Study optical properties of the thin HfO$_2$ coatings deposited by DC reactive magnetron sputtering

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Abstract. Thin HfO$_2$ films were deposited on polished microscope glass substrates by DC magnetron sputtering at bias voltages of -85 V, -100 V, -115 V, -130 V and -145 V. The deposited films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and UV-VIS-NIR spectrophotometry. The XRD results show the presence of a polycrystalline monoclinic phase. The roughness calculated from the AFM images increases as the bias voltage is raised to -130 V and then starts decreasing. The effect was also investigated of the bias voltage on the optical properties of the HfO$_2$ films.

1. Introduction

The deposition of thin oxide films with precisely controlled properties is an indispensable part of the development of modern technologies. Hafnium oxide (HfO$_2$), a refractory dielectric, has been the subject of intense research in the past few years due to its unique properties [1]. Its outstanding chemical stability, electrical and mechanical parameters, high dielectric constant, and wide band gap make it suitable for several industrial applications in the fields of electronics, microelectronics, structural ceramics, and optoelectronics [2]. Furthermore, its relatively high band gap ($E_g > 5$ eV) and refractive index ($n \sim 2$), and its excellent transmittance and good transparency over a wide wavelength range make the HfO$_2$-based thin films and coatings attractive for optical applications, such as optical filters, ultraviolet (UV) and heat mirrors, antireflection coatings and scintillation materials [3]. In the field of electronics, it is a leading candidate to replace the SiO$_2$ dielectrics in gate oxides due to the low electron tunneling effect and the high permittivity [4].

Hafnium oxide has been synthesized by various deposition techniques – chemical vapor deposition [5,6], atomic layer deposition [7] and electron beam evaporation [8]. A number of studies have reported the optical properties of HfO$_2$ films depending on the different technological conditions. The optical properties from the visible to the far-infrared ranges of HfO$_2$ films with different thicknesses from about 180 nm to 500 nm were deposited using magnetron sputtering onto Si substrates and the results were reported in [9]. In [10], the authors investigated the effect of the O$_2$/Ar gas flow ratio on the optical properties and mechanical stress of sputtered thin HfO$_2$ films. The effect of the substrate temperature
ranging from room temperature to 500 °C on the structural and optical properties of the HfO₂ films was described in [11]. This brief review of the literature makes it clear that a number of researchers have studied the influence of the processing parameters on the properties of HfO₂ deposited films by magnetron sputtering. However, the relationship between the applied negative bias voltage on the structural and optical properties of the HfO₂ coatings thus prepared is yet to be studied in detail.

In our study, we deposited HfO₂ films by direct current (DC) magnetron sputtering with the substrate bias voltage ranging from -85 V to -145 V and followed the effects on the crystallographic structure, the morphology and the optical properties of the grown films.

2. Experimental details

We deposited the HfO₂ films by a DC magnetron at the bias voltages of -85 V, -100 V, -115 V, -130 V and -145 V. The sputtered target of high-purity Hf (about 99.8%) had a diameter of 100 mm. Deltalab polished glass microscope plates with dimensions 40×26×1 mm³ were used as substrates. Before the deposition process, the vacuum chamber was evacuated to a pressure of 1.5×10⁻⁵ mbar. The substrates were cleaned by Ar⁺ plasma sputtering for 10 min to eliminate contaminations from their surface. During deposition, the substrates were kept at a temperature of 300 °C. The process took place in Ar-O₂ atmosphere at a pressure ratio between the reactive/inert gases of 0.2. To achieve better uniformity and density of the HfO₂ films, the substrates were placed at an angle of 15°.

The crystallographic structure of the coatings was assessed by grazing incidence X-ray diffraction (GIXRD) at an angle of incidence of 2° with Cu Kα radiation (1.54 Å), a 20 scale from 20° to 60°, a step size of 0.05° and a step scan time of 1.5 s. The phases were identified using the International Center for Diffraction Data (ICDD) database.

