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Study of rapid thermal annealing on ultra thin high-*k* HfO_2 films properties for nano scaled MOSFET technology

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ABSTRACT

The effect of rapid thermal annealing on structural and electrical properties of high-*k* HfO_2 ultra thin films deposited by rf-sputtering system is investigated. The films properties were investigated for optimum rapid thermal annealing temperature in oxygen and nitrogen ambient, respectively to get the best electrical results as a MOS device structure. Detailed studies of temperature induced annealing effects on the HfO_2/Si interface are done using Fourier Transform Infrared Spectroscopy (FT-IR). The film thickness, composition and microstructure is studied by Ellipsometry, XRD and AFM, respectively, and the effect of annealing on these parameters is shown. The *I–V* and *C–V* characteristics of the annealed dielectric film were investigated employing Si/HfO_2/Si MOS capacitor structure. The results showed that the HfO_2/Si stack with rapid thermal annealing (RTA) in nitrogen ambient showed improved physical and electrical performance than with in oxygen. It is shown that RTA improves the interface properties of HfO_2/Si and the densification of HfO_2 ultra thin films. The as deposited films were amorphous and orthorhombic after annealed at 700 °C in nitrogen and oxygen, respectively. We found that the nitrogen annealed samples exhibit a reduced equivalent oxide thickness, interfacial density of states, capacitance–voltage hysteresis and leakage current; additionally it also showed negligible charge trapping under positive voltage bias and temperature stress. The results are presented and discussed.

1. Introduction

High-*k* dielectric materials have been considered as alternative gate oxides to overcome the scaling limit of SiO_2 due to high tunneling and reliability concerns.

Among the various high-*k* dielectrics materials HfO_2 is considered as one of the most promising materials [1–7]. HfO_2 exhibits desirable properties including a high dielectrics constant, high density, large bandgap, and a good thermal stability in contact with silicon relative to the other high-*k* materials. For ultrathin regime of equivalent oxide thickness (EOT) <1 nm, penetration of oxygen and impurities should be suppressed to maintain low EOT and reduce flatband voltage fluctuation. Many issues such as electrical performance and thermal stability are directly affected by that interface [8–10]. Other studies on the thermal behavior of HfO_2 reported relatively poor stability and formation of metallic silicide [11–14]. Those studies report crystallization and morphological changes in the HfO_2 films. Some annealing studies reported changes in the interfacial chemical structure that suggest silicide formation [15]. However, the physical and electrical properties of HfO_2 suffer from its crystallization at high temperature during post deposition annealing, which in turn induces higher leakage current and severe boron penetration issues [16,17]. High temperature annealing leads to fast diffusion of oxygen through the HfO_2, resulting in the growth of uncontrolled low-*k* interfacial layers [11]. The uncontrolled low-*k* layers pose a serious limitation to further scaling of the equivalent oxide thickness (EOT) for HfO_2 gate dielectrics. Nevertheless, several integration challenges remain for these films in terms of their chemical stability, crystallinity and stoichiometry. Variables affecting overall gate stack quality include surface cleaning, specific deposition process (layer thickness, material composition and microstructure, structural defects) and post deposition annealing methodologies. All of these could have an impact on the gate stack quality and electrical properties such as equivalent oxide thickness (EOT), gate leakage current, and transistor characteristics such as the threshold voltage shift.

In this study, ultra thin HfO_2 gate dielectric films were deposited on Si(1 0 0) substrate at room temperature and rapid thermal heat treatment was given in nitrogen and oxygen ambient to study the effect on the structural and electrical properties of HfO_2 thin films.

