ray geometry with secondary target it is possible to increase the sensitivity of X-ray fluorescent analysis [1, 2]. But to reveal and measure element trace impurities in the bulk materials, special mass standards are necessary to apply. Usually for measuring trace impurities, various diluted solutions are used as mass standards. However, the main drawback of such mixtures is inhomogeneity, so, their application is limited. Other techniques for standard sample preparation described in [3].

The developed technology of X-ray mirrors [4, 6, 7] allows preparing metal nano-layers which remain stable for a long time, thus, such objects may be used as mass standards for nano-trace measurements. Magnetron sputtered super-thin (of the order of 1 nm) extra-smooth layers on substrates are analyzed by X-ray reflectivity method [4, 5] in order to determine film thickness (d) and density (ρ). Thus, by $\rho \times d$ value the mass of film substance can be measured with high accuracy (3-5%).

The present work is purposed to studying thin film mass standards in the nano-gram range.

2. SAMPLES AND INVESTIGATION METHODS

DC magnetron sputtered cobalt films deposited onto silicon substrates were analyzed. The preparation procedure is described in details in [6]. The deposition was carried out in cycle manner. 500 cycles of deposition corresponded to film thickness near 20 nm. The samples were covered by 2 nm amorphous carbon layer to protect oxidation.

X-ray fluorescent (XRF) analysis was carried out using the energy-dispersive spectrometer SPRUT-K (AO Ukrrentgen, Ukraine) with Si(Li) X-100 detector (Amptek, USA) in the arrangement with a Ge secondary target. The shooting-through type Ag anode was used in the X-ray tube BS-22 in the regime $U = 35$ kV, $I = 250$ μ m, and exposure time 300 s. The optic scheme aperture was 8×10^{-6} (tube anode – irradiator, irradiator – sample, sample – detector).

he sample irradiated area was determined by the intensity variation of Ca-K α fluorescence line when the 2 mm paper square moved relative to the sample-holder in vertical and horizontal directions with 1 mm step.

The high homogeneity of the films allowed obtaining mass standards less than 50ng using additional cutting the films.

The values $\rho \times d$ were determined by three different methods: (i) by X-ray reflectivity oscillations [4, 5]; (ii) by XRF method measuring Co-K α line intensity [8]; and (iii) by film absorption of the substrate Si-K α fluorescent signal [8].

In the first case the cobalt mass was calculated as

$$M_n = \frac{H_{500}}{500} \cdot \rho_{Co} \cdot n \cdot S_n, \quad (1)$$

where H_{500} corresponds to Co thickness obtained for 500 deposition cycles; ρ_{Co} is cobalt density; n is the number of deposition cycles; S_n is the area of n -th sample.

According to (1), the cobalt mass 53 ng was obtained for 7 deposition cycles at $S_n = 0.28$ cm². Using a diamond knife, the sample was cut into sections of 0.03, 0.04, and 0.09 cm².

By the second method $\rho \times d$ value was determined as follows [8]:

$$\rho \cdot d = \left(\frac{\mu_{Co}^{Ge}}{\sin \varphi} + \frac{\mu_{Co}^{Co}}{\sin \psi} \right)^{-1} \cdot \ln \left(1 - \frac{I_{\rho d}^{Co}}{I_{d=\infty}^{Co}} \right), \quad (2)$$

where μ_{Co}^{Ge} and μ_{Co}^{Co} are, respectively, absorption mass coefficient of Ge-K α radiation of the secondary target, and one of the film Co-K α analytical line, – by cobalt; φ and ψ are, respectively, an incident angle of the secondary target radiation and the exit angle of fluorescent radiation recorded by detector; $I_{\rho d}^{Co}$ and $I_{d=\infty}^{Co}$ are Co-K α analytical line intensities at $d \neq \infty$ and at "infinite" thickness of the sample.

Using the third method, $\rho \times d$ value calculated by film absorption of the substrate Si-K α fluorescent signal [8]:

$$\rho \cdot d = \left(\frac{\mu_{Co}^{Si}}{\sin \varphi} + \frac{\mu_{Co}^{Si}}{\sin \psi} \right)^{-1} \cdot \ln \left(\frac{I_{d=0}^{Si}}{I_{\rho d}^{Si}} \right), \quad (3)$$

where μ_{Co}^{Si} is cobalt mass coefficient of absorption of the substrate analytical signal Si-K α ; $I_{\rho d}^{Si}$ is the substrate Si-K α analytical line intensity with partial absorption of the radiation by the film; $I_{d=0}^{Si}$ is the intensity of the same line in the absence of the film.

3. RESULTS AND DISCUSSION

In Fig.1, the dependences $\rho \times d$ on the cycle number obtained by the three methods described above are shown. The value $\rho \times d = 13.44 \cdot 10^{-6} \text{ g/cm}^2$ was determined by X-ray reflectivity method (1) for the 16.8 nm sample. Almost the similar values we obtained the for

