Physica B 482 (2016) 43–50

Contents lists available at ScienceDirect

Physica B

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

# Interface and electrical properties of ultra-thin $HfO_2$ film grown by radio frequency sputtering

Madhuchhanda Nath, Asim Roy *

*Department of Physics, National Institute of Technology Silchar, Silchar 788010, Assam, India*

ARTICLE INFO

*Article history:*
Received 28 November 2015
Accepted 5 December 2015
Available online 8 December 2015

*Keywords:*
Thin film
rf sputtering
High-k

ABSTRACT

Interfacial composition and electrical properties of ultra-thin hafnium oxide ($HfO_2$) films on p-type $<100>$ Si substrate are reported. Hafnium oxide ($HfO_2$) thin films are prepared using radio-frequency sputtering method and subsequently annealed at different temperature. The effect of post-deposition annealing on the interfacial and chemical state of $HfO_2$/Si gate stack has been characterised by means of X-ray reflectivity and X-ray photoelectron spectroscopy studies. Peaks of X-ray photoelectron spectroscopy spectra at 530.50 and 532.25 eV originate from Hf–O–Si bond illustrated the creation of Hf-silicate based interfacial layer at the high-k/Si interface. X-ray reflectivity fitting result also corroborated the formation of Hf silicate interfacial layer. Capacitance-voltage measurements revealed insignificant hysteresis in case of film annealed at 600 °C. Interface trap density has been extracted using Terman method and is found to be $3.18\times10^{-11}$ cm$^{-2}$ eV$^{-1}$ at $-1.0$ V. Minimum equivalent oxide thickness (EOT) of 1.3 nm was obtained for the film annealed at 600° C. The gate leakage current density of the $HfO_2$ film annealed at 600 °C is $1.5\times10^{-5}$ A/cm$^2$ at a bias voltage of $-2$ V.



## 1. Introduction

With the down scaling of advanced complementary metal oxide semiconductor (CMOS) field effect transistors, the $SiO_2$ gate oxide has become too thin ($<2$ nm) to prevent leakage currents resulting from tunnel effects [1–4]. Reduction of leakage current for CMOS with 22 nm node will demand an effective oxide thickness (EOT) value in the order of 1 nm [5–7]. Once the gate thickness reduces to 1–5 nm range, parameters like interface state density and interface of gate oxide with the substrate dominates the electrical characteristics of MOS capacitor. Therefore, examination of the features of the interface between the high-k and the Si substrate is essential. Recently many high-k dielectric have been introduced with thickness in the sub-nanometre range to replace $SiO_2$ gate dielectric material [8–12]. Out of these, $HfO_2$ appeared to be a probable gate dielectric in MOS capacitor as this material has some better qualities over other oxides such as dielectric constant (24), a wide energy band gap $E_g$ (5.7 eV) and better compatibility with Si substrate [13–15]. A large number of reports claimed that the oxide charges present in the bulk oxide and the interface state charges greatly influence the performance of high-k oxide [16]. The oxygen vacancies which get incorporated in the bulk oxide during deposition are the principal sources of oxide charges and bulk defect in $HfO_2$ thin films [17]. These defects can be efficiently reduced by post deposition heating in oxygen environment. Annealing also leads to a decrease in leakage current. But it causes a decrease in capacitance due to an unwanted interfacial layer formed at the semiconductor-oxide interface [18]. It still remains a critical challenge to simultaneously obtain both high capacitance density and low current density. Hence, it is essential to examine the performance of $HfO_2$ thin films for various annealing temperatures and optimise the temperature at which MOS capacitor shows the best performance. Researchers have prepared $HfO_2$ thin films by various methods for example, atomic layer deposition [19,20] (ALD), electron beam evaporation [21] (EBE), sol–gel method, chemical vapour deposition (CVD) [23,24] pulsed laser deposition (PLD) [22], and sputtering [25,26]. Out of all the mentioned techniques, radio-frequency (RF) sputtering is used very often to prepare oxide films as this method provides some advantages compared to other deposition methods [27,28]. Here, we report the effect of annealing at different temperatures on the electrical characteristics of $HfO_2$ films prepared by RF sputtering using a $HfO_2$ target. The electrical properties of a MOS capacitor can be best judged by analysis of its (*C–V*) and (*I–V*) characteristics. The (*C–V*) curves in case of an ideal MOS capacitor are frequency independent. But, frequency dispersion in (*C–V*) curves occur primarily due to the existence of interface states. The changes in frequency response of the interface states can be observed from the $G_p/\omega$ vs frequency curves at different voltages. Such detailed analysis of electrical properties of $HfO_2$ thin film will