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2. Experiments

The HfO_2 thin films were deposited by Dielectrics Sputter System (Advanced Processing Technology) on the 4–7 Ω cm p-type Si(100) wafers at forwarding power of 150 W, base pressure of 1.6×10^{-5} mbar and operating pressure .016 mbar for 45 s. High purity (99.999 pure) 5 in. HfO_2 sputtering target was used to deposit ultra thin films. All the samples were treated with an RCA preclean process before high-*k* dielectric deposition. This cleaning process is found to improve the interface and initial growth of the high-*k* dielectrics. After the deposition of HfO_2 films, rapid thermal annealing (RTA) treatments were performed in RTP Annealsys AS-ONE-150 system at temperature of 700 °C in N_2 and O_2 ambient for 30 s. The physical thickness of the ultra thin high-*k* dielectric measured using the SENTECK SE800 Ellipsometer. The electrical properties were studied using metal–oxide–semiconductor (MOS) capacitor with Al electrode deposition by evaporation system over a circular area of 2.2×10^{-4} cm^2. Al thin film was deposited on the back side of the silicon wafer for back electrical contact. The post metallization annealing (PMA) was done in forming gas, N_2 (90%) + H_2 (10%), at 400 °C before the electrical measurement. Fourier Transform Infrared Spectroscopy (FT-IR) was used to observe transmission spectra of different chemical bonds and the change of bonding state after the thermal processing. Each spectrum was measured with a resolution of 4 cm^{-1} and a range of 400–1400 cm^{-1} and transformed from transmission to absorption. The crystal structures of the films were investigated using an X-ray diffracto-meter with Cu Kα radiation at 1.54 Å. The electrical properties of the films were characterized by capacitance–voltage (*C–V*) and current density–voltage (*J–V*) measurements using Keithley 4200-SCS semiconductor parameter analyzer.

3. Results and discussion

FT-IR analysis is a reliable and powerful method for characterization of material composition due to rapid and non-destructive measurement. Fig. 1 shows the FT-IR spectra of the HfO_2 ultra thin films samples annealed at 700 °C in N_2 and O_2 ambient for 30 s each. There are three peaks, at 750, 650, and 600 cm^{-1}, attributed to the Hf–O chemical bonds in the spectra, and the peaks at 1100 and 970 cm^{-1} are assigned to Hf–O–Si stretching vibrations. Comparing the spectra (N_2 and O_2 ambient annealed at 700 °C), the intensities of the peaks at 1100 and 970 cm^{-1} are seem to increase with the oxygen annealed sample [17–21]. This could be due to the formation of Hf–O–Si chemical bonds at the HfO_2/SiO_2 interface. The formation of silicate cannot be avoided during the thermal process. During this annealing process, Hf-silicate is formed by the atomic diffusion mechanism. As a result of Si diffusion into HfO_2, the Hf-silicate should be formed in the original HfO_2 layer, thus increasing the interfacial layer thickness. As observed in Fig. 1 the annealing at 700 °C in N_2 and O_2 ambient generates absorption peaks due to Hf–O–Si stretching vibrations indicating the intermixture and formation of Hf-silicate after the rapid thermal annealing.

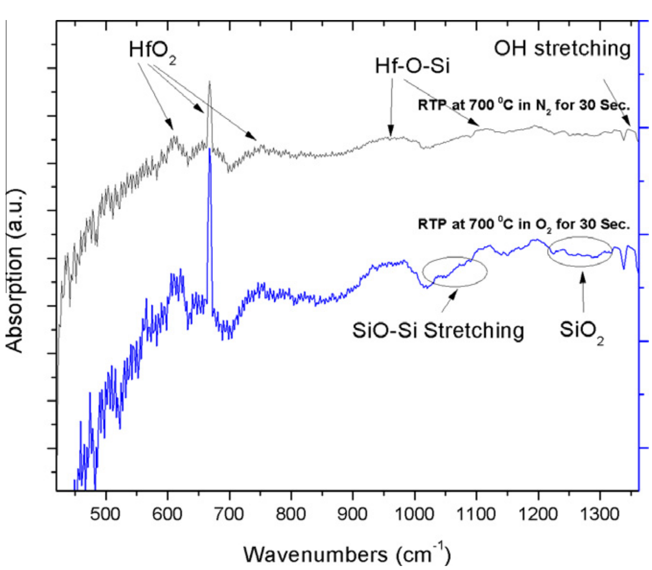

Fig. 1. FT-IR spectra of HfO_2 thin film after rapid thermal annealing in oxygen and nitrogen ambient at 700 °C for 30 s.

