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Optical properties of ferroelectric films $Hf_xZr_yO_2$ and $La:Hf_xZr_yO_2$ according to ellipsometry data

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Recently ferroelectric properties have been found in hafnia-based nanosized films. Such films are of the utmost interest for development of a universal memory, which combines the advantages of random access memory and flash memory. The paper studies optical properties of hafnia-zirconium oxide films $Hf_xZr_yO_2$ and lanthanum-alloyed hafnia-zirconium oxide films $La:Hf_xZr_yO_2$. Fluctuations of thickness in $Hf_xZr_yO_2$ do not exceed 3.5%, fluctuations of thickness in $La:Hf_xZr_yO_2$ films — 3.2%. Optical properties are analyzed based on effective-medium theory. According to effective-medium theory data, $Hf_xZr_yO_2$ films contain 46% HfO_2, 54% ZrO_2, $La:Hf_xZr_yO_2$ films contain 47.5% HfO_2, 52.4% ZrO_2, 2.5% La_2O_3.

Keywords: ferroelectric, refraction index, spectral ellipsometry, effective-medium theory.

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Introduction

Segnetoelectric (or ferroelectric in English literature) memory is of the utmost interest for development of a universal memory, which combines advantages of random access memory (high speed response) and flash memory (nonvolatility, information storage with power off) [1]. However, memory based on perovskite films (such as $SrTiO_3$) does not enable scaling to small design norms because of large thickness of a ferroelectric film [2]. Recently, it has been found that thin (≈ 10 nm) hafnia-based films have ferroelectric properties [3]. However, such memory has a number of reprogramming cycles of $\sim 10^{10}$, which is by orders less than the number of reprogramming cycles of random access memory ($\sim 10^{14}$). It has been found that alloying with lanthanum ($La:Hf_xZr_yO_2$) causes increased number of reprogramming cycles [4,5]. Optical properties of $Hf_xZr_yO_2$ and $La:Hf_xZr_yO_2$ films are not studied currently.

The objective of this paper is to study the optical properties of ferroelectric hafnia–zirconium oxide films $Hf_xZr_yO_2$, lanthanum-alloyed hafnia–zirconium oxide films $La:Hf_xZr_yO_2$, and to analyze data based on effective-medium theory.

Experimental part

$Hf_xZr_yO_2$ and $La:Hf_xZr_yO_2$ films on silicon substrates were produced by atomic layer deposition method. Technology details for $Hf_xZr_yO_2$ films are described in [4], and $La:Hf_xZr_yO_2$ technology — in [5].

Spectral dependencies of ellipsometric parameters $\Psi(E)$ and $\Delta(E)$ were measured on ellipsometer „Ellipse–1891" (Rzhanov Institute of Semiconductor Physics, Siberian Branch of Russian Academy of Sciences, Novosibirsk) [6] under the following conditions. Spectral range by photon energy $E = 1.13-4.60$ eV, spectral resolution 0.01 eV, sample light incidence angle 70°, time of single spectrum measurement did not exceed 20 s. Measurements were conducted using four-zone method with subsequent averaging to increase measurement accuracy. Measured spectral dependencies of ellipsometric parameters $\Psi(E)$ and $\Delta(E)$ were further used to calculate dispersion dependencies of refraction index $n(E)$ and thickness of $Hf_xZr_yO_2$ and $La:Hf_xZr_yO_2$ films using method of adjustment of experimental and model spectra according to the model of single layer reflecting structure in accordance with the technique described previously [7].

To describe dispersion dependencies, polynomial Cauchy formula is used [8]:

$$n(E) = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4}, \qquad (1)$$

where a, b, c are coefficients. Optical constants n, k of Si substrate were taken from a database [9].

For numerical assessment of $Hf_xZr_yO_2$ and $La:Hf_xZ_yO_2$ film composition, Bruggeman's effective medium model is

