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Evolution of microstructural and electrical properties of sputtered HfO_2 ceramic thin films with RF power and substrate temperature

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Abstract

Hafnium oxide (HfO_2) ceramic thin films were deposited on p-type silicon substrate by radio frequency magnetron sputtering at various RF powers and substrate temperatures. The morphological and electrical properties of the sputtered films were investigated and a correlation between the surface and interface properties of the HfO_2 films was established with the variation of sputtering parameters. The evolution of monoclinic structure of the hafnium oxide thin films was observed by XRD studies. The surface of the HfO_2 ceramic thin films became smooth with the decrease in grain size for higher power and growth temperature. The characteristic FTIR absorption peaks in the range from 550 cm^{-1} to 900 cm^{-1} depicted the formation of Hf–O bond for all the samples. The oxide charge density and leakage current density was found to be increased with the increase in RF power and substrate temperature, which was mainly due to the evolution of smaller grains. HfO_2 thin films, grown at room temperature with a RF power of 150 W, have shown better electrical properties.

Keywords: Hafnium oxide; Ceramic thin films; Sputtering; SEM; *C–V*

1. Introduction

In recent years, tremendous research on the development of high quality Zirconia (ZrO_2), Hafnia (HfO_2), Titania (TiO_2) ceramic thin films are under active consideration in order to replace the conventional low-k dielectric material such as SiO_2 [1–3]. However, ZrO_2 thin films are not compatible with polysilicon gate electrode because of formation of Zr-silicide, which in fact gives rise to high leakage current and electrical shorting of the poly/ZrO_2 metal oxide semiconductor (MOS) capacitors [4]. On the other hand, TiO_2 thin films are not thermodynamically stable with silicon for electronic applications [5]. Therefore, hafnium oxide (HfO_2), a high temperature refractory ceramic material, has drawn great interest in the field of structural ceramics, optics, electronics and electroceramics due to its high density (~ 10 g/cm^3), wide bandgap (>5 eV), good thermal and chemical stability, high dielectric constant, low leakage current and excellent mechanical properties [2,6–13]. In addition, HfO_2 thin film has ability to reduce the mobility of 2-D semiconductor based transistors due to the suppression of both charged impurity scattering as well as phonon scattering [14–15]. Therefore, an extensive research on the development of high quality HfO_2 ceramic thin film is highly required prior to its incorporation into the low-dimensional semiconductor technology. Various methods such as Pulsed Laser Deposition [16], Chemical Vapor Deposition [17], e-beam evaporation [18] and radio frequency (RF) magnetron sputtering [19] were adopted to deposit the HfO_2 films on the silicon substrate. Among them, RF magnetron sputtering technique has several advantages such as low thermal budget, ease of handling, less consumption of source materials, nontoxic nature, possibility of multi-target processing, good reproducibility and ability to produce films of better quality. The electrical properties of the ceramic thin films not only depend on the methods of fabrication, but also mostly

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depend on the growth parameters. Therefore, a systematic study on the evolution of microstructural properties of HfO$_2$ ceramic thin film is utmost important in order to understand its electrical behavior. In the present work, microstructural and electrical properties of the HfO$_2$ thin films are investigated and correlated with the variation in the sputtering parameters such as RF power and substrate temperature.

2. Experimental

Hafnium oxide thin ceramic films were deposited by RF magnetron sputtering technique on p-type silicon [(100), 1–10 Ω cm] wafers using pure hafnium target (99.995%) in presence of high purity argon and oxygen gases at a flow ratio of 3:2. Ceramic thin films were sputtered at 4×10^{-3} mbar by varying RF power from 75 W to 300 W. Thereafter, a series of experiments were performed by varying substrate temperature from room temperature to 300 °C. During the entire deposition process, the substrates were rotated in order to obtain uniform ceramic thin films. The thickness of HfO$_2$ films was kept around 20 nm.

The structural properties of HfO$_2$ ceramic thin films were investigated by X-ray diffraction system (Rigaku ultima IV), whereas the morphological studies were carried out using scanning electron microscope (JEOL JSM-7001F) and atomic force microsope (Asylum research system). Fourier transform infrared spectroscopy (FTIR) studies were carried out using Thermo scientific Nicolet 6700 system in order to get the bonding information. The MOS capacitors were fabricated, through shadow mask, by thermal evaporation technique with Al as top and bottom electrodes. The capacitance–voltage (C–V) and leakage current density–voltage (J–V) measurements for the Al/HfO$_2$/Si MOS structures were performed using an Agilent E4980A precision LCR meter and Keithley 6487 Picoammeter/ Voltage source, respectively.