The study of the crystalline structures of the films prepared under the RTA at 700 °C N_2 and O_2 ambient for HfO_2 ultra thin films was realized by XRD measurements. The diffraction patterns for RTA annealed ultra thin films are shown in Fig. 2. A stronger peak of the orthorhombic phase identified as corresponding to the HfO_2 characterized by (402) diffraction peaks was observed in the past [22]. It is evident that the intensity of the HfO_2 peaks increasing with nitrogen annealed sample, suggesting a higher concentration of HfO_2 and a better crystallization. Also the peaks seem to be shifted towards higher 2θ values with respect to the oxygen ambient annealed sample. According to the Bragg's law, the reduction of the lattice parameter produces the increase of 2θ values. The full width of half maximum (FWHM) of nitrogen annealed sample found to be FWHM = 0.2362 lesser than that of oxygen annealed samples which is FWHM = 0.2952, implying that increasing the grain size with nitrogen annealing, thus improving the crystallinity and quality of the film in nitrogen ambient. Fig. 3(a) and (b) shows the 2D-AFM pictures of the HfO_2 ultra thin films after the rapid thermal annealing in oxygen and nitrogen ambient at 700 °C for 30 s. The nitrogen annealed sample is significantly smoother, with average roughness of 0.082 nm and an RMS roughness of 0.103 nm. In comparison, the oxygen annealed films has a average roughness of 0.128 nm and an RMS roughness of 0.183 nm. Fig. 4(a) and (b) shows 3D images of ultra thin films of HfO_2 after the rapid thermal annealing in oxygen and nitrogen ambient at 700 °C for 30 s and the effects are clearly shown. The smooth gate dielectrics surface plays a very important role for MOS capacitors because it could induce much less interface defects and improve the performance and stability of devices. The very smooth thin films surface is in favor of fabrication of high-quality MOS devices. The surface roughness is a very important factor for the gate oxide applications as it signifies film homogeneity and or particle formation. Assuming that the minimum thickness at which a deposited film remains continuous is directly related to its peak to valley roughness, significantly thinner and thus more transparent films can be obtained using rf-sputtering and RTA annealing in nitrogen ambient.

Figs. 5 and 6 present the electrical properties for both nitrogen and oxygen annealed samples. As illustrated in Fig. 5, nitrogen and oxygen annealed sample have accumulation capacitance 6.629×10^{-9} and 4.6×10^{-9} F, respectively. Similarly, the flatband voltage for nitrogen and oxygen annealed sample is -0.87 and -1.074 V as shown in Table 1. It indicates a significant increase in accumulation capacitance and positive side shifts in the flatband band voltage in nitrogen annealed sample with respect to the oxygen annealed sample. Higher reduction in number density of fixed oxide charges after the nitrogen annealing treatment compared to oxygen annealing is also observed. Furthermore, the interface states density (D_{it}) were estimated from the *C–V* curves are given in Table 1. Fig. 6(a) and (b), demonstrates the hysteresis behavior of the ultra thin HfO_2-based MOS capacitor under the nitrogen ambient annealed samples. It is clearly seen from the Fig. 6(a) and (b) that nitrogen annealed sample shown negligible hysteresis compare to the sample annealed in oxygen ambient. It demon-

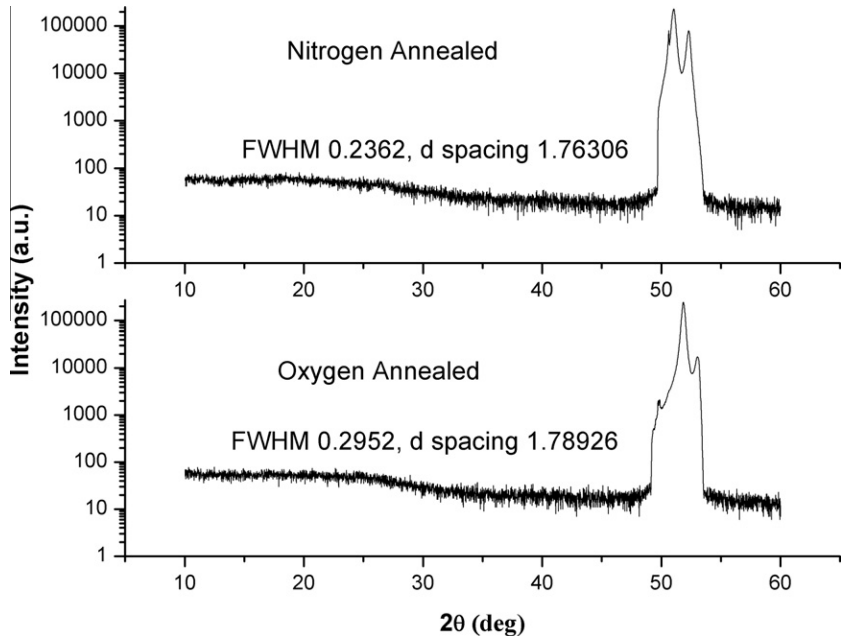

Fig. 2. XRD spectra of HfO_2 thin film after rapid thermal annealing in oxygen and nitrogen ambient at 700 °C for 30 s.