The ellipsometry measurements were performed using a Woollam M2000D rotating-compensator spectroscopic ellipsometer with a wavelength range from 193 nm to 1000 nm. The data acquisition and analysis software employed was Complete EASE 5.10 (J. A. Woollam Co., Inc). To determine the thickness of the layers, the spectroscopic ellipsometry data Ψ and Δ (taken at angles of incidence of 55°, 65° and 75°) were analyzed using a model consisting of a Si substrate and a Cauchy layer (HfO₂ layer) as a second layer in the transparent wavelength range of 500 nm – 1000 nm.

A Universal Nanomechanical AFM Tester (UNMT, Bruker Surface Analysis, USA) was used to characterize the surface nano-topography by a silicon tip with a 10-nm radius of curvature. The studies were implemented in a non-contact mode with each surface being scanned at different locations with a scanning area of 50×50 µm². The data were analyzed and the average roughness parameter S₅ was calculated.

The optical properties of the as-deposited HfO₂ coatings were determined based on transmittance measurements in the ultraviolet, visible and near infrared ranges by an SF-46 spectrophotometer with a working range 190 – 1100 nm. The reflection and absorption coefficients were measured by an optical microprocessor system developed by us using a semiconductor laser at the wavelength of 630 nm. The system is based on an ARM Cortex STM 32 processor allowing measurements with high accuracy. It is capable of measuring simultaneously the incident power, the transmitted power and the reflected power, thus determining the losses in the deposited film. A current-voltage (230 V) converter with a linear characteristic is utilized with pin photodiodes sensors with a working range of 630 nm.

3. Results and discussion

XRD patterns of the DC-sputtered HfO₂ films deposited at different bias voltages are shown in figure 1. In all cases, the films are single phase and polycrystalline, with the diffraction peaks attributed to the hafnium dioxide monoclinic phase (ICDD PDF#43-1017) [12]. The diffraction patterns lack amorphous-like halos, thus proving a high degree of crystallinity of the coatings deposited. Therefore, one should conclude that applying different bias voltages does not result in shifts of the 20 peak positions, i.e., does not lead to changes in the lattice parameters, neither does it result in additional residual stresses, strains, etc.
The thickness of the HfO$_2$ films prepared was calculated to be 480 nm, 508 nm, 535 nm, 545 nm and 514 nm at -85 V, -100 V, -115 V, -130 V and -145 V bias voltage, respectively. As can be noted, the films’ thickness grows linearly with raising the deposition bias voltage to -130 V. However, the further increase of the bias voltage to -145 V reduces the thickness to 514 nm. This could be due to the increased ion energy leading to the formation of a denser microstructure, or to re-sputtering of the coating [13].

Figure 2 presents the surface topography of the HfO$_2$ films prepared at different bias voltages.

**Figure 1.** XRD patterns of HfO$_2$ films deposited at different substrate bias voltages.

**Figure 2.** AFM images of HfO$_2$ films grown at (a) – 85 V; (b) –100 V; (c) –115 V; (d) –130 V; (e) –145 V; (f) – substrate without film.
The three-dimensional AFM images demonstrate a big difference in the surface roughness of the deposited films. As seen, increasing the bias voltage to -130 V increases the surface roughness of the coatings by a factor of almost three in comparison to the sample grown at a bias of -85 V. The further increase of the bias voltage, to -145 V, results in a slight decrease of the surface roughness. According to the authors of [14], the surface roughness is strongly related to the grain size, with larger crystallites corresponding to a rougher surface, and vice-versa. Increasing the bias voltage to -130 V increases the grains size due to the enhanced ion bombardment and the formation of a larger number of defects blocking the grain boundaries migration. A further increase in the bias voltage leads to the effects of the higher ad-atom energy and mobility becoming predominant. Thus, the voids between the grains are filled, the large column growth is broken down, and more nucleation sites are created, all of which increases the grains density and refinement.

Figure 3 shows the transmittance spectra of the samples deposited on microscope glass substrates.