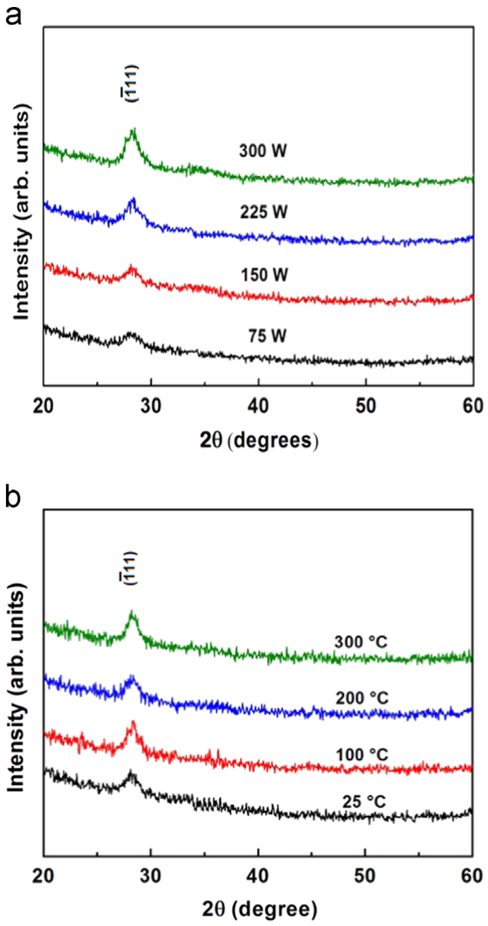

Fig. 1. XRD patterns of the HfO$_2$ thin films deposited at different (a) RF powers, and (b) substrate temperatures.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the HfO$_2$ thin films deposited at different RF powers on silicon substrates. A weak and broad $\left(\bar{1}11\right)$ peak is observed for all the samples, which is attributed to the monoclinic phase of HfO$_2$ films [20]. Similar results are obtained by other researchers [21,22]. The broadening of weak diffraction peaks signifies the existence of a mixed structure of amorphous and crystalline phase in the ceramic thin films, where small crystallites being present in an amorphous matrix as reported by Vargas et al. [21]. The appearance of only dominated $\left(\bar{1}11\right)$ may be due to the lower film thickness, where the initial few interfacial Hf–O–Si layer may have amorphous like behavior, which limits the growth of other crystalline phases [21,23]. The presence of the anisotropy nature in the crystalline material is due to the differences in the strain energy densities, which varies with the variation of the crystalline direction. Hence, the growth favors such a direction, where the strain energy becomes minimum [23]. The appearance of $\left(\bar{1}11\right)$ orientation of HfO$_2$ films may be due to the minimizations of the internal strain-energy in the film during the film growth. The $\left(\bar{1}11\right)$ peak intensity marginally improved with power, which may be due to the increase in adatoms energy at higher RF power. Fig. 1(b) indicates the evolution of HfO$_2\left(\bar{1}11\right)$ peak at various substrate temperatures. However, the increase in substrate temperature did not show any significant improvement on the crystallinity of the sputtered ceramic films.

The SEM images of HfO$_2$ thin films, deposited at various RF powers, are shown in Fig. 2. Uniform surface morphology with homogeneously distributed grains is observed for the sputtering power of 300 W. SEM micrographs of HfO$_2$ films with different substrate temperatures are shown in Fig. 3, where a uniform surface morphology is observed for the films deposited at higher substrate temperature. The average grain size was decreased from 30 nm to 24 nm with the increase in RF power, whereas a reduction in the average grain size from 32 nm to 19 nm is observed for the rise in substrate temperature. The three dimensional (3-D) surface topography and atomic structures were examined using atomic force microscopy with a scanning area of 1 μm × 1 μm. The AFM micrographs of the features of HfO$_2$ film deposited by different RF power and substrate temperature are shown in the Fig. 4 and Fig. 5 respectively. The root mean square (RMS) roughness was estimated by using the standard expression [24]. The estimated RMS roughness of the ceramic thin films is plotted in Fig. 6 with different sputtering parameters, where the