Electrical and Optical Reliability Improvement of HfO2 Gate Dielectric by Deuterium and Hydrogen Incorporation


Abstract

Electrical and optical reliability characteristic of Pt/HfO2 gate stack have been investigated. Incorporating deuterium and hydrogen treatment during post-metallization annealing is employed to improve both the electrical and optical reliability of Pt/HfO2 gate stack. For comparison, deuterium-treated technology provides slightly better reliability improvement on both the electrical and optical reliability of Pt/HfO2 gate stack devices.

1. Introduction

High dielectric constant (high-k) materials implemented in CMOS technologies as gate dielectrics will eventually be needed to relieve the rapid gate current increase associated with aggressive oxide thickness scaling. The increased dielectric constant allow for increased physical thickness at similar driving capability. Among the many potential high-k materials under investigation, HfO2 films have been widely considered one of the most promising candidates because of its relative high electric constant ($\varepsilon \sim 20$) and low leakage current density ($10^3$~$10^6$ less than SiO2 of equivalent CET). Optimization of interfacial layer and bulk high-k layer is known to be important due to the instability is one of the most challenging issues to implement high-k gate dielectric. Several studies on HfO2 have been reported with the polysilicon gates electrode [1, 2].

Metal gate electrodes are generally well accepted to eliminate gate depletion effect, additional polysilicon gates/high k interfacial layer, and high gate resistance problems that are associated with conventional polysilicon gates. In addition to gate depletion, recently polysilicon gates have also shown to suffer from Fermi level pinning on high-k dielectrics [3]. These issues warrant the investigation of metallic gate electrodes on high-k dielectrics. In this paper, we will present both the electrical and optical reliability improvement of Pt/HfO2 gate stack by deuterium and hydrogen incorporation.

2. Experiment

The HfO2 films were deposited by atomic layer chemical vapor deposition (ALCVD) [4] on the p-type, 1-10 $\Omega$cm, (001) orientation silicon substrate wafers, followed by a post-deposition-annealing (PDA) at 600 °C for 300 sec in N2 by rapid thermal annealing (RTA). ALD might be the leading deposition process for High-K gate dielectrics [5, 6] due to its thickness control and good conformality. In ALD, materials are deposited layer by layer in a self-limiting fashion, allowing for inherent atomic scale control. The metal-insulator-silicon (MIS) capacitor structure had Pt gate electrode with circular areas defined by the shadow mask. Pt electrodes were deposited using DC magnetron sputtering. The area of capacitor was $3 \times 10^{-4}$ cm$^2$. The Al contact is on the back of the wafers. The furnace post-metallization annealing was done in forming gas to incorporate deuterium ($D_2 / N_2=1 / 9$) and hydrogen ($H_2 / N_2=1 / 9$) at 400 °C for 30 min. In this experiment, the C-V, I-V characteristics, and reliability measurement was carried out using an HP 4156A semiconductor parameter analyzer. Time evolutions of light emission intensity measurement are employed to examine the optical reliability.

3. Results and Discussion

Fig. 1 Cross-section TEM micrograph of HfO2 on p-type Si wafer, after 300 sec post deposition annealing at 600 °C.
It is clearly observed from the cross-section transmission electron microscopy (TEM) micrograph, as Fig. 1 shows, that ~0.7 nm interfacial layer is formed in addition to the 2nm (physical thickness) HfO₂ film after 300 sec post deposition annealing at 600 °C. The capacitance equivalent thickness (CET) is 1.3 nm. Note that the CET value is obtained by two-frequency (500 kHz & 100 kHz) correction method [7]. The CET have constant values before and after hydrogen and deuterium treatment indicating that it will not increase the interfacial layer thickness.

There are significantly reductions (more than 3 orders) of current density at inversion bias after post-metallization annealing incorporating deuterium and hydrogen at 400 °C for 30 min (Fig. 2 and Fig. 3). The little difference of Jg-Vg curves before and after constant voltage stress at -3 V exceed 4000 sec show the good stability of HfO₂ films after PMA to incorporate deuterium and hydrogen treatment. Fig. 4 shows the time evolutions of HfO₂ gate current after H₂ and deuterium treatment under constant voltage stress (CVS) at gate voltage (Vg) of -3 volts. Note that the hydrogen-treated device shows the observable gate current discontinuous occurs during the CVS, as compared to the deuterium-treated device (the smoother curve) under the same conditions. The reliability of Pt/HfO₂ gate dielectric stack is effectively enhanced by introducing deuterium treatment PMA at 400 °C for 30 min, as compared to hydrogen.