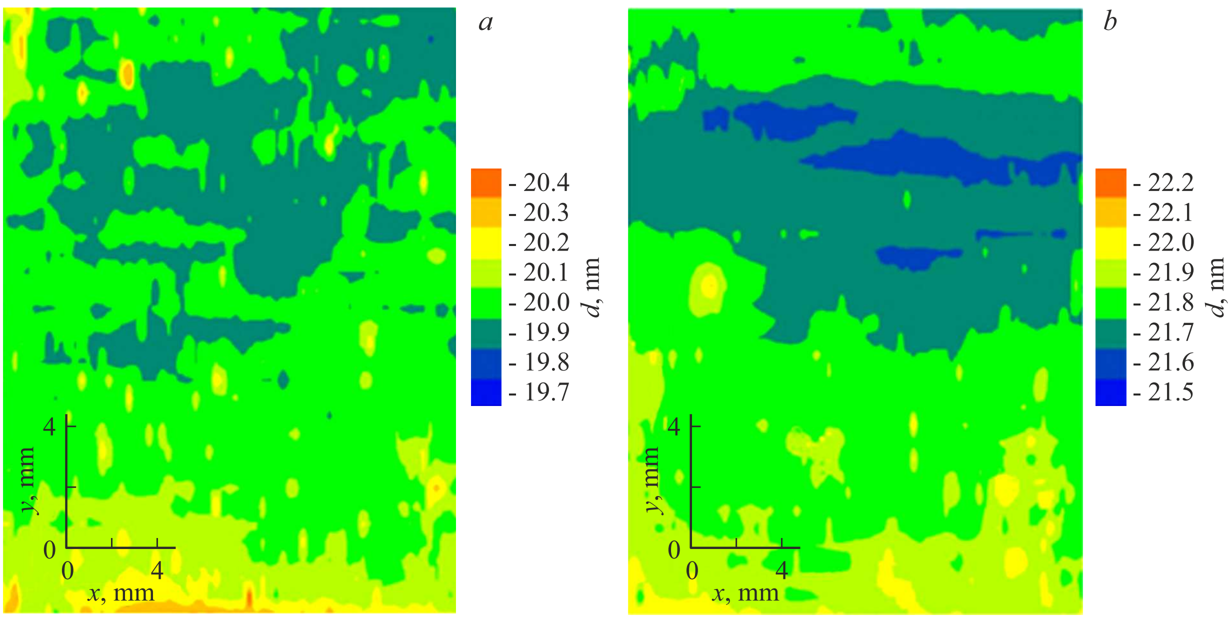

Figure 1. Chart of film thickness distribution for samples 1 (a) and 2 (*b*).

used [7]:

$$\sum_i \left(q_i \frac{\varepsilon_i - \varepsilon_{ef}}{\varepsilon_i + 2\varepsilon_{ef}} \right) = 0, \qquad (2)$$

where q_i is the part of ith component of composite material; ε_i, ε_{ef} are dielectric constants of ith component and effective medium, accordingly.

To assess homogeneity of film thickness on the sample surface, scanning ellipsometer with high spatial resolution was used „Microscan−3M" (Rzhanov Institute of Semiconductor Physics, Siberian Branch of Russian Academy of Sciences) [10]. Measurements were conducted on the surface area 20−15 mm with pitch along axes x and y 0.2 and 0.5 mm accordingly. Light spot diameter during scanning made 10 μm. Source of light in the ellipsometer is HeNe-laser ($E = 1.96$ eV). Sample light incidence angle is 60°. Calculation of film thickness in each point of the scanned sample was conducted independently under the above method; values of the refraction index n for $E = 1.96$ eV were taken from spectral measurements (table).

Results and discussion

Composition and optical properties of $Hf_xZr_yO_2$ and $La:Hf_xZr_yO_2$ film samples studied within this paper are given in the table. According to the data of X-ray photoelectron spectroscopy (XPS) samples 1 and 2 include in their composition approximately equal parts of HfO_2 and ZrO_2 oxides; in addition to that sample 2 contains approximately 2% La_2O_3. $Hf_xZr_yO_2$ and $La:Hf_xZr_yO_2$ films are homogeneous in thickness: the spread in the central part of the sample does not exceed 0.5 nm (Fig. 1).

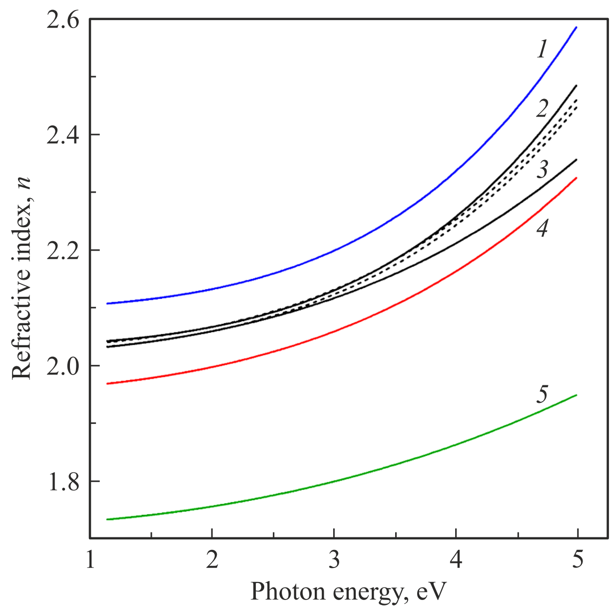

Figure 2. Dispersion dependencies $n(E)$ calculated according to Cauchy formula for samples 1 (curve *2*) and 2 (*3*), and also dispersion dependencies of oxides ZrO_2 (*1*), HfO_2 (*4*) and La_2O_3 (*5*) [12]. Dashed lines — results of calculation of $n(E)$ for $Hf_xZr_yO_2$ and $La:Hf_xZr_yO_2$ films according to Bruggeman's model, where the lower describes the film alloyed with lanthanum.