The films are transparent down to a wavelength of 300 nm. The highest transmission value (89%) in the visible region is exhibited by the coating deposited at -115 V. A further increase of the bias voltage to -130 V and -145 V reduces the transmittance level to 87% and 85%, respectively. In addition, the films grown under the conditions described are homogeneous, as evidenced by the maximum in their transmittance (89%) being almost equal to the transmittance of the uncoated substrate (92%). The surface roughness and transparency have an inverse relationship, the former causing light scattering, which, in turn, decreases the films’ transmission if the roughness is sufficiently high [15]. In our experiments, the highest surface roughness was 440.4 nm, i.e., sufficiently high to have a significant effect on the transparency. The oscillations in the spectra are probably due to interference.

Figure 4 illustrates the films’ reflection and absorption coefficients dependences on the bias voltage. It is seen that the reflection coefficient increases slightly, with the highest value (29%) achieved at -130 V. Applying a higher negative bias voltage (-145 V) reduces the reflection. The good anti-reflection properties of HfO$_2$ films can be useful in some optical devices by reducing effectively the Fresnel losses [8].
Figure 4. Dependence of the reflection and absorption coefficients on the bias voltage.

4. Conclusion
Thin HfO$_2$ films were deposited on polished microscope glass substrates at bias voltages of -85 V, -100 V, -115 V, -130 V and -145 V by DC magnetron sputtering with the purpose of studying the bias voltage effect on the coatings’ structural, morphological and optical properties. The XRD patterns demonstrate the growth of a polycrystalline monoclinic phase, with the lack of amorphous halos proving the high degree of crystallinity of the coatings deposited. The AFM results show that a rise in the bias voltage to -130 V leads to the deposition of HfO$_2$ coatings with a high degree of roughness, an effect hindering the films’ potential use in optoelectronic applications. The highest value of the bias voltage (-145 V) results in a smoother, denser and more uniform surface. Moreover, all the coatings deposited exhibit a good transparency of 85% – 89% in the visible wavelength range depending on deposition bias voltage.

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References
[1] A, Rubio E, Abhilash K and Ramana C 2013 Opt. Mater. 35 1728–1734
[2] Aygun G and Yildiz I 2009 J. Appl. Phys. 106 014312
[3] Wilk G, Wallace R and Anthony J 2001 J. Appl. Phys. 89 5243–5275
[4] Wang Y, Yu Z, Zahid F, Liu L, Zhu Y, Wang J and Guo H 2014 J. Appl. Phys. 116 023703
[5] Lo W, Kamath A, Kher S, Metzner C, Wen J and Chen Z 2004 J. Mater. Res. 19 1775–1782
[6] Smirnova T, Yakovkina L, Kitchai V, Kaichev V, Shubin Yu, Morozova N and Zherikova K 2008 J. Phys. Chem. Sol. 69 685–687
[7] Mändar H, Rammula R, Aidla A and Aarik J 2013 J. Mater. Res. 28 1680–1686
[8] Wang Y, Lin Z, Cheng X, Xiao H, Zhang F and Zou S 2004 Appl. Surf. Sci. 228 93–99
[9] Bright T, Watgen J, Zhang Z, Muratore C and Voevodin A 2012 Thin Solid Films 520 6793–6802
[10] Jena S, Tokasa R, Misal J, Rao K, Udupa D, Thakur S and Sahoo N 2015 Thin Solid Films 592 135–142
[11] Du Q, Wang W, Li S, Zhang D and Zheng W 2016 Thin Solid Films 441 60821
[12] International Center for Diffraction Data 1999 ICDS Powder Diffraction File No 34–104
[13] Ding J, Zhang T, Mei H, Yun J, Jeong S, Wang Q and Kim K 2018 Coatings 8 8010010
[14] Zhang T, Gan B, Park S, Wang Q and Kim K 2014 Surf. Coat. Technol. 253 115–122
[15] Wiatrowski A, Obstarczyk A, Mazur M, Kaczmarek D and Wojcieszak D 2019 Coatings 9 106–126