strates that the nitrogen annealed sample shows improved interface as compared with the sample annealed in oxygen ambient. This improvement in the HfO_2 thin films also confirmed from the forward and reverse bias *C–V* plots. The computed values of hysteresis from capacitance–voltage characteristics for each sample are given in Table 1. This significant shift in *C–V* hysteresis for nitrogen annealed samples as compared to oxygen indicates the improvement in dielectric layer, which supports the previous observation of reduction in fixed oxide charges after nitrogen treatment [8,23,24]. Since hysteresis is commonly observed in high-*k* material in *C–V* characteristics and need to be minimize for the memory applications. The dielectric constant of nitrogen and oxygen annealed sample measured from the accumulation capacitance was about 24 and 17, respectively. It is attributed that pure HfO_2 thin films annealed in nitrogen ambient, SiO and Hf silicate generally formed instead of SiO_2 which increase in the accumulation capacitance. On the other hand, in the oxygen annealed samples, the formation of SiO_2 is easy than that of SiO and Hf silicates which generally causes the decrease of the accumulation capacitance. But the interpretation for the exact cause of this kind of behavior is not found [25]. Here we try to explain the main cause of increase of the accumulation capacitance on the basis of change in the structural properties. From the literature it is evident that pure HfO_2 thin films when annealed transform towards crystalline structure, which depends upon the sample preparations, annealing time, temperature, and annealing ambient. It is found that the sample after RTA in oxygen ambient exhibits a low capacitance value in accumulation and a larger flatband voltage shift, suggesting a poorly crystallized HfO_2 structure and a high oxide charge density. The decrease in flatband and increase in capacitance value after RTA in nitrogen ambient indicate that the oxide formation is possible to a well crystallized microstructure in the HfO_2 matrix, which is consistent with the XRD spectra of these ultra thin films. From the XRD plot, it is clear that after annealed at temperature 700 °C, HfO_2 thin films become crystalline. The change of the crystalline phase of films causes the change in the dielectrics properties [26–28].

In order to explain the enhanced dielectric constant of HfO_2 thin films, the effect of the crystal structure on the electrical properties should be considered. The Clausius Mossotti equation identifies the relationship between the dielectric constant (k), the molecular polarizability (α), and the molar volume (V_m) of a material from the equation [29],

$$k = \frac{(V_m + 2\alpha/3)}{(V_m - \alpha/3)}$$

Assuming that the molecular polarizability is independent of HfO_2 crystal structures because the polarizability contribution to the dielectric constant is equal to the square of the refractive index, which was found to be 2.1 for all HfO_2 phases, a larger increase in the dielectrics constant can be achieved by decreasing the molar volume. Fig. 7 depicts the gate leakage current as a function of gate voltage across the HfO_2 based MOS-capacitor. The gate leakage current is an important device parameter. To evaluate the gate leakage performance of the MOS devices, the *I–V* characteristics is measured both in accumulation and inversion region. From Fig. 7, it is clear that the leakage current of nitrogen annealed sample have the smaller leakage current density than the oxygen annealed sample which is consistent with the results of CV curve and XRD data. The HfO_2 device shows a $10^4\times$ leakage current reduction as compared to the SiO_2 device, and Hf-silicate devices show about one order of magnitude or less leakage current reduction as compared to the SiO_2 device. As shown in the experimental result the relatively larger leakage current for the oxygen annealed sample is attributed to the formation of oxide interfacial layer as compared to the sample annealed in nitrogen. The quality of thin films of HfO_2 gets improved after annealing in nitrogen ambient, which is also confirmed by the Bias Temperature Instability (PBTI). Figs. 8(a) and 8(b) show the PBTI results of nitrogen and oxygen annealed samples, respectively. Gate dielectric of the MOS capacitor were stressed at DC = 5 V at temperature 125 °C for time varying from 1 to 1000 s. Nitrogen annealed sample shows the small variation in accumulation region than the oxygen annealed samples. There is a very small variation in flat band and threshold voltage change in nitrogen annealed compared to the oxygen annealed samples. It is our conjecture that the accumulation capacitance density of HfO_2 films is affected by the chemical states rather than the physical layer thickness under the N_2 annealing atmosphere. In contrast, the tendency of the accumulation capacitance density in O_2-annealed samples is fitted to $t_{\mathrm{Interface}}/t_{\mathrm{HfO_2}}$ ratios as shown in Fig. 8(b).