Small spread of thickness is important for development of reproducible semiconductor instruments of memory based on ferroelectric effect in hafnia-based films.

Spectral ellipsometric measurements of $Hf_xZr_yO_2$ and $La:Hf_xZr_yO_2$ films with subsequent analysis according to

Composition and optical properties of samples $Hf_{0.5}Zr_{0.5}O_2$/Si and La : $Hf_{0.5}Zr_{0.5}O_2$/Si

№	Sample	d, nm	n (1.96 eV)	Cauchy coefficients			**Fraction		
				a	$b \times 10^2$	$c \times 10^4$	Hf	Zr	La
1	$Hf_xZr_yO_2$	20.2	2.065	2.032	6.681	4.743	46 (48)	54 (52)	0 (0)
2	La : $Hf_xZr_yO_2$	21.9	2.057	2.019	9.284	1.781	45.7 (46.5)	52.4 (51)	1.9 ($\sim$ 2.5)
	*HfO_2	78.5	1.995	1.955	9.635	2.179	–	–	–
	*ZrO_2	82.4	2.130	2.097	6.539	5.396	–	–	–
	*La_2O_3	65.3	1.754	1.722	8.249	0.381	–	–	–

* — data from [12]; ** — data of X-ray photoelectron spectroscopy and calculated according to Bruggeman's model (in brackets).

the model of homogeneous single-layer structure demonstrated that such thin films are transparent in the studied spectral range and, accordingly, may be described by polynominal Cauchy dependence without absorption ($k = 0$). Found Cauchy coefficients of all measured samples and their thicknesses are given in the table. Figure 2 represents dispersion dependencies $n(E)$ calculated according to Cauchy formula for samples 1 (curve *2*) and 2 (curve *3*).

To describe $Hf_xZr_yO_2$ and La : $Hf_xZr_yO_2$ composite films, Bruggeman's effective medium model was used [11]. This model describes well the composite optical medium as a mixture of separate chemically separate phases of ZrO_2 and HfO_2 and La_2O_3, each having own dielectric constants ε_i and fraction value q_i. $Hf_xZr_yO_2$ and La : $Hf_xZr_yO_2$ films were calculated using Bruggeman's model with dispersion dependencies of ZrO_2, HfO_2 and La_2O_3 [12], which are shown in Fig. 2 (curves *1, 4* and *5*). Figure 2 shows results of the calculation according to Bruggeman's model for dispersion dependencies of refraction index $n(E)$ of $Hf_xZr_yO_2$ and La : $Hf_xZr_yO_2$ films with dashed lines, the lower of which describes a lanthanum-alloyed film. From calculation results it is seen that the best compliance with experimental data occurs when fractions of ZrO_2 and HfO_2 are equal accordingly to 0.52 and 0.48, which is very close to figures produced from XPS measurements (0.54 and 0.46, table). Content of La_2O_3, assessed by ellipsometric measurements (0.025), is slightly higher than XPS data (0.19), which may be caused by features of La_2O_3 film formation, in particular, higher content of bound water in the layer resulting in dispersion dependency change. It should be noted that dispersion dependencies of $Hf_xZr_yO_2$ and La : $Hf_xZr_yO_2$ films are noticeably different in the short-wave area of the spectrum.

Conclusion

Fluctuations of refraction index and thickness of $Hf_xZr_yO_2$ and La : $Hf_xZr_yO_2$ nanometer films were studied. Dispersion of refraction index and composition of films are analyzed with the help of effective-medium theory based on the model considering the mixture of HfO2, ZrO2 and La_2O_3. Fluctuations of thickness in $Hf_xZr_yO_2$ films do not exceed 3.5%, fluctuations of thickness in La : $Hf_xZr_yO_2$ films — 3.2%. According to data of effective-medium theory, $Hf_xZr_yO_2$ film contains 46% HfO_2, 54% ZrO_2, La : $Hf_xZr_yO_2$ film — 47.5% HfO_2, 52.4% ZrO_2, 2.5% La_2O_3.

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Conflict of interest

The authors declare that they have no conflict of interest.

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