Rare Metal Materials and Engineering
Volume 38, Issue 2, February 2009
Online English edition of the Chinese language journal

Cite this article as: Rare Metal Materials and Engineering, 2009, 38(2): 0189–0192.

ARTICLE

Interfacial and Electrical Characterization of HfO_2 Gate Dielectric Film with a Blocking Layer of Al_2O_3

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Abstract: HfO_2 gate dielectric films with a blocking layer of Al_2O_3 inserted between HfO_2 layer and Si layer (HfO_2/Si) were treated with rapid thermal annealing process at 700 ℃. The interfacial structure and electrical properties were reported. The results of X-ray photoelectron spectroscopy showed that the interfacial layer of SiO_x transformed into SiO_2 after the annealing treatment, and Hf-silicates and Hf-silicides were not detected. The results of high-resolution transmission electron microscopy indicated that the interfacial layer was composed of SiO_2 for the annealed film with blocking layer. The results of the electrical measurements indicated that the equivalent oxide thickness decreased to 2.5 nm and the fixed charge density decreased to -4.5×10^{11}/cm^2 in comparison with the same thickness of HfO_2 films without the blocking layer. Al_2O_3 layer could effectively prevent the diffusion of Si into HfO_2 film and improve the interfacial and electrical performance of HfO_2 film.

Key words: gate dielectrics; HfO_2; blocking layer; Al_2O_3.

HfO_2 film as a candidate of high-*k* dielectric materials has been extensively studied. The main challenge is the formation of interfacial layer (IL) at high-*k*/Si interface during the deposition/annealing process, and IL was composed of SiO_x, Hf-silicates or Hf-silicides. These by-products of processing suppress the effective dielectric constant and degrade the electrical performances of devices[1]. Recently, Al_2O_3 is used as a reaction blocking layer (BL) for HfO_2 due to its high temperature thermal stability[2]. Park et al. studied the effect of Al_2O_3 blocking layer to suppress the growth of IL at Si interface[3]. Katamreddy et al. reported that Al_2O_3 layer could also control the growth of Hf-silicates and Hf-silicides during the post-deposition annealing treatment[4]. However, how the blocking layer of Al_2O_3 controlled the interfacial reaction and how it affected the electrical performance need to be further studied.

In this paper, HfO_2 films with BL of Al_2O_3 were treated with rapid thermal annealing (RTA) process to improve the interfacial and electrical performance of HfO_2 gate dielectric film.

1 Experimental

p-type (10-20 Ω·cm) (100) silicon substrates were cleaned and etched in a diluted hydrofluoric solution. 1 nm Al_2O_3 and then 5 nm HfO_2 was deposited onto Si substrates by electron-beam evaporation (EBV) method. In order to study the impact of Al_2O_3, 6 nm HfO_2 film was also deposited onto Si substrate. Background pressure of the main chamber was 10^{-6}-10^{-7} Pa, and the substrate temperature was kept at 300 ℃. High purity sintered HfO_2 and Al_2O_3 pellets were evaporated at the rate of 2-5 nm/s and the thickness of the films was monitored by quartz crystal oscillator. Then the wafer was cut into several parts, and some of them were treated with RTA process in N_2 at 700 ℃ for 3 minutes. MIS capacitors were formed with aluminum top and bottom electrodes. All MIS capacitors were treated with RTA at 300 ℃ for 30 minutes to form ohm contact.

The interfacial structure was investigated by X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM), and the

Received date: 2008-01-27
Foundation item: Supported by National Natural Science Foundation of China (50402026)
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electrical properties were studied with metal-insulator-semiconductor (MIS) capacitors.

2 Results and discussion

XPS analysis was performed with all peaks referring to the Si2p peak at the binding energy (BE) of 99.2 eV.