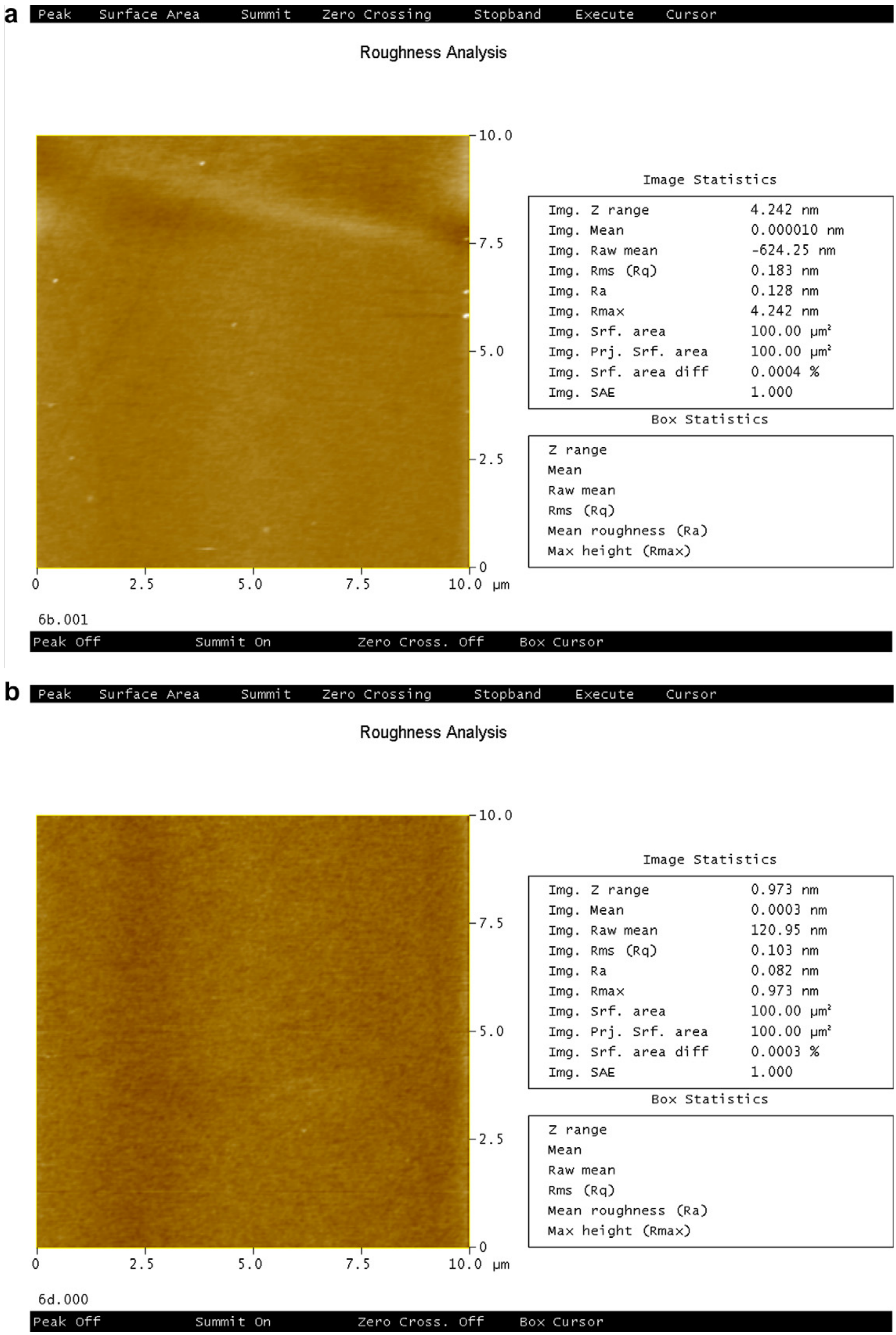

Fig. 3. AFM-2D image of HfO_2 ultra thin films after RTA annealing in (a) oxygen and (b) nitrogen ambient at 700 °C for 30 s.