* Corresponding author.
*E-mail address:* 28.asim@gmail.com (A. Roy).

http://dx.doi.org/10.1016/j.physb.2015.12.007
0921-4526/

improve the understanding of Physics of $HfO_2$ based MOS device reliability.

## 2. Experimental details

We have prepared hafnium oxide ($HfO_2$) thin films with thickness in the range of 5 nm by radio-frequency (rf) sputtering technique. P-type Si (100) having resistivity 1–20 Ω/cm is used as a substrate. Piranha cleaning method has been used for cleaning the Si substrate. Various parameters during the deposition of $HfO_2$ were set as follows; rf power 100 W, time of sputtering 30 min, working pressure 0.180 mbar. The detailed procedure is described elsewhere [25]. Post deposition annealing were performed in an oxygen ambient for 60 min in a resistive quartz furnace at four different temperatures 400 °C, 500 °C, 600 °C and 700° C. Aluminium was deposited by using thermal evaporation technique to form gate electrode on $HfO_2$ thin film through shadow mask. The area of the fabricated capacitor is $7.06 \times 10^{-4}$ cm$^2$. The electrical characterisations of the fabricated MOS capacitors were performed using Keithely semiconductor parameter analyser (4200 SCS). The film thickness was measured by grazing incidence X-ray reflectivity (GIXRR) measurements. Grazing incidence X-ray reflectivity measurements were performed with CuKα ($\lambda = 0.15418$ nm) radiation in a Philips X-Pert PRO-MRD diffractometer operated at 45 kV and 40 mA. The reflectivity measurement was made in $\theta$–$2\theta$ scan. The angular resolution of the goniometer is 0.0002°. The chemical states of $HfO_2$/Si structures were studied by X-ray photoelectron spectroscopy (XPS) (ULVAC, PHI, Inc., Japan). For easy reference, the sample annealed at 400 °C, 500 °C, 600 °C and 700 °C are named as S4, S5, S6 and S7.

## 3. Result and discussion

### 3.1. X-ray photoelectron spectroscopy

To examine the interface and its chemical composition of the $HfO_2$/Si heterostructures, XPS studies were accomplished for $HfO_2$ films after heat treatment at 600 and 700 °C. Peak positions of the XPS spectra will enable to identify the chemical composition of the interfacial layer. Calibration of core levels was done by setting the carbon 1s peak at 284.6 eV. XPS spectra of the samples annealed at 600 and 700 °C are presented in Fig. 1. Peaks at the BE of 17.58 eV and 19.12 eV as shown in Fig. 1 correspond to Hf $4f_{7/2}$ and Hf $4f_{5/2}$, respectively, which is related to Hf–O bonding in $HfO_2$ for the sample annealed at 600 °C [29]. The obtained spin–orbit splitting (~1.54 eV), matches well with the reported value obtained by many researchers [30,31]. Above analysis confirm the formation of $HfO_2$ film. The shift of peak positions to 18.11 and 19.65 eV corresponding to Hf $4f_{7/2}$ and Hf $4f_{5/2}$, respectively, in the spectrum of sample S7 ( annealed at 700 °C) may be attributed to the oxidation of more Hf elements and also the formation of Hf silicate during the annealing process [32,33].