Hf4f spectra with and without BL are shown in Fig. 1a and Fig. 1b, respectively. In the case of the samples with BL, the peaks were around 16.8 eV and 18.4 eV for the as-deposited samples, and shifted slightly to 17.0 eV and 18.6 eV for the annealed ones. The peak shifts by annealing would be due to the incorporation of Al into HfO_2 during the annealing, since Hf is a more ionic cation than Al, and thus the charge transfer may contribute to the increase of Al concentration[5]. In the case of the samples without BL, the corresponding peaks were located at 16.9 eV and 18.4 eV for the as-deposited samples, and shifted significantly to 17.5 eV and 19.1 eV, and moreover, a new peak at 16.2 eV appeared for the annealed ones in comparison with the samples with BL. Wilk et al. pointed out that the diffusion of Si atoms into HfO_2 would lead to Hf4f peaks up-shift [6]. It was also reported[7] that O atoms diffused easily to Si substrate through HfO_2, where Si substitutional defects were most likely to form, and the formation energy of neutral oxygen vacancies in SiO_2 was lower than that in HfO_2. Therefore, the high BE in the case without BL was due to the formation of Hf-silicates at Si interface, which would further grow during high temperature annealing, as indicated by the up-shift of the peaks for the annealed sample. The peak at 16.2 eV was attributed to Hf-silicides, which were easily formed during high temperature annealing in oxygen-deficient ambient[8]. These observations indicated that the diffusion of Si atoms into HfO_2 films was significant for HfO_2 films without BL.

Si2p spectra with and without BL are shown in Fig.2a and Fig. 2b, respectively. Si2p spectra were de-convoluted into two peaks with peak 1 originating from Si substrate and peak 2 corresponding to oxidized states. In the case with BL, the peak 2 was shifted from 102.5 eV for the as-deposited samples to 103.3 eV for the annealed counterparts; meanwhile, the peak intensity increased obviously. These indicated that Si sub-oxides IL transformed into SiO_2 with the increase of thickness. For the samples without BL, the peak 2 was located at a higher BE of 103.3 eV and with a higher intensity for the as-deposited ones. It is noted that it was shifted to lower BE of 102.8 eV and with no detectable change of intensity for the annealed counterparts. Takahashi et al. pointed out that the diffusion of Si during high temperature annealing could make HfO_2 transformed into $HfSi_x$ and HfSiO, where the BE of Si oxidized state was lower than that of SiO_x[9]. Our previous study also showed that the peak relating to Si oxidized state would downshift after annealing treatment[10]. The results were consistent with these shown in Fig.1, where the peak relating to Hf-silicides was clearly observed. That is, the diffusion of Si atoms into HfO_2 was serious, and Hf-silicides were formed during post deposition annealing treatment. However, a blocking layer of Al_2O_3 could effectively prohibit the diffusion of Si atoms, keeping IL composition of SiO_2.

O1s spectra with and without BL are shown in Fig. 3a and Fig. 3b, respectively, and Al2p spectra are shown in Fig. 3c. For the samples with BL, O1s peak was located at 530.5 eV with a shoulder at 532.6 eV for the as-deposited samples, but it moved to 532.6 eV for the annealed film. Won et al. indicated that the peak at 530.5 eV corresponds to O1s electrical state in HfO_2, and 532.6 eV is attributed to that in SiO_2 or in Al_2O_3[11]. It means that IL was grown further and transformed to SiO_2, which was in consistent with the observation of Fig.2a. In contrast, for the samples without BL, O1s peak was at 532.4 eV for the as-deposited film, and it shifted to lower BE of 531.7 eV. Lee et al. reported that the peak at 531.5 eV

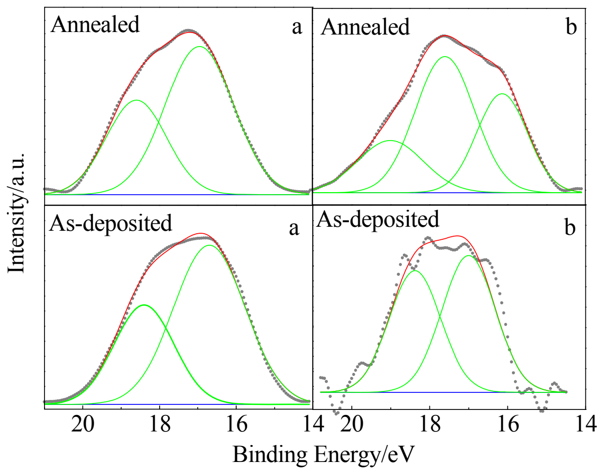

Fig.1 Hf4f spectra for the as-deposited film and the annealed film, respectively: (a) with a blocking layer, (b) without blocking layer