4. Conclusion

In summary, ultra thin films of HfO_2 were prepared using rf-sputtering. The effects of rapid thermal annealing on the film microstructure, chemical composition and electrical properties in ultra thin HfO_2 films are studied. It is shown that RTA improves the interface properties of HfO_2/Si and the densification of HfO_2 ultra thin films. The as deposited films were amorphous and that were orthorhombic after annealed at 700 °C in nitrogen and oxygen atmosphere. It is found that nitrogen annealed samples exhib-

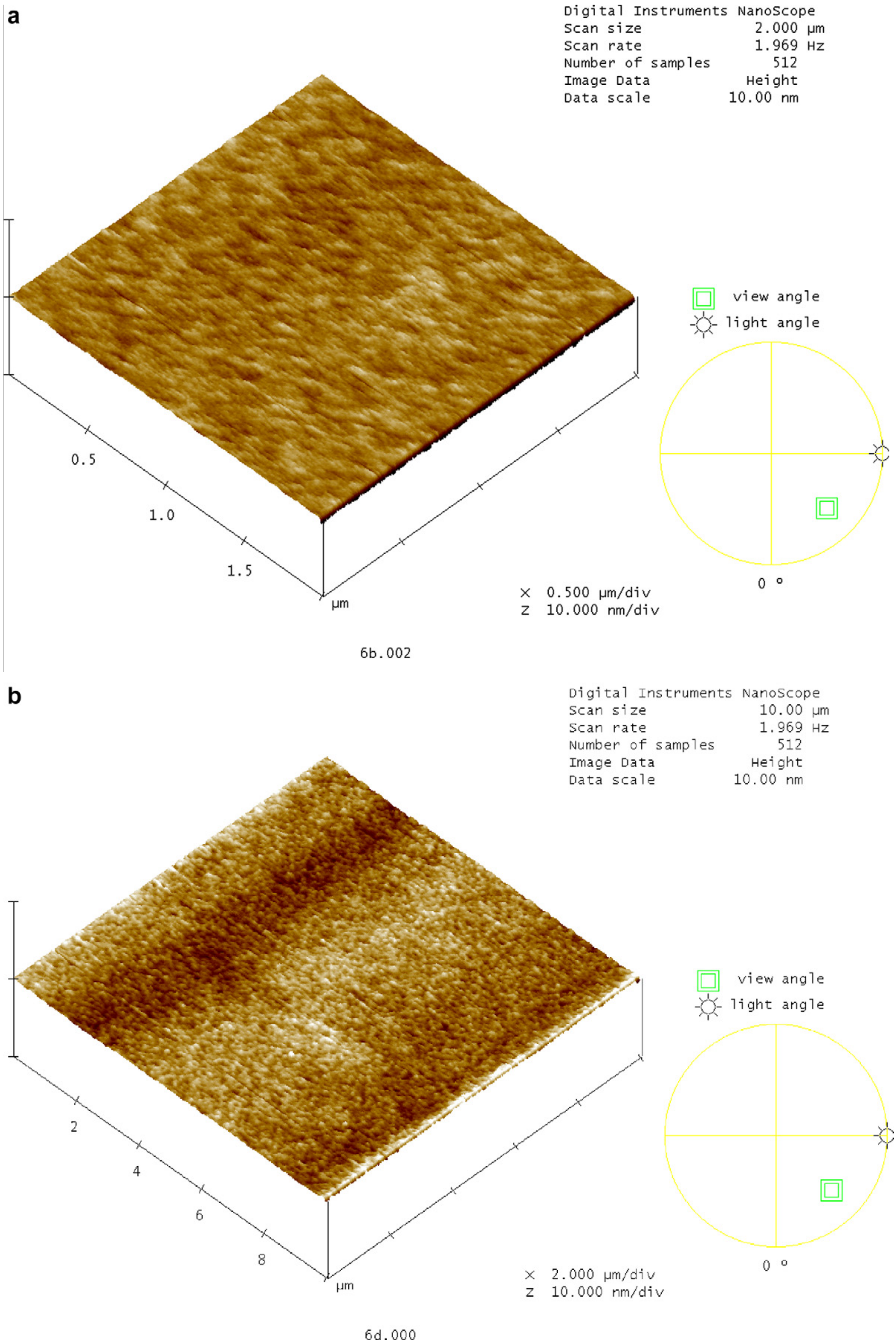

Fig. 4. AFM-3D image of HfO_2 ultra thin films after RTA annealing in (a) oxygen and (b) nitrogen ambient at 700 °C for 30 s.

