Vacuum 155 (2018) 339–344

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Effects of annealing on quality and stoichiometry of HfO_2 thin films grown by RF magnetron sputtering

Arun Vinod, Mahendra Singh Rathore, N. Srinivasa Rao*

Department of Physics, Malaviya National Institute of Technology Jaipur, J L N Marg, Jaipur, 302017, India

ARTICLE INFO

Keywords:
HfO_2 films
Annealing
XPS
Leakage current
Skewness
Kurtosis

ABSTRACT

In this paper, the effects of annealing temperature on HfO_2 thin films prepared by RF sputtering have been investigated. Thin films of hafnium oxide were deposited using sputtering onto p-type Si substrates and the pristine films were annealed at different temperatures in air atmosphere to obtain crystallinity. The Raman and XRD results of the as-deposited films show amorphous nature, whereas the annealed films at 600 °C results in crystallization. AFM was used to study the surface morphology of the films and to estimate the skewness, kurtosis and the roughness values. The core level orbitals of Hf 4f spectra of as-deposited films not only reveal the formation of hafnium rich hafnium oxide but also nearly stoichiometric composition of HfO_2 and exhibit a shift in binding energy with annealing. Electrical measurements of the films suggest that the leakage current is increased for crystalline films as compared to the as-deposited ones. The effects of annealing temperature on quality and stoichiometry of hafnia thin films and their possible applications are reported.

1. Introduction

In recent years, the demand for low cost, faster and reliable electronic devices with high efficiency has attracted considerable attention. For decades, the silicon industry relied on SiO_2 gate dielectric until the scaling down of the dielectric has reached both technological and theoretical limits [1,2]. Further shrinkage of SiO_2 gate dielectric thickness restrained due to permittivity and electron tunneling effect [3]. Due to the aforementioned difficulties, an alternative replacement for SiO_2 gate material has gained great interest. Among various dielectric materials such as Al_2O_3, ZrO_2, La_2O_3, SrO, Y_2O_3 and HfO_2, hafnium oxide has received significant focus due to its thermodynamical stability, reasonable energy gap, excellent electrical properties and high dielectric constant [4]. Moreover, the unique combination of structural, optical and electrical properties of HfO_2 films is used for various electronics and optoelectronics applications.

In optoelectronic applications, hafnium oxide thin films are very useful for anti-reflection coating in optical waveguide devices to reduce the Fresnel loss [5]. HfO_2 thin films are also being used as protective coating for electrical applications due to the hydrophobic effectiveness for outdoor insulators [6]. Moreover, in the electrical application, the presence of large conduction band offset in HfO_2 helps to attain lower operational voltage and makes it suitable for low leakage current application. The electrical properties such as capacitance and leakage current density of HfO_2 thin films drastically change with annealing [7]. For industrial application, low temperature annealing is required in the production process and HfO_2 thin films undergo phase transition from amorphous to crystalline even at low temperatures [8]. The formation of grain boundary due to crystallization, increases the leakage current and degrades the device performance [9]. Thus, the growth of high purity, quality and stoichiometry thin films and modulation of their properties under various conditions are of great interest for solid-state devices and communication. This attracts huge demand for the growth and optimization of high-quality HfO_2 thin films.

There are various physical and chemical methods employed to grow HfO_2 thin films such as electron beam evaporation, reactive dc sputtering, RF magnetron sputtering, metal-organic molecular beam epitaxy and atomic layer deposition [10–15]. RF magnetron sputtering has various advantages like less wastage of the material, high adhesion of films and excellent uniformity with good packing density as compared to other methods. Recently, Das et al. had reported the utmost importance of high-quality HfO_2 thin films and its incorporation into a low dimensional semiconductor technology [16]. Nam et al. and He et al. reports the formation of stoichiometric HfO_2 thin films at high temperature annealing [17,18]. The variation in electrical and structural properties of HfO_2 based MOS capacitance with low surface roughness was studied by Khairnar and Mahajan [10]. This study shows that there is an utmost need to correlate stoichiometry, surface roughness and crystallinity for better electrical application. Our work aims at the systematic and detailed study of the growth and optimization of RF

