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Plasma enhanced atomic layer deposition of HfO_2 with in situ plasma treatment

Dawei Xu [a,b,*], Xinhong Cheng [a], Youwei Zhang [a], Zhongjian Wang [a,b], Chao Xia [a,b], Duo Cao [a,b], Yuehui Yu [a], DaShen Shen [c]

[a] State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Micro-System and Information Technology, Chinese Academy of Sciences, Changning Road 865, Shanghai 200050, PR China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China
[c] Department of Electrical and Computer Engineering, University of Alabama in Huntsville, Huntsville, Alabama 3589, USA

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ABSTRACT

Plasma-enhanced atomic layer deposition was explored to produce thin HfO_2 films, where oxygen plasma acted as oxidant. The interfacial layer (IL) was controlled by in situ pre-oxygen plasma treatment (PRO) and pre-ammonia plasma treatment (PRN). Post oxygen plasma treatment (POP) to HfO_2 film was in situ executed. The IL thickness was 1.1 nm, which was detected to be HfSiON by X-ray photoelectron spectroscopy (XPS). With 4 nm thick amorphous HfO_2 film, an equivalent oxide thickness (EOT) of total gate dielectric stacks of 0.87 nm was obtained. Small leakage current density of 0.02 mA/cm^2 was measured at a gate bias of $|V_g - V_{fb}| = 1$ V.

As the feature size of transistor continues to scale down, the thickness of traditional SiO_2 gate dielectrics has reduced to the sub-nanometer range, the leakage current caused by direct tunneling significantly increases. Consequently, the on/off characterization and power consumption are becoming a big concern [1]. High dielectric constant (high-k) gate dielectrics provides a solution to increase capacitance density and reduce leakage current without increasing the equivalent oxide thickness (EOT) [2,3]. Among many candidates, Hf based oxide and silicate not only have relatively high dielectric constant and wide band gaps but also have been demonstrated to display impressive thermal stability in contact with the silicon substrate [4,5]. But there are still many challenges, such as the existence of relatively low dielectric constant interfacial layer (IL) which limits the continuous scaling probability of high-k dielectric stacks. In addition, the poor interfacial properties may result in degradation of mobility of MOSFET devices. Therefore, a buffer layer (BL) between Si substrate and HfO_2 layer is needed to improve the electrical properties of the interface as well as preventing the increase of EOT [6,7]. A buffer layer, such as an ultra thin SiO_2 [8], or a nitrided ultrathin Al_2O_3 film [9] was used before HfO_2 film deposition to improve the HfO_2/Si contact properties.

Atomic layer deposition (ALD) is a widely used technique for high-k film deposition. ALD is based on the principle of self-limited reaction mechanism, where two or more precursors are alternately pulsed into the reaction chamber, and are chemically adsorbed at the surface of the samples, and then react with each other to form dielectric films. The film thickness can be precisely controlled, and the film properties are uniform [10,11]. In thermal ALD, the operating temperature is around 300 °C. A common oxidant for thermal ALD is H_2O which will induce OH bonds into high-k film and degrades its properties. In addition, the high growth temperature would increase thermal budget and decrease the growth rate. In contrast, plasma-enhanced ALD (PEALD) method, where oxygen plasma can be used as oxidant to avoid the incorporation of OH bonds, and high-k films with high density can be grown at high growth rate when the deposition temperature was relatively low. HfO_2 and ZrO_2 gate dielectrics were prepared by PEALD with a small EOT and low leakage current [12]. $SrTiO_3$ film was deposited by PEALD at low temperature with a low carbon residue [13]. Moreover, oxygen plasma and ammonia plasma can be in situ used to improve the performance of the interface and high-k films. Notice that, HfO_2 film deposited by PEALD usually showed thicker interfacial layer (IL) than that of conventional thermal ALD method. This is because oxygen plasma interacts with Si surface to form Si oxide. Therefore, it is very important to optimize the deposition parameters, including the growth temperature, the power of RF plasma generator, the pulse, the purge time and the cycle numbers in PEALD process.