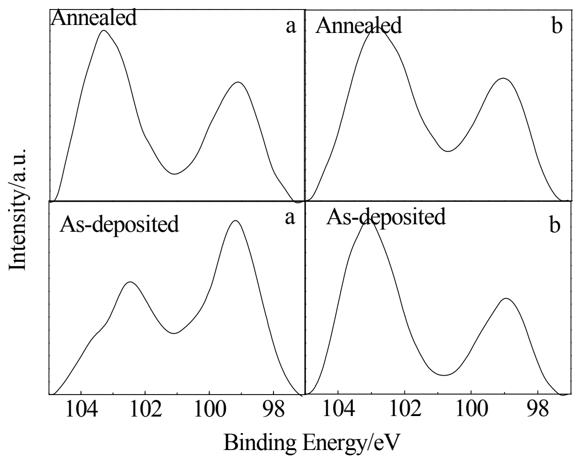

Fig.2 Si2p spectra for the as-deposited film and the annealed film,

respectively: (a) with a blocking layer, (b) without blocking layer

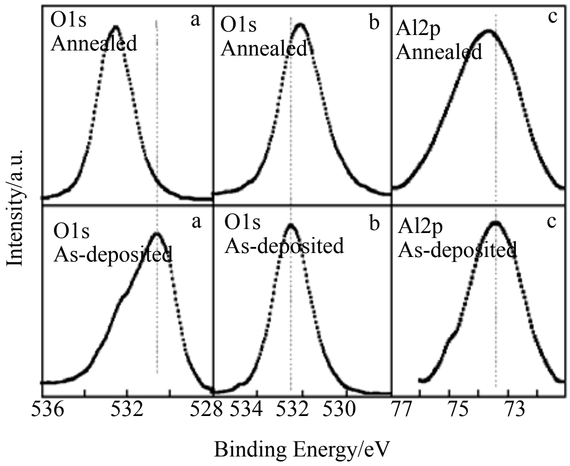

Fig.3 XPS spectra for the as-deposited film and the annealed film, respectively: (a) O1s spectra with a blocking layer, (b) O1s spectra without blocking layer, and (c) Al2p spectra

originated from O1s electronic state in Hf-silicates[12]. In addition, according to the analysis of Fig. 2b, it is clear to see that IL was composed of SiO_x and Hf-silicates for the as-deposited samples without BL. The above mentioned is helpful to conclude that the peak at 531.7 eV attributed to the components of IL, and peak downshift was due to the further growth of Hf-silicates as observed in Fig. 1b.

Al2p spectra for annealed sample are shown in Fig.3c. In contrast to that of the as-deposited sample, Al2p spectrum for annealed sample became broader and an up-shift of the peak was observed. It would be due to that Al atoms contacted with O atoms in HfO_2 or SiO_2 to form tetrahedral structure[13], and the distribution of electronic cloud changed during annealing treatment. The slight up-shift of H4f peaks for the annealed sample shown in Fig.1a also indicated that Al diffusion took place.

HRTEM images for the samples with a blocking layer were shown in Fig. 4. For the as-deposited film, there was an IL between Si substrate and Al_2O_3, which was composed of SiO_x(x<2). However, for the annealed film, the existence of IL of SiO_2 was clearly shown, indicating that annealed treatment could transform the interfacial layer from SiO_x into SiO_2, which was consistent with what observed in Fig.2.

Typical capacitance-voltage (C-V) curves of MIS capacitors are shown in Fig.5, which were measured at 1 MHz using HP4194A impedance analyzer. Equivalent oxide thickness (EOT) was estimated to be 2.5 nm, and the fixed charge density was -4.5×10^{11}/cm^2 for the annealed HfO_2 films with BL.

