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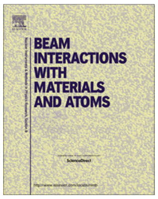

Changes in the Young Modulus of hafnium oxide thin films

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ABSTRACT

Hafnium-oxide (HfO_2)-based materials have been extensively researched due to their excellent optical and electrical properties. However, the literature data on the mechanical properties of these materials and its preparation for heavy machinery application is very limited. The aim of this work is to deposit hafnium oxide thin films by DC reactive magnetron sputtering with different Young's Modulus from the Ar/O_2 concentration variation in the deposition chamber. The thin films were deposited by DC reactive magnetron sputtering with different Ar/O_2 gas concentrations in plasma. After deposition, HfO_x thin films were characterized through XRD, AFM, RBS and XRF. In this regard, it was observed that the as-deposited HfO_2 films were mostly amorphous in the lower Ar/O_2 gas ratio and transformed to polycrystalline with monoclinic structure as the Ar/O_2 gas ratios grows. RBS technique shows good compromise between the experimental data and the simulated ones. It was possible to tailored the Young Modulus of the films by alter the Ar/O_2 content on the deposition chamber without thermal treatment.

1. Introduction

Hafnium-oxide (HfO_2)-based materials have been extensively researched due to their excellent optical and electrical properties. They present a high refractive index and high dielectric constant ($k \sim 25$) that makes it an interesting replacement for silicon dioxide in microelectronic applications [1–4]. Intensive efforts have been dedicated to the research of the electrical properties of hafnium oxide thin films. However, the literature data on the mechanical properties of these materials and its preparation for heavy machinery application, even though of critical importance, is very limited [5,6].

The Young Modulus has a major role on the electrical properties and the thermal stability of coatings. It is related to the energy bond between the atoms, where the higher the Young's Modulus is, the greater the atomic bonding energy will be. Thus, the higher the heat capacity and the shear strain resistance are the minor the volume variation of the film will be. Thus, high-temperature coatings are critical technologies for future power-generation systems and industries since the thin film will be stable at elevated temperatures prior to performing the phase transformations [7–9]. On this perspective, tailoring the mechanical properties of the thin films allows to produce a material for any specific application.

Hafnium oxide thin films are produced by several deposition techniques, among which we highlight: RF magnetron sputtering, atomic layer deposition and CVD. These processes enable rapid and homogeneous deposition of thin films and are widely discussed in review articles [10–12]. On the other hand, DC reactive magnetron sputtering have the ability to produce also nonstoichiometric films with high quality and reproducibility, generating homogeneous coatings with low deposition rate and different oxygen concentration allowing in that way, the deposition of a wide range of structures [13,14]. The aim of this work is to deposit hafnium oxide thin films by DC reactive magnetron sputtering with different Young's Modulus from the Ar/O_2 concentration variation in the deposition chamber.

2. Material and methods

HfO_x thin films were deposited on Si (100), soda-lime glass and high purity graphite substrates by reactive DC magnetron sputtering technique. The Si (100) wafers and the soda-lime glass were cleaned in ultrasound during 10 min with isopropyl alcohol, washed with acetone and then washed in DI water. High purity graphite substrates were mirror polished up to grade 4000 sandpaper. A 99.95% pure hafnium target was used as starting material. The vacuum chamber was pumped to a pressure of at least 5×10^{-5} Pa and then filled with a mixture of argon (Ar 6.0) and oxygen (O_2 5.0) until the working pressure of 2×10^{-1} Pa was reached. In the sputtering process the power source (Advanced Energy USA) was maintained constant power of 100 W. The depositions of the films were dynamically controlled by the Ar/O_2

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partial pressure ratio using a gas analyzer attached to de vacuum chamber. This system allows to produce oxide coatings with structures from the metal phase to the stoichiometric oxide, as presented on Table 1. Each Ar/O_2 condition was deposited on all the substrates in one single process. The Ar and O_2 partial pressures were controlled and monitored using a mass gage controller (QMG) inside a differential chamber, which is attached to the main deposition chamber. Detailed information about the deposition equipment can be found at Hübler [15].

HfO_x films deposited on soda-lime glass and Si (1 0 0) were used for X-ray diffraction patterns (GAXRD), X-ray fluorescence (XRF) and instrumented hardness tests (IHT) characterizations. GAXRD was performed by a XRD 7000 Shimadzu equipment, with Bragg – Brentano geometry, applying a Cu Kα radiation (0.15406 nm). The X-ray tube was kept on 3° and 2θ varied between 0° and 40°, always using the sample randomizer (rotating at 60 rpm) in order to standardize the diffraction intensities. IHT were carried out on a Fisherscope HV100 equipment, applying a 5 mN load-unload cycle, during 120 s. IHT were performed according to ISO 14577 regulations. Coatings on graphite were evaluated by Rutherford backscattering spectrometry (RBS) using a Tanden equipment applying an incident alpha particle beam (He++) with energy of 2.0 MeV perpendicular to the samples ($\theta = 0°$) and $\varphi = 15°$. Energy calibration was made with Au film with 2.0 MeV energy and an Hf film with 1.5 MeV. RUMP software was used to simulate and to compare theoretical and experimental samples spectra [16]. The morphological analysis was made using Bruker Dimension Icon® Atomic Force Microscope equipment in tapping mode analysis and the images were acquired in a 1 µm area with a 256 × 256 matrix and using a 1 Hz scan rate.