* Corresponding author.
E-mail address: srnelamarri.phy@mnit.ac.in (N. Srinivasa Rao).

https://doi.org/10.1016/j.vacuum.2018.06.037
Received 25 November 2017; Received in revised form 11 June 2018; Accepted 12 June 2018

magnetron sputtered HfO_2 thin films and the correlation of the effects of annealing temperature (200,400 and 600 °C) in air atmosphere on the stoichiometry, surface roughness and crystallinity of HfO_2 thin films for various applications from a basic and applied scientific perspective.

2. Experimental details

Hafnium oxide thin films were deposited by RF magnetron sputtering method onto a p-type silicon (100) substrates with resistivity of 1–10 Ωcm. The substrates were thoroughly cleaned by standard Radio Corporation of America (RCA) I and II process before deposition. For sputtering, HfO_2 target purchased from ACI Alloys, USA of purity 99.999% (5 N) was used. The target was placed in a 2-inch holder, at a distance 10 cm from the substrates. Initially, the chamber was evacuated to a high vacuum pressure of 6×10^{-6} mbar using a rotary assisted turbo pump. The working pressure was maintained at 3×10^{-3} mbar by introducing high purity Ar gas (99.99%) into the chamber using mass flow controller. The Ar flow rate and RF power were kept constant (20 sccm and 100 W) during deposition. Prior to deposition, the target was pre-sputtered for 10 min to remove surface contamination, if any, present. The substrate holder was rotated at low rpm to get uniform films, and the thickness of the film was around 25 nm as measured by a digital thickness monitor (DTM). After the deposition, annealing of the samples was carried out using a muffle furnace in air at different temperatures viz. 200 °C, 400 °C and 600 °C for 30 min with a ramp rate of 10 °C/min.

Raman spectra of the films were obtained using confocal micro-Raman spectrometer, which incorporates a solid-state laser of 532 nm. The crystal structure and the orientation of the films have been investigated using PANalytical X'pert Powder X-ray diffractometer with Cu K_α radiation (1.5406 Å). The surface morphology of the films was studied using Bruker atomic force microscopy and the roughness, skewness and kurtosis values were estimated using NanoScope Analysis software. The chemical states and composition of films were examined using X-ray photoelectron spectroscopy (XPS) with a monochromatic Al K_α (hυ = 1486.6eV) X-ray radiation under a base pressure of 6×10^{-10} mbar using an Omicron Nanotechnology (ESCA+) from Oxford Instruments. For electrical measurements, Al contacts with diameter ~1 mm and thickness around 250 nm were deposited using electron beam evaporation. The electrical measurements were carried out using B1500A Semiconductor Device Analyzer with frequency 1 MHz at room temperature.

3. Results and discussion

The Raman spectra of HfO_2 thin films in the range of 120–600 cm^{-1} are depicted in Fig. 1. The broad peak around 150 cm^{-1} for the films annealed at 200 °C indicates the amorphous nature of the hafnia films. The peaks around 302 and 520 cm^{-1} correspond to acoustic and optical phonon modes the Si substrates [19,20]. For samples annealed at 600 °C, the origin of a new peak at 147 cm^{-1} is observed, which is attributed to the A_g mode in HfO_2 monoclinic structure. It is evident from the spectra that crystallinity increases with an increase in annealing temperature and there is a phase transformation from amorphous to crystalline structure at high temperature. Theoretical analysis predicts that for monoclinic structures, there are 36 phonon modes present, out of which 18 ($9A_g + 9B_g$) are Raman active modes, 15 are IR active modes and other three are zero-frequency translation modes [21]. In addition, the modes of HfO_2 have been studied by Zhou et al. [22] using density functional perturbation theory. The results obtained are in good agreement with the reported phonon modes of monoclinic structures [21–25]. The bands occurred at 130-300 cm^{-1} are mainly due to Hf-Hf vibrations [25].