![Fig. 2](image1.png)  
**Fig. 2** $J_g$-$V_g$ curves of HfO₂ gate stack MIS capacitors incorporating H₂ treatment.

![Fig. 3](image2.png)  
**Fig. 3** $J_g$-$V_g$ curves of HfO₂ gate stack MIS capacitors incorporating D₂ treatment.

![Fig. 4](image3.png)  
**Fig. 4** Time evolutions of gate current of HfO₂ gate stack MIS capacitors incorporating H₂ and D₂ treatment under -3 V constant voltage stress.

![Fig. 5](image4.png)  
**Fig. 5** Interface trap density of Pt/HfO₂ gate stack MIS structure before/after H₂ (D₂) treatment and after stress, respectively.
The interface trap density (Dit) at the midgap energy was estimated using the high-low (500 kHz & 50 Hz) frequency method (Fig. 5). The Dit values of as-deposited devices are about \(10^{11} \text{cm}^{-2}\text{eV}^{-1}\), and are slightly decreased after deuterium and hydrogen treatment. The Dit value of hydrogen-treated devices increases significantly (one order of magnitude higher) after CVS at -3 V exceeds 4000 sec, as compared to the constant Dit of deuterium-treated devices. That is another evidence for deuterium-technology to provide a better Pt/HfO₂ gate stack reliability improvement.

![Fig. 6](image)

**Fig. 6** Time evolutions of light emission intensity for (a)H₂- and (b)D₂-treated devices under constant current stress at 100 mA.

To further investigate the optical characteristic of the Pt/HfO₂ gate stack, the time evolutions of light emission intensity due to the electron-hole plasma recombination is measured [8]. Fig. 6 shows the time evolutions of light emission intensity for hydrogen-treated and deuterium-treated devices under constant current stress at 100 mA. The fresh devices are initially measured under constant current stress at 100 mA for \(10^4\) sec, followed by the post-metallization annealing in forming gas at 400 °C for 30 min to incorporate deuterium or hydrogen. As the Fig. 6 shows, the normalized light emission intensity of deuterium-treated device is stable and with less fluctuation (12.5%) compared to the fresh device (25%). Note that the hydrogen-treated device shows small gate current fluctuation at the beginning, and a significantly drop and fluctuation after 5500 sec.

It is interesting to note that the \(J_g-V_g\) characteristic of inversion current regarding to constant current stress with hydrogen and deuterium-treatment are recoverable. As Fig. 7 shown, solid line indicates \(J_g-V_g\) curve of the fresh devices. The inversion current increased 5 orders of magnitude higher after the first constant current stress at 100 mA for \(10^4\) sec (the solid circle). After post-metallization annealing was done in forming gas to incorporate hydrogen (H₂ / N₂=1 / 9) at 400 °C for 30 min, the significantly reductions of current density is observed (triangle). The inversion current density degrades to high magnitude after another constant current stress at 100 mA for \(10^4\) sec is carried out.

The deuterium-treated samples were processed with the same procedure except replacing hydrogen by deuterium. Fig. 8 shows the similar recoverable characteristic of the deuterium-treated devices.

![Fig. 7](image)

**Fig. 7** Recoverable \(J_g-V_g\) curves incorporating H₂ treatment with constant current stress at 100 mA for \(10^4\) sec.

![Fig. 8](image)

**Fig. 8** Recoverable \(J_g-V_g\) curves incorporating D₂ treatment with constant current stress at 100 mA for \(10^4\) sec.
4. Conclusions

The Pt/HfO₂ gate stack reliability is enhanced by introducing deuterium and hydrogen treatment during the post-metallization annealing. For comparison, deuterium-treated technology provides slightly better reliability improvement on both the electrical and optical reliability of Pt/HfO₂ gate stack devices. Due to the interfacial layers, the results are similar to SiO₂ gate dielectrics.

Acknowledgments

The HfO₂ deposition by ASM is highly appreciated.

References


