Effect of the annealing temperature on the structural properties of hafnium nanofilms by magnetron sputtering

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Abstract. In this work investigated the effect of the annealing temperature on hafnium nanofilms obtained by DC magnetron sputtering on Si substrates. The nanofilms annealed through 100°C to 700°C by a High-Temperature Strip Heater Chambers (HTK-16N) on an X-ray Diffractometer (XRD). The microstructure and morphology of the films at different temperatures were investigated by XRD, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Raman Microspectrometer (RS). It was found that annealing affects changes in the lattice strains, texture, grain size, and roughness of Hf nanofilms. According to XRD data, the structure of the thin films showed amorphous from room temperature to 100°C and starting from a temperature of 200°C were changed crystallization. At 500°C a monoclinic structure corresponding to hafnium dioxide HfO₂ was formed in hafnium nanofilms.

1. Introduction

Studies of structural and morphological changes occurring in thin films upon annealing are of great interest both for understanding the fundamental and relaxation processes occurring in these films and for solving various practical problems. In recent years, nanostructured materials have become widely used in various fields of electronics, optics, for recording and storing data on magnetic media, as catalysts, in ceramic materials and nanocomposites [1-3]. For example, HfO₂ films in optoelectronic devices, optical filters, mirrors have a high reflectivity, which is applicable in high-power lasers because of their characteristic high refractive index, wide band gap, laser damage threshold, or transparency [2]. According to studies, thin HfO₂ films can crystallize at annealing temperatures above 500°C [4, 5]. The crystal structure of HfO₂ strongly affects the optical and electrical properties. The demand for inexpensive, fast and reliable electronic devices with high efficiency that has formed over the past decade has been built on silicon electronics with a native oxide high-κ gate dielectric SiO₂ until both technological and physical limits have been reached [6, 7].

The low dielectric constant of silicon dioxide (ε₀ = 3.9) is insufficient at nanometer thickness to prevent significant gate leakage currents. Among various dielectric materials hafnium oxide has attracted an acceptable band gap, excellent electrical properties and high dielectric constant [8]. High dielectric materials are also gaining increasing interest as MIM capacitors for analog/mixed signals and RF integrated circuits due to their smaller capacitor area with higher capacitance density. The electrical properties of hafnium oxide (HfO₂) and other metal oxides with high dielectric constants are currently being investigated with great interest, especially in connection with the promising
possibilities that these materials have found to replace silicon oxide in metal oxide semiconductor (MOS) transistors, involved be used carbon nanotube and bipolarity memristor [9-12].

2. Experimental materials and methods
Hafnium nanofilms were deposited on silicon substrates by direct current magnetron sputtering (DC MS) using a MVU TM Magna T. When the working chamber was evacuated, a vacuum of no more than $5 \times 10^{-4}$ Pa was achieved in it. The magnetron discharge occurred at an Ar (99.998%) working pressure of 0.5 Pa. Before deposition, the substrates were heated to 130°C for 60 seconds, then ionic cleaning was carried out (60 mA, 120 s). The targets were products of GIRMET LLC made of Hf (99.99%). They were in the form of a disk with the following dimensions: diameter – 100 mm, thickness – 6 mm. Magnetron nanofilms were deposited on silicon wafers with dimensions of 18×5 mm. Sputtering was carried out at a power of 300 W for 300 s, an argon flow rate of 0.7 liter per hour (l/h).

X-ray structural analysis was performed on a GBC EMMA diffractometer with (HTK-16N). Surface morphology was studied using an atomic force microscope (Smart SPM AistNT) minimum scanning area 1 μm² with spatial resolution along the Z coordinate – 30 pm. Changes in the chemical structure of nanofilms were studied by Raman scattering using an OmegaScope AIST-NT confocal Raman microspectrometer with high spatial and spectral resolutions: ~ 250 nm, 0.8 cm⁻¹, accordingly.

