MEASUREMENT OF THE THICKNESS
NONUNIFORMITY OF NANOFILMS
USING AN ELECTRON PROBE METHOD

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We propose an electron-probe method for measuring thickness nonuniformity in nanofilms, using the dependence of the ratio of the intensities of the characteristic x-ray film elements on its thickness. The calibration dependence is computed simulating the interaction of electrons with the sample by a Monte-Carlo method.

Keywords: *low-voltage electron probe x-ray microanalysis, nanofilm, thickness measurement, Monte-Carlo method.*

Films of nanometer thickness constitute an important element of modern electronic technology. One of the most promising methods for creating such films is the method of atomic layer deposition, which yields uniform film thickness with a given composition [1]. The uniformity of thickness is a parameter of fundamental importance for the practical application of nanofilms.

The paper presents a method of rapidly measuring the non-uniformity of nanofilms on silicon substrates with thickness of 5–25 nm. The selected objects of study are films with composition $Hf_{0.5}Zr_{0.5}O_2$, produced by atomic layer deposition on single crystal silicon substrates. For measurements, we used the signal of the characteristic x-ray radiation (CXR) excited by an electron probe with energy 4–6 keV. If the chemical composition of the film is constant, the changes in the CXR line intensities of oxygen, hafnium and zirconium included in its composition will cause non-uniform thickness.

Experiments were carried out with a scanning electron microscope JSM 6460 LV (JEOL, Japan) equipped with energy-dispersive x-ray spectrometer INCAx-sight (Oxford Instruments, UK). We used an electron probe with energy 6 keV, current strength of the probe – 2 nA, spectral collection time – 1000 sec. Selection of energy is conditioned by the fact that the observed CXR spectrum is the sum of the CXR spectra of the film and the substrate. For all energies sufficient for effective excitation of the CXR lines of oxygen, hafnium and zirconium, the run of electrons significantly exceeds the thickness of the film, so its influence on the intensity of the CXR emission lines in the substrate (in the indicated thickness range) can be ignored [2]. With an initial energy of 6 keV, the run of the electron probe in silicon was approximately 600 nm; the attenuation occurred in the substrate material [3].

In Fig. 1, we show the CXR spectrum of $Hf_{0.5}Zr_{0.5}O_2$ film on a silicon substrate. The first peak is the carbon line CK_α ($E = 0.277$ keV) caused by contaminated film formed on the surface of the sample due to the extended spectral collection time; the next peak is the oxygen line OK_α ($E = 0.525$ keV); the weak peak (arrow) corresponds to the hafnium electron

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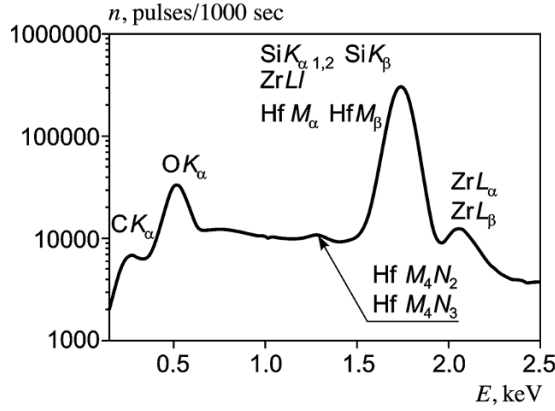
Fig. 1. x-Ray spectrum of the $Hf_{0.5}Zr_{0.5}O_2$ film on a silicon substrate.

transitions HfM_4N_2 and HfM_4N_3 ($E = 1.280$ keV). The highest peak in the spectrum is the imposition of the lines of the silicon K-Series SiK_α ($E = 1.740$ keV), SiK_β (E = 1.836 keV); the lines of the hafnium M-series HfM_α ($E = 1.646$ keV), HfM_β ($E = 1.700$eV) and the line of ZrL_1 zirconium ($E = 1.792$ keV). The last peak is the unresolved lines of the zirconium $ZrL_{\alpha1,2}$ ($E = 2.042$ keV) and ZrL_β ($E = 2.129$ keV). Energy lines are given in [4]. The unresolved lines HfM_4N_2, HfM_4N_3, $ZrL_{\alpha1,2}$ ($E = 2.042$ keV), ZrL_β have no impositions and can be used to determine the film thickness.

For measuring the film thickness by the electron-probe method, one usually calculates the k-ratio (the ratio of the intensities of element peaks in the test and standard samples), and a calibration graph of k-ratio and film thickness. This method assumes the stabilization of an electron beam or its control during the experiment, which is not always possible. Otherwise, the probe current instability introduces additional error in [5, 6].

In this paper, for the measurement of film thickness non-uniformity we used a dimensionless ratio r, i.e., the ratio of the intensities of lines of zirconium and silicon, normalized to the intensity of the corresponding lines of pure zirconium and silicon:

$$r = 100\left[\left(\frac{I_{Zr}}{I'_{Zr}}\right) \Big/ \left(\frac{I_{Si}}{I'_{Si}}\right)\right] = 100\left(\frac{I_{Zr}}{I_{Si}}\right)\left(\frac{I'_{Si}}{I'_{Zr}}\right), \tag{1}$$

where I_{Zr}, I_{Si}, I'_{Zr}, I'_{Si} are the intensities of the zirconium lines $ZrL_{\alpha1,2} + ZrL_\beta$ and the silicon lines $SiK_\alpha + SiK_\beta$ of the test sample and the pure element, respectively.