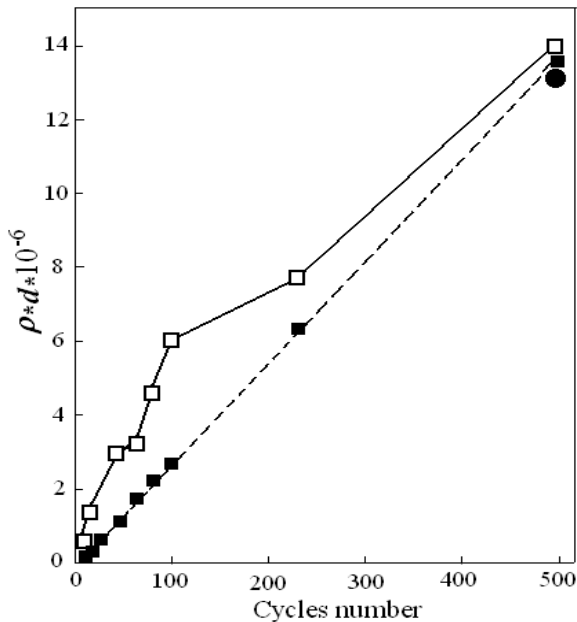


Fig. 1 – $\rho \times d$ ($\text{g/cm}^2 \times 10^{-6}$) values versus the number of deposition cycles for three independent methods: (●) by X-ray reflectivity oscillations; (■) by film fluorescence radiation intensity (Co-K α line); (□) by substrate fluorescence radiation intensity (Si-K α line) absorption.

the same sample using other methods: $13.87 \cdot 10^{-6} \text{ g/cm}^2$ – by the intensity of film fluorescent radiation (2 method); and $14.04 \cdot 10^{-6} \text{ g/cm}^2$ – by cobalt film absorption of the substrate fluorescent radiation (3 method) at relative inaccuracy not more than 2%. The $\rho \times d$ plot obtained by Eq. (2) is linear according to the linear dependence ‘intensity – element mass’ of fluorescent radiation. As it is seen, the plot obtained by the 3 method gives a non-linear plot with higher values $\rho \times d$ than the previous one. This behavior we explain by the non-planar film surface in the beginning of the growth when the coating is inhomogeneous and broken [5]. So, the model of substrate radiation absorption by the flat film is inadequate. As the whole substrate becomes completely coated by the film (after 500 cycles), the values $\rho \times d$ become similar for the three methods.

The model used for calculation by (1) also considers the film as homogeneous over whole substrate surface. Therefore, for thicknesses less than 50 nm, we obtained overestimated mass values. As the second method is less sensitive to the coating inhomogeneity, we obtain reliable results in the whole range of thicknesses.

Using the cobalt mass calculated by Eq. (1) we built a calibration function of Co-K α fluorescence intensity versus Co film mass (Fig. 2).

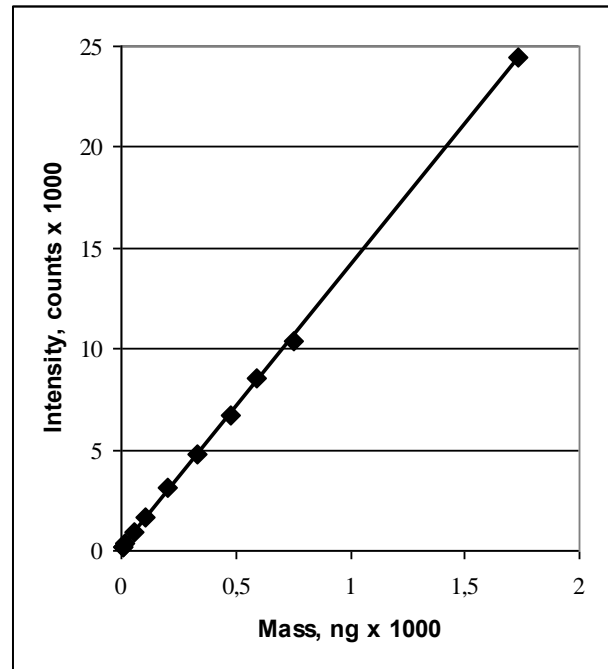


Fig. 2 – A calibration function “fluorescence intensity-film mass” in the range from 5 ng to 1800 ng

The threshold of detectability for i -th sample is

$$m_{\min} = \frac{3m_i \sqrt{I_{Bi}}}{I_{Ci}},$$

where I_{Bi} and I_{Ci} are integral intensities of background and analytical signals, respectively, and m_i is cobalt mass in i -th sample. The standard deviation \bar{S}^2 for the calibration function (Fig. 2) scattering was 8 ng. Thus, mass certification is possible in the range from 1 to 17 ng with accuracy about 1 ng according to the threshold of detectability, while in the range from 17 to 1800 ng the accuracy is not worse than 8 ng.

The film standards may be applied for any other element, but for $Z < 27$, the accuracy decreases. For recalculation of the calibration function it is necessary to introduce a coefficient K [8]:

$$K_i = \frac{\frac{S_{qi} - 1}{S_{qi}} \cdot \mu_i^{Ge} \cdot \omega_{qi} \cdot \rho_i}{\frac{S_{qs} - 1}{S_{qs}} \cdot \mu_s^{Ge} \cdot \omega_{qs} \cdot \rho_s} \quad (4)$$

where S_{qi} and S_{qs} are absorption jump values of for i -th element and the standard, respectively; μ_i^{Ge} and μ_s^{Ge} are mass attenuation factors of the secondary target Ge-K α radiation by i -th element and the standard, respectively; ω_{qi} and ω_{qs} are fluorescence yields of i -th element and the standard; ρ_i and ρ_s are densities of i -th element and the standard, respectively.

4. CONCLUSIONS

The magnetron sputtered metal layers onto single-crystalline substrates are super-smooth, homogeneous, high stable and may be certified using different methods. So, these are promising mass standards in the wide nano-gram range (1–1800 ng). In the range from 1 to 17 ng, the accuracy is about 1 ng, and in the range

from 17 to 1800 ng it is not worse than 8 ng.

In comparison of obtained Co film standards with for water solution State Standards, the firsts showed the advantages of high stability and homogeneity at good accordance of calibration functions.

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