3. Results and discussion
X-ray diffraction patterns of nanofilms in the initial state and after annealing are shown in figure 1. In the spectra up to 100°C, the nanofilms were characterized by an amorphous structure. The structural transition from the amorphous to the crystalline state appeared in nanofilms upon annealing, starting from a temperature of 200°C. Obviously, it is caused by thermal activation sufficient for crystallization of nanofilms. Starting annealing from 500°C and up to the 700°C, the formation of a monoclinic structure characteristic of hafnium dioxide is appeared: Hf + O₂ → HfO₂ — plane (-111), which correlates with the data [13].

![Figure 1. Changes in the crystal structure of hafnium and hafnium dioxide nanofilms at the corresponding annealing temperatures by XRD.](image-url)
The chemical structure and its rearrangement upon heating the hafnium magnetron film was studied by the RS method (figure 2). RS spectra are represented by lines of basic hafnium oxide, analysis of changes in the intensity of the most characteristic lines of hafnium oxide (HfO₂ (A_g – 148, 370, 470 cm⁻¹) in the RS spectrum [14]. The theoretical group estimated that the monoclinic structure possesses 18 modes related to the Raman-active modes (9A_g + 9B_g). In the RS spectrum, those observed at 300 and 521 cm⁻¹ are characteristic Si lines, and the corresponding FWHM is ~ 3.4 cm⁻¹. At T_an = 700°C, the RS spectrum note an increase in the background by several times with the retention of the characteristic lines HfO₂ (148, 370, 470 cm⁻¹).

![Raman spectrum of hafnium and hafnium dioxide nanofilms at different temperatures: from 25 to 600°C.](image)

Figure 2. Raman spectrum of hafnium and hafnium dioxide nanofilms at different temperatures: from 25 to 600°C.

The calculations of the roughness values were carried out according to the standard equations for calculating the mean and root-mean-square values [15]:

\[ R_s = \frac{1}{N} \sum R_i \]  

(1)

with summation over \( I = 1, 2, 3, \ldots, N \). \( R_i \) is the change in the height of the nanostructures along the Z-coordinate, determined from the profile of the AFM image shown in table 1. Magnetron sputtering mode, in which the values of \( R_s \) (1) satisfy at least one of the following conditions:

\[ R_s = \min \{ R_{i_{min}} \} \]  

(2)

corresponded to the mode of MF formation with the highest quality surface.

In addition, according to XRD data calculated the crystallites size and the lattice strains \( \varepsilon \) from the Debye – Scherer equation [16, 17]:

\[ D = \frac{0.9 \lambda}{\beta \cos(\theta)} \]  

(3)

\[ \varepsilon = \frac{\beta}{4 \tan(\theta)} \]  

(4)

Here \( \beta \) is the peak width at half height, \( \lambda \) is the wavelength of x-ray radiation, \( \theta \) is the Bragg angle.
The XRD peak intensities in the preferred crystallographic orientation should be high compared to other XRD peaks. In partially preferred oriented thin film samples, some other XRD peaks with relatively higher intensities may also appear. Later many other researchers are also used the texture coefficient value to determine the orientation parameter for thin films sample. Texture coefficient of the \((hkl)\) planes for the films can be calculated as follows [15]:

\[
T_{\text{tex}} = \frac{I(hkl)}{\sum_{i=1}^{N} I_i(hkl)},
\]

where \(I(hkl)\) is the intensity measured from XRD pattern and \(I_i(hkl)\) is standard intensity taken from ICDD data card for a particular \((hkl)\) planes, and \(N\) is the number of diffraction peaks. The calculating results \(D\), \(\varepsilon\), \(T_{\text{tex}}\) in according equations (3), (4) and (5), analogy (2) for the roughness \(R_a\) were represented in table 1.