XRD patterns of the pristine and annealed films are shown in Fig. 2. The XRD spectra of the as-deposited and films annealed upto 400 °C reveal amorphous nature. A phase transition from amorphous to

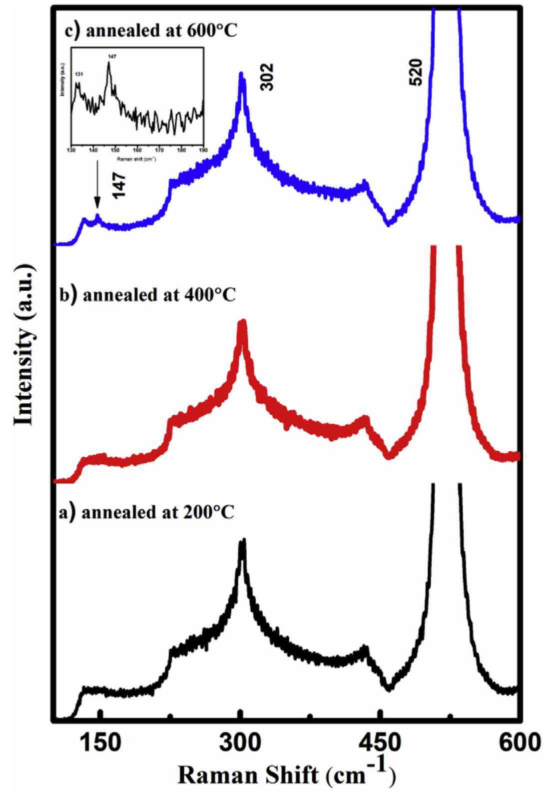

Fig. 1. Raman spectra of HfO_2 thin films annealed at a) 200 °C b) 400 °C c) 600 °C.

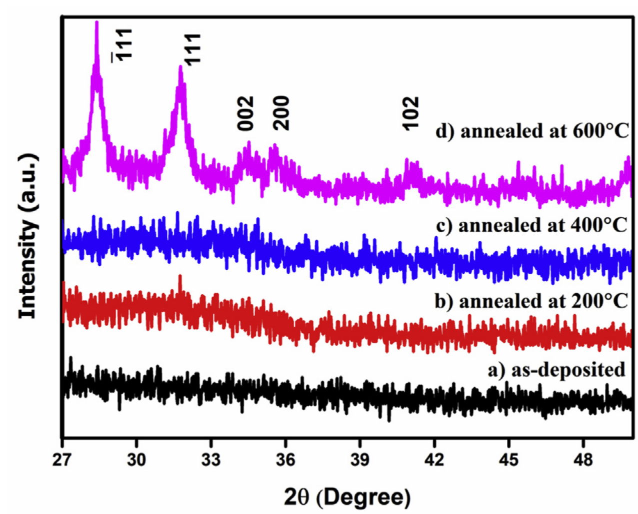

Fig. 2. X-ray diffraction pattern of as-deposited and annealed HfO_2 thin films.

crystalline observed for films annealed at 600 °C. The phase transition could be due to the attainment of required activation energy in the form of temperature for rearrangement of atoms leading to crystallization of films [26]. The films annealed at 600 °C exhibit monoclinic phase of HfO_2 with polycrystalline nature as evident from ($\bar{1}$11), (111), (002), (200) and (102) planes [27]. The crystallite size is calculated using Scherrer formula [28] and it is found to be around 17 nm.

The surface morphology of the as-deposited and annealed films is presented in Fig. 3. AFM images show rms roughness of pristine and annealed films up to 400 °C is around 0.20 nm. The images indicate that films are smooth, uniform and high-quality without any cracks, which make them suitable for the possible optoelectronic application. Further,