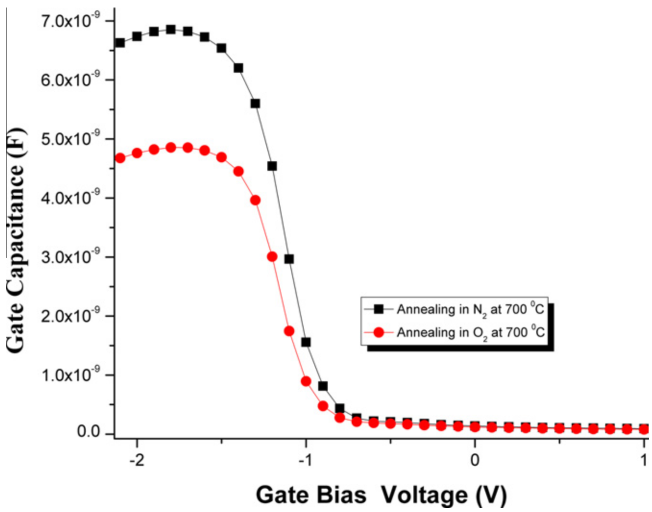

Fig. 5. CV characteristics of HfO_2 thin film after rapid thermal annealing in different ambient at 700 °C for 30 s.

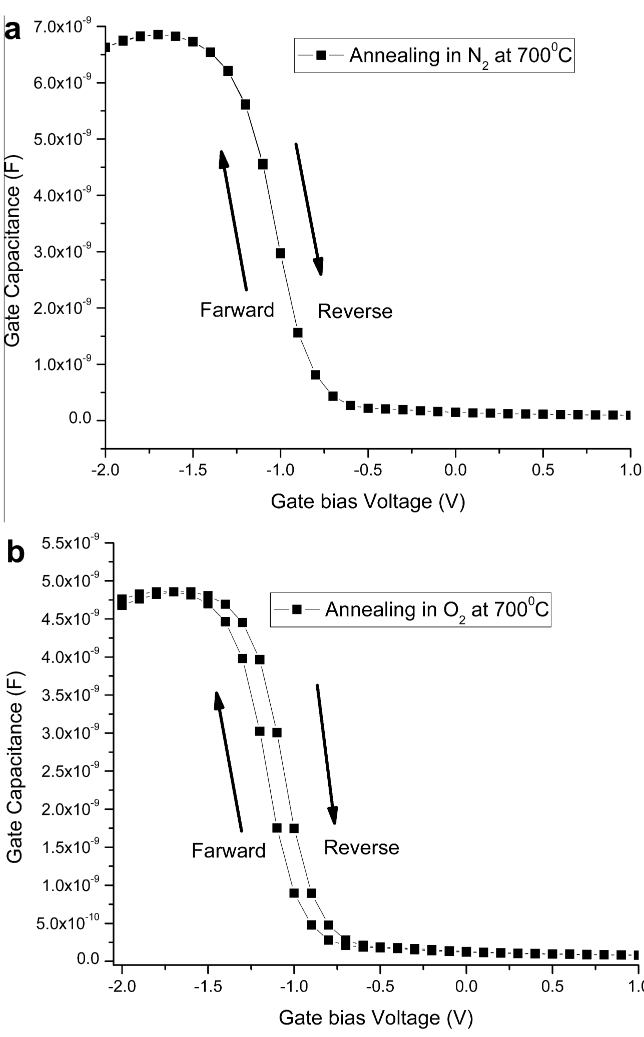

Fig. 6. The *C–V* characteristics of HfO_2 based MOS capacitor under forward and reverse bias for each samples (a) nitrogen annealed at 700 °C for 30 s and (b) oxygen annealed at 700 °C for 30 s.

Table 1
RTA effects on the electrical and physical properties of ultra thin HfO_2 films in nitrogen and oxygen ambient.