* Corresponding author at: State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Micro-System and Information Technology, Chinese Academy of Sciences, Changning Road 865, Shanghai 200050, PR China.
E-mail address: dwxu@mail.sim.ac.cn (D. Xu).

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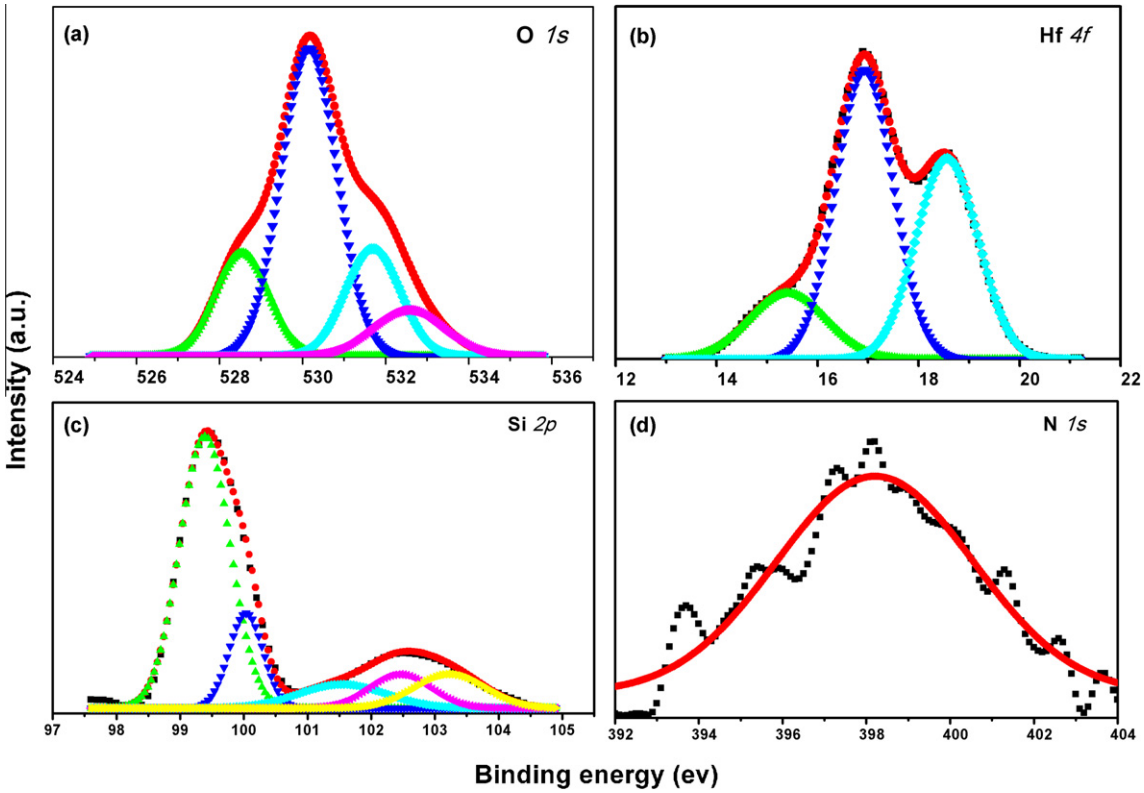

Fig. 1. XPS spectra of PEALD HfO_2 film with PRO, PRN and POP process: (a) O 1s peak, (b) Hf 4f peak, (c) Si 2p peak, and (d) N 1s peak.

In this work, HfO_2 film was deposited by a remote PEALD system which was connected to an RF generator. At the top of the reactor chamber, there is an upper aluminum plate electrode with gas inlets and a lower aluminum grid electrode, they are the same size as the reactor chamber substrate. Oxygen plasma and ammonia plasma were generated between them and carried by argon vertically into the reactor chamber. Through the optimization of key parameters, an IL composed of HfSiON was formed. HfO_2 film with EOT of 0.87 nm and leakage current of 0.02 mA/cm^2 at a gate bias of $|V_g - V_{fb}| = 1$ V were achieved.