3. Results and discussion

IHT analyses were conducted as soon as the deposited films were removed from the vacuum chamber. Fig. 1 shows the hardness values obtained for each of the deposited coatings. Sample R23 presented the highest hardness value (20 GPa) and sample R2.5 the lowest one (9 GPa). Hardness and Young Modulus presented the same behavior. The values of hardness and elastic modulus presented in the literature vary widely depending on the thermal treatment and mechanical efforts. In general, the reported hardness values are between 1.5 GPa and 22 GPa for the metallic hafnium and from 8.5 GPa to 21 GPa for hafnium oxide, however, these properties have yet to be studied in more detail. The variation of concentration Ar/O_2 in the chamber produced thin films with different mechanical properties. Fig. 2 shows the load unload curves for the HfO_x samples where it is possible to observe distinct behaviors for the mechanical response of the films to the load. These regions, however, can be separated into four different ones, due to their diffraction patterns as showed in Fig. 3. Sample R23 presented the characteristic pattern of metallic hafnium hexagonal structures. Sample R17 presented an amorphous structure composed by a mixture of hexagonal metal structure

Table 1
The Ar/O_2 partial pressure ratio and film thickness for each samples.

Ar/O_2 ratio	Partial pressure (mbar)		Film thickness (nm)
	Ar	O_2	
R23	$6.72 \cdot 10^{-7}$	$2.92 \cdot 10^{-8}$	2312
R17	$5.57 \cdot 10^{-7}$	$3.24 \cdot 10^{-8}$	2248
R10	$8.27 \cdot 10^{-7}$	$8.07 \cdot 10^{-1}$	1714
R5	$7.92 \cdot 10^{-7}$	$1.73 \cdot 10^{-7}$	612
R2.5	$1.39 \cdot 10^{-6}$	$5.62 \cdot 10^{-7}$	328
R0.5	$1.46 \cdot 10^{-6}$	$2.62 \cdot 10^{-6}$	374

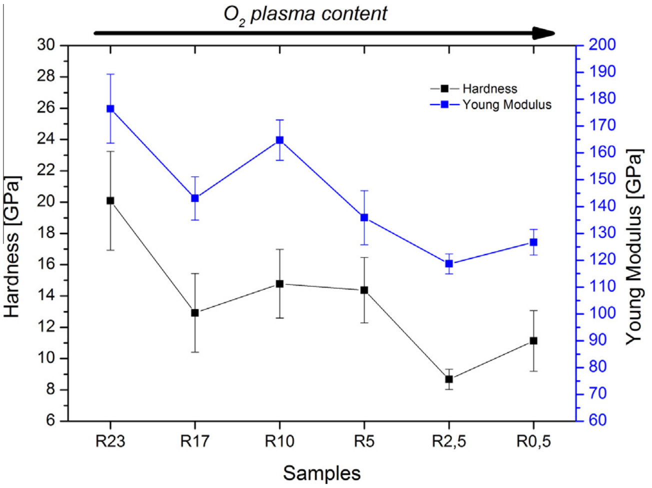

Fig. 1. Hardness and Young's Modulus for which HfO_x thin film as-deposited.

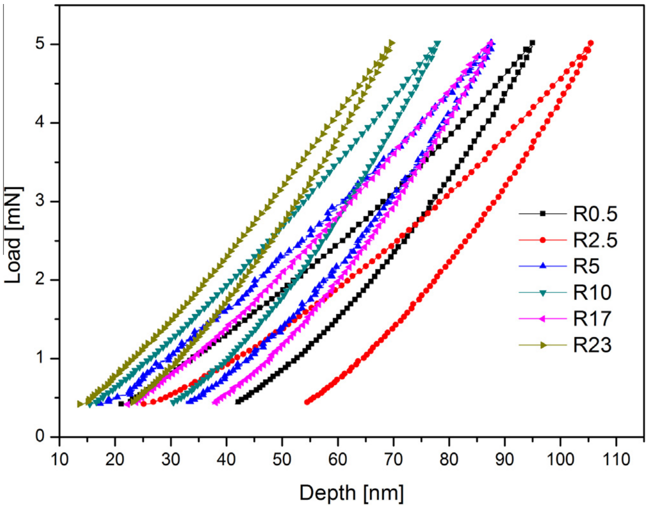

Fig. 2. Typical IHT curve for the deposited HfO_x thin films.

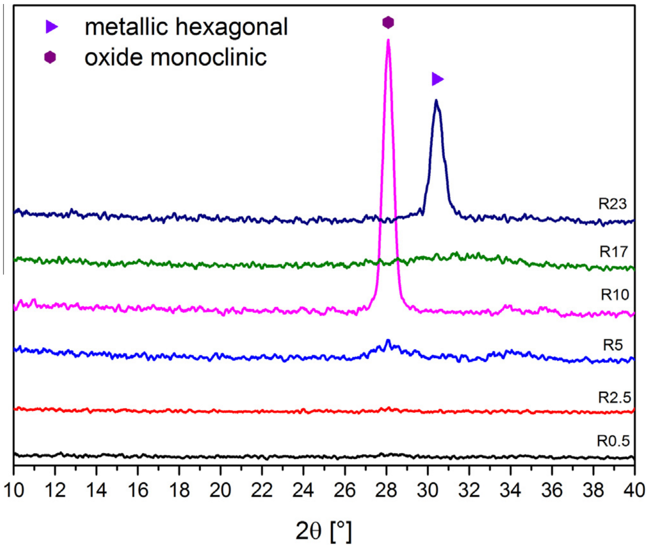

Fig. 3. GAXRD patterns for the HfO_x thin films.