Annealing temperature/ ambient	Surface roughness rms (nm)	C_{OX} (F)	Flat band voltage (V)	Hysteresis (V)	Interface state density, N_{it} (cm^{-2})
700 °C in nitrogen	0.103	6.629×10^{-9}	−0.87	0.0012	1.9×10^{11}
700 °C in oxygen	0.183	4.6×10^{-9}	−1.074	0.101	2.06×10^{12}

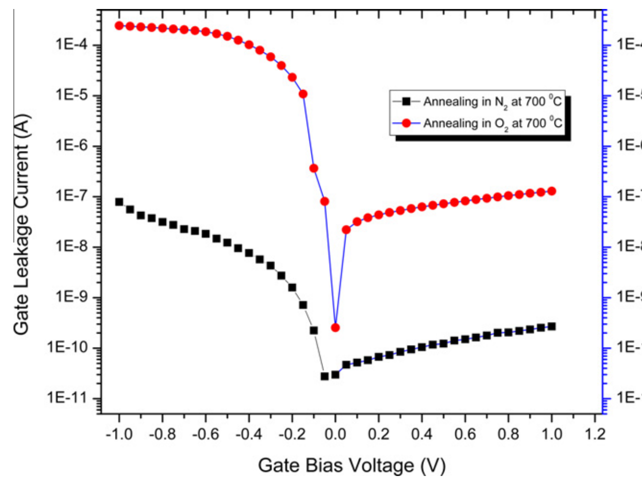

Fig. 7. IV characteristics of HfO_2 thin film after rapid thermal annealing in oxygen and nitrogen ambient at 700 °C for 30 s.

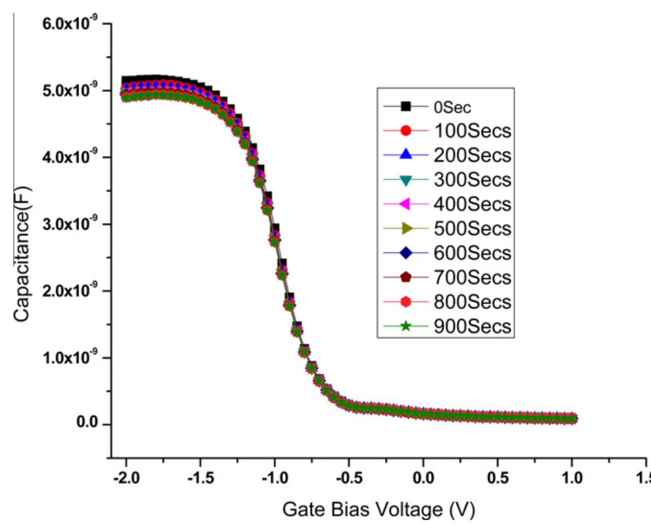

Fig. 8a. Stress CV characteristics of HfO_2 thin film after rapid thermal annealing effects in nitrogen ambient at 700 °C for 30 s.

ited a reduced equivalent oxide thickness, interfacial density of states, leakage current and *C–V* hysteresis; it also showed negligible charge trapping under high electric voltage stress. We attribute this behavior to the orthorhombic phase perfectly crystalline and suppressing the formation of interfacial layer and silicate at the HfO_2/Si interface. The ultra thin high-*k* HfO_2 annealed in nitrogen is most stable gate dielectric materials for advanced nano electronic devices.

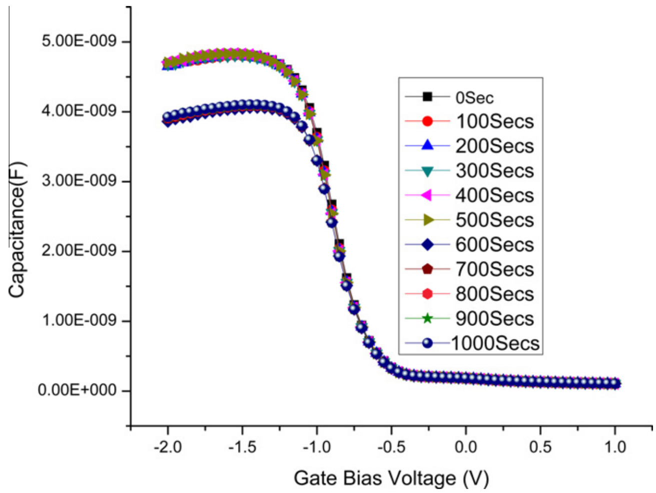

Fig. 8b. Stress CV characteristics of HfO_2 thin film after rapid thermal annealing effects in oxygen ambient at 700 °C for 30 s.

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