**Table 1.** Surface roughness, crystallite size, lattice strains and the texture results of the Hf films.

| \(T_{\text{an}}\) (°C) | 25  | 100 | 200 | 300 | 400 | 500 | 600 | 700° |
|-------------------------|-----|-----|-----|-----|-----|-----|-----|------|
| \(D\) (nm)              | 9   | 10  | 16  | 16  | 15  | 14  | 13  | 11   |
| \(\varepsilon\)         | 0.65| 0.59| 0.37| 0.36| 0.39| 0.41| 0.43| 0.69 |
| \(T_{\text{tex}}\)      | 0.5 | 0.5 | 0.9 | 0.9 | 0.9 | 0.9 | 0.8 | 0.7  |
| \(R_a\) (nm)            | 1.4 | 1.5 | 1.9 | 2.1 | 2.0 | 2.1 | 1.4 | 1    |

* – corresponded \((-111)\)

The structural phase transition of the first order, which occurs when magnetron nanofilm is heated from Hf in air at \(T_{\text{an}} = 400\)°C, was also confirmed by the calculating measurements of \(R_a\), \(D\) according to which, at the same temperature its jump-like growth occurs. According to the tabular data \(D\), \(\varepsilon\), \(T_{\text{tex}}\) and \(R_a\) have an inflection point: \(dR_a/dT_{\text{an}}\), \(dT_{\text{tex}}/dT_{\text{an}}\), \(dD/dT_{\text{an}} > 0\), but \(d\varepsilon/dT_{\text{an}} < 0\), hence \(dR_a/dT_{\text{an}}\), \(dT_{\text{tex}}/dT_{\text{an}}\), \(dD/dT_{\text{an}} < 0\), but \(d\varepsilon/dT_{\text{an}} > 0\). It was corresponds to the phase transformation Hf + O₂ = HfO₂.

**Figure 3.** Typical 2-D AFM surface topography and corresponding surface profiles of hafnium and hafnium dioxide in difference annealing temperature.

The two dimensional (2-D) typical surface topography and corresponding surface profiles were shown in figure 3 (at temperature 25, 200, 400 and 700°C) that examined using AFM with a scanning area of 1×1 µm². After annealing at a temperature of 700°C, when the surface of the nanofilm is already completely oxidized and is represented only by HfO₂, the roughness is characterized by several dimensions. It is proved that the mechanism of cluster coalescence is dominant in magnetron
sputtering of hafnium due to the additive contribution of both ballistic and kinetic aggregation, under the action of which films are formed from nanoparticles of small sizes - about 20 nm and large ones - up to 145 nm, respectively. At annealing temperatures no higher than 100°C and in the initial state, nanofilms were formed from metal hafnium height of nanoparticles size about 8 nm. Starting from 200°C and up to 600°C, nanofilms are represented by height of nanoparticles sizes up to 12 nm, increase height of nanoparticles sizes 20 nm at 700°C.

The results of particles size distributions – \( N(d) \) from AFM images of magnetron nanofilms from Hafnium are shown in figure 4, which shows the values of \( d \) - the maximum value of the particle size, as well as the interval of changes \( \Delta d \) at the level of 0.5. The characteristic particle dimensions varied in the range: \( d \pm \Delta d = [29 \pm 16 \text{ nm} \ (T_R), \ 27 \pm 15 \text{ nm} \ (100°C), \ 29 \pm 15 \text{ nm} \ (200°C), \ 31 \pm 14 \text{ nm} \ (300°C), \ 35 \pm 20 \text{ nm} \ (400°C), \ 46 \pm 20 \text{ nm} \ (500°C), \ 43 \pm 30 \text{ nm} \ (600°C) \) and 28 \pm 9 nm (700°C)]. A Gaussian normal distribution is superimposed on this particle size diagram: \( N(d) = 1/(2\pi\sigma^2)^{1/2}\exp[-(d - d_{av})^2/(2\sigma^2)] \), where \( d_{av} = \Sigma d_i/N \) – is the average value of the cluster size, \( \sigma = [\Sigma(d_{av} - d_i)^2/(N(N-1))]^{1/2} \) - root-mean-square value of the cluster size or variance. The granulometric data coincide most fully with the Gaussian dependence at \( \sigma = 0.7 \) in the region of nanoparticles with large sizes (more than 28 nm), whereas in the region of small nanoparticles this distribution obeys the Cauchy-Lorentz distribution: \( P(x, m, b) = (1/\pi b)/[(x-m)^2 + b^2] \), where, \( m \) is the mean value, \( b \) is the scale parameter of the half-width at half-height [18].