Negative value of fixed charge perhaps resulted from the negatively charged Al^{3+} ions with the tetrahedral coordination, which are in contact with the O atoms of HfO_2 and SiO_2. It is

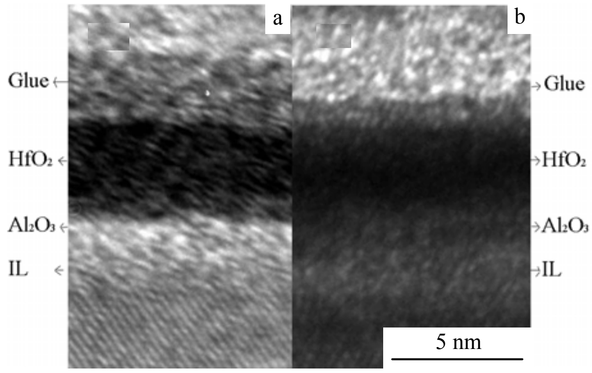

Fig.4 HRTEM images for the samples with blocking layer: (a) annealed and (b) as-deposited

indicated further that Al atoms diffused into HfO_2 and SiO_2 layer. In contrast, the annealed HfO_2 films without IL showed a relatively poor electrical performance with an EOT of 2.9 nm and a fixed charge density of 7.3×10^{11}/cm^2. The improvement of electrical performance was most likely due to that BL prevented the diffusion of Si atoms, keeping IL composition of SiO_2, leading to an optimal SiO_2/Si interface. It is noted that the hysteresis and the reduction in accumulation capacitance at negative bias were not detected clearly for all the annealed films, but were obvious for all the as-deposited films. In addition, the decrease of the accumulation capacitance due to the growth of IL was also not observed clearly for the annealed films. Therefore, though the annealing treatment in- creased the thickness of IL, as shown in Fig.2, it also made the films denser, reducing defect density and slowed interface state density, leading to a negligible hysteresis and a flat accumulation capacitance region.

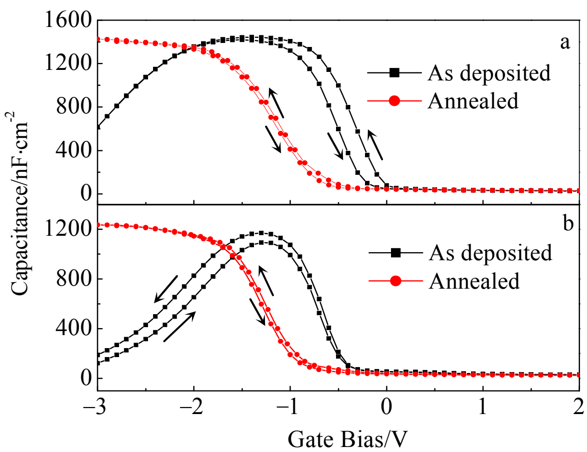

Fig.5 Capacitance characteristics of MIS capacitors made of the as-deposited film and the annealed film, respectively: (a) with a blocking layer, (b) without blocking layer

3 Conclusion

A blocking layer of Al_2O_3 inserted between HfO_2/Si would control the diffusion of Si atoms into HfO_2 films, suppress the formation of Hf-silicates or Hf-silicides at Si interface, keep IL composition of SiO_2, and lead to an optimal SiO_2/Si interface. In addition, it could enhance gate capacitance density and reduce fixed charge density. Therefore, this method could effectively improve the interfacial and electrical performance of HfO_2 gate dielectric film.

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具有Al_2O_3阻挡层的HfO_2栅介质膜的界面和电学性能的表征

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摘 要：研究了经过700 ℃快速热退火的并在Si界面处插入Al_2O_3阻挡层的HfO_2栅介质膜的界面结构和电学性能。X射线光电子谱表明，退火后，界面层中的SiO_x转化为化学当量的SiO_2，而且未发现铪基硅酸盐和铪基酸化物。由电学测试提取出等效栅氧厚度为2.5 nm, 固定电荷密度为$-4.5\times10^{11}/cm^2$。发现Al_2O_3阻挡层能有效地阻止Si原子扩散进入HfO_2薄膜，进而改善HfO_2栅介质膜的界面和电学性能。

关键词：栅介质；HfO_2；阻挡层；Al_2O_3

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