To inspect the nature of the interfacial layer on the silicon substrate, the xps spectra of O1s core-level of the annealed films are obtained as shown in Fig. 2. O 1s core level spectra located at 529.75 eV for the film annealed at 600 °C shifts to 530.50 eV after annealing at 700 °C, as shown in Fig. 2. Furthermore, upon close observation of the curve for the sample annealed at 700 °C, a kink appears at about energy 532.25 eV in addition to the main peak at 530.50 eV. However, no such kink or shoulder is observed in the spectrum of sample S6, which implies the non-formation of silicate at oxide-semiconductor interface for S6. The peaks located at 529.75 and 530.50 eV for the sample S6 and S7, respectively, is attributed to O in $HfO_2$ film which is similar to other reported

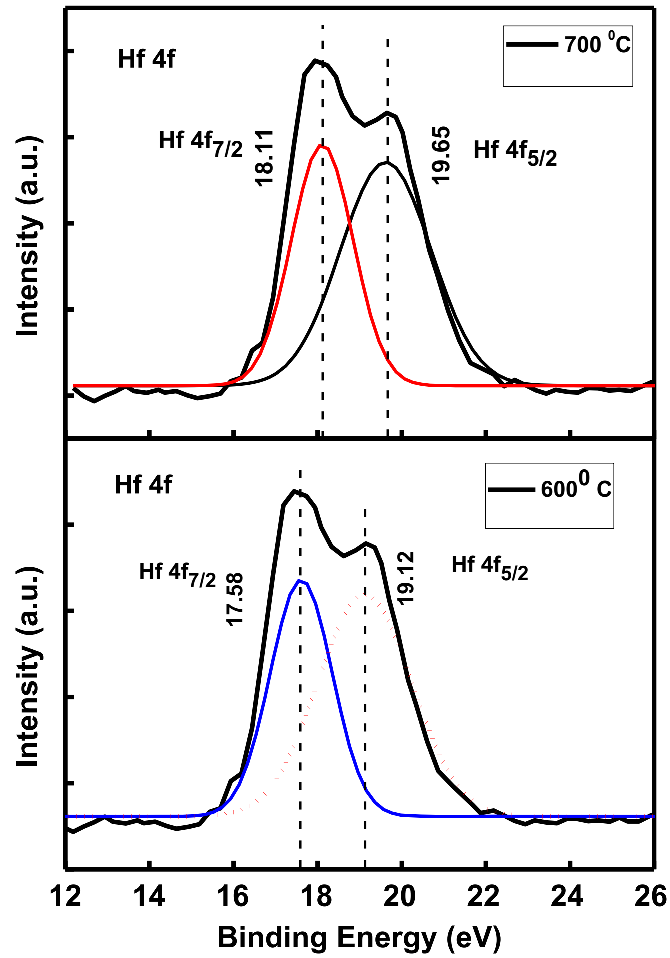


**Fig. 1.** Hf 4f regions XPS spectra of $HfO_2$ ultrathin films deposited on Si and annealed at 600 and 700 °C.

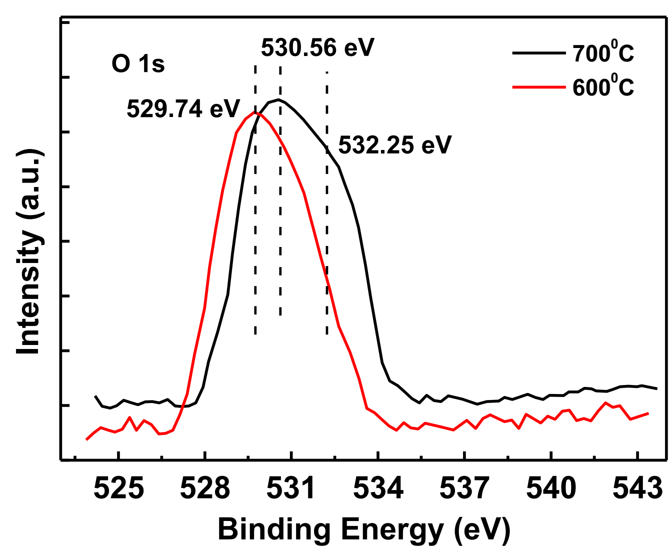


**Fig. 2.** XPS spectra of the $HfO_2$ ultrathin films as a function annealing temperatures.

values [34–36]. Wang et al. reported that fully oxidized $HfO_2$ has O 1s peak at 530.6 eV. The appearance of the peak at 532.25 eV in case of sample S7 may be attributed to oxygen in Hf-silicate or in O–Si bonds and in general cannot be differentiated the source of origin from the spectrum alone [37].