The multiplier 100 is introduced because of the large difference in the intensities of the lines for the film and the substrate. The value r does not depend on the electron probe current, since the intensities I_{Zr}, I_{Si} are measured simultaneously, and the ratio of intensities of the lines of pure elements is a constant, which greatly simplifies the experimental procedure, since no stabilization or special current control is required. Using silicon line intensity is justified, despite the imposition (on the silicon line) of hafnium and zirconium lines. The normalization of the intensity of pure elements reduces the number of input data such as the fluorescence yield of the corresponding element. The ratio I'_{Si}/I'_{Zr} is found experimentally and used in further calculations as a constant.

The program developed by the authors for calculating the CXR intensity using a Monte Carlo method was applied to the screened Rutherford elastic scattering cross section [6] in differential form with a modified electron deceleration law due to Joy–Luo [7]. In the calculation of the CXR intensity, the ionization cross-section is expressed in the form

$$Q = K(\ln U/U^m), \tag{2}$$

where K is a coefficient depending on the type of atom and CXR spectral series; $U = E/E_{ab-}$ is the overvoltage (ratio of the energy of an electron interacting with the atom, and the absorption edge of the recorded spectral series); the uncertainty $m = 0.9$ [8].
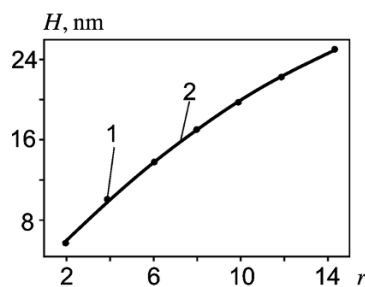
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Fig. 2. The calibration curve: *1*) results of calculations;
2) second-degree polynomial approximation.

TABLE 1. Thickness Measurement Results for $Hf_{0.5}Zr_{0.5}O_2$ Film

Parameters	Index of region										
	1	2	3	4	5	6	7	8	9	10	11
r	5.52	5.19	5.05	5.03	5.26	4.93	4.87	4.95	5.03	4.93	4.94
H, nm	12.90	12.20	12.00	12.00	12.40	11.80	11.70	11.80	12.00	11.80	11.80

Data on mass attenuation coefficients and ionization potentials are taken from [5, 9]. Modeling was performed with the number of electrons $N = 5 \cdot 10^6$ for each thickness. The calibration dependence $H = f(r)$ of the film thickness H on the defined ratio r (cf. (1)) is constructed in the range for the $Hf_{0.5}Zr_{0.5}O_2$ film on the silicon substrate (Fig. 2).

The calibration equation for the film thickness in nanometers, obtained by fitting the results of the Monte-Carlo calculations, has the form

$$H = 1.5 + 2.33r - 0.049r^2. \tag{3}$$

The line intensities of zirconium $I_{Zr}(ZrL_{\alpha 1,2} + ZrL_\beta)$ and silicon $(SiK_\alpha + SiK_\beta)$ are the sum of recorded x-ray quanta within an energy range $(E_{max} - \Delta E/2, E_{max} + \Delta E/2)$ with no background in it. At the same time, ΔE is the full peak width at half maximum and E_{max}, the position of the peak maximum. As a result of the ten-fold measurements, one establishes the ratio I'_{Si}/I'_{Zr}.

The thickness of the film was measured in 11 regions of the scanning area of 300×300 μm at distances of 500 to 1000 μm from one another. The measurement results for r and the thickness calculated from (3) are presented in Table 1.

The measurement error for the thickness from (3) is determined by the statistical error of measuring the parameter r, i.e., the measurement error of the intensities of the characteristic x-ray lines, calculated by (1), as well as the error of obtaining the calibration curve. Under the conditions of this experiment, the statistical error of measuring the parameter r was less than 1%.

The calibration curve calculation error is due to: the final number of analyzed electrons $N = 5 \cdot 10^6$ (calculations showed this data component of the error does not exceed 0.2%); the uncertainty m in (2) (for $\Delta m = 0.1$, the relative measurement error of film thickness is less than 2%); the uncertainty of the ionization potential for the elements of the film and the substrate (which contributes no more than 1% to the relative measurement error); the approximation error is less than 1%. The overall error in constructing the calibration curve is no more than 3.5% at a significance level 0.95 and confidence interval of ±0.5 nm (cf. Table 1).

Within the range of variation of $r = 4.87$–5.52, relationship (3) can be replaced by

$$H = A + B(r - 4.87),$$

where $A = 11.68$, $B = 1.83$ are parameters in Monte-Carlo calculations, introducing an additional error of not more than 0.1%. In this case, the film thickness deviation from its average value is given by the expression

$$\delta H = B(r - \tilde{r}), \tag{4}$$

where $\tilde{r}$ is the average thickness of the film.

Studies of the effect of uncertainty of parameters used in Monte-Carlo calculations, for $r = 4.87$–5.52 showed that the error in the derivation of the parameter B does not exceed 3%.

On the basis of experimental data (cf. Table 1), we calculated the maximal deviation of film thickness from its mean value (4), $\delta H_{max} = 0.9$ nm (7.5%), which can be regarded as an indicator of the non-uniformity of film thickness. The estimate of measurement uncertainty δH_{max} carried out in accordance with [10] using error estimates in the determination of B in (4) and r. The error $\Delta(\delta H_{max}) = 0.2$ nm confirms the validity of the existence of non-uniformity of the film thickness.

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