![Figure 4](image_url)

**Figure 4.** The particles size distributions of nanofilms from hafnium and hafnium dioxide.

The SEM images of the HfO\(_2\) films, annealing at different temperature are shown in figure 5. The amorphous structure of the nanofilms is evident in the annealing temperature growth at \( T_R \). The crystalline nature of the \( T_{an}=500-700°C \) possess a uniform distribution of dense particles spherical in shape, the EDS analysis of the HfO\(_2\) thin film shown in figure 5e. The average particles size was
increase 70 nm ($T_R$) to 78 nm with the increase $T_{an}$ up to 500°C but the decrease in particles size from 78 nm (500°C) to 65 nm (600°C) and 55 nm (700°C) by the effect of monoclinic structure thin film.

![Figure 5. SEM images of the HfO$_2$ films growth at various annealing temperature (a-d) and the EDS analysis (e).](image)

4. Conclusions
Magnetron hafnium nanofilms deposited on a single-crystal silicon substrate by DC magnetron sputtering in a mode satisfying the quality criterion. By increasing of the annealing temperature the value of the roughness, texture and size of nano crystallite is increased, but can see after annealing the 500°C these values are decreased. The lattice strains of hafnium and hafnium dioxide are decreased by the increasing of annealing temperature. Based on the XRD, AFM and SEM analysis of the deposited and annealed HfO$_2$ samples in O$_2$ ambient, we have shown that higher temperature annealing will lead about the transformation of amorphous structure to crystalline structure (monoclinic phases) and result in smoother surface and spherical finer uniform grain.

References
[1] Ananthakumar Ramadoss, Karthikeyan Krishnamoorthy and Sang Jae Kim 2012 Mater. Res. Bull. 47(9) 2680
[2] Khan S B, Hui W, Ma L, Hou M and Zhang Z 2017 Advanced Materials Interfaces 4(6) 1600892
[3] Vargas M, Murphy N R and Ramana C V 2014 Opt. Mater. 37 621-8
[4] Shim J, Rivera J A and Bashir 2013 Nanoscale 5(22) 10887-93
[5] Miyata N 2018 Appl. Phys. Lett. 113 251601
[6] Kim M-K, Jin Sub Jang, Soon-Gil Yoon, Ju-Youung Yun and Nak-Kwan Chung 2020 Materials 13(9) 13092008
[7] Tianran Li et al 2020 Nature Electronics 3 473-8
[8] Rudenja S, Minko A and Buchanan D A 2010 Appl. Surf. Sci. 257(1) 17-21
[9] Martínez F L, Toledano-Luque M, Gandía J J, Cárabe J, Bohne W, Röhrich J, Strub E and Mártí I 2007 J. Phys. D: Appl. Phys. 40(17) 5256
[10] Khairnar A G and Mahajan A M 2013 Solid State Sci. 15 24-8
[11] Daneshvar F, Chen H, Noh K and Sue H-J 2021 Nanoscale advances 3 942-62
[12] Aleshin A N, Zenchenko N V and Ruban O A 2021 Tech. Phys. Lett. 47(13) 39-42 [in Russian]
[13] Sadaf Bashir Khan, Zhengjun Zhang and Shern Long Lee 2020 J. Alloy. Compd. 816 152552
[14] Vescio G, López-Vidrier J, Leghrib R, Cornet A. and Cirera A 2016 Journal of Materials Chemistry C 4(9) 1804-12
[15] Kuzmenko A P, Naw Dint, Kuzko A E, Myo Min Tan, Thant Sin Win and Kolpakov A I 2016 Materials of Electronics Engineering 19(3) 195-203 [in Russian]
[16] Prajapati C S and Sahay P P 2011 Sensor. Actuat. B-Chem. 160(1) 1043-9
[17] Pandey A, Dalal S, Dutta S and Dixit A 2021 J. Mater. Sci-Mater. El. 32(2) 1341-68
[18] Budaev V P and Khimechenko L N 2008 Problems of Atomic Science and Technology, ser. Thermonuclear Fusion 3 34-61 [in Russian]