Si(100) p-type substrates with a resistivity of 8–13 Ω cm were cleaned with a piranha solution (H_2SO_4:H_2O_2 = 4:1) for 10 min to remove organic particles, rinsed in deionized water, and then etched in a diluted hydrofluoric acid solution (HF:H_2O = 1:100) to remove oxides. After that, the substrate was immediately put into the plasma reactor chamber and protected by argon. Oxygen plasma and ammonia plasma treatments (PRO and PRN) were applied on Si substrate with optimal parameters to yield a thin IL, where the power of plasma source was 150 W. The pulse time for the oxygen plasma was 4 s, and for the ammonia plasma 40 s. Then HfO_2 films was in situ grown at a substrate temperature of 160 °C. The metal precursor was Tetrakis (ethylmethylamino) hafnium $[(CH_3)(C_2H_5)N]_4$ Hf (TEMAH), the oxidant was oxygen plasma, and the carrying gas was argon. The basic cycle for HfO_2 film deposition consisted of supplying hafnium precursor 1 s, purging 3 s, exposing oxygen plasma at 150 W for 2 s. After HfO_2 film deposition, post oxygen plasma treatment (POP) was performed to reduce oxygen vacancies in the HfO_2 layer. The control sample without PRO, PRN, but with POP process was also fabricated. All these processes were executed in the same plasma reactor chamber, which can avoid environmental impurity incorporation. The samples were taken out of reactor chamber and cut into small pieces. Some samples were treated by rapid thermal annealing (RTA) at 500 °C for 1 min in N_2. In order to examine the electrical property, MIS capacitor was fabricated with the top electrode of Au and back electrode of Al. Post metallization annealing (PMA) was carried out in forming gas (95% N_2 + 5% H_2) at 400 °C for 3 min. Capacitance–voltage (*C–V*) measurement and leakage current–voltage (*I–V*) measurement were performed using Agilent B1500A Semiconductor Device Analyzer. Chemical bonding state was determined by X-ray photoelectron spectroscopy (XPS), and the binding energy (BE) was calibrated with the position of C 1s peak at 284.8 eV. High-resolution transmission electron microscope (HRTEM) was used to study the microstructure of films.

Fig. 1 depicts the XPS O 1s, Hf 4f, Si 2p and N 1s spectra of the HfO_2 prepared by PEALD film with PRO, PRN and POP process. As shown in Fig. 1(a), O 1s XPS spectra was deconvoluted into four Gaussian–Lorentzian features corresponding to four different chemical states. The main peak at a binding energy of 530.1 eV is attributed to Hf–O bonds in HfO_2. The peaks at 532.5 eV and 531.7 eV correspond to interfacial O atoms in SiO_x and nonstoichiometric $HfSi_xO_y$, respectively. Considering N incorporated into the interfacial layer, the lower binding energy at 528.5 eV was likely related to N–Hf–O bonds. As shown in Fig. 1(b), Hf 4f XPS spectra was deconvoluted into three Gaussian–Lorentzian features. The peak at a binding energy of 16.9 eV corresponds to the Hf–O bonds [14], and the lower peak at a binding energy of 15.4 eV is likely attributed to O–Hf–N bonds. As shown in Fig. 1(c), Si 2p XPS spectra was deconvoluted into six peaks, the strong peak at 99.3 eV related to Si substrate, the peak at 102.4 eV is attributed to Si–O–Hf bonds, and the peak at 103.2 eV originated from Si in SiO_2. As shown in Fig. 1(d), N 1s spectra has a main peak at 398.2 eV, corresponding to N–Hf bonds [15]. The peak signal was weak, indicating that only a small amount of N atoms was incorporated during the PRN process.

From XPS analysis, it is concluded that the PRO and PRN together with the PEALD process led to the formation of IL that was composed of HfSiON. The PRO and PRN made the IL more