TDDB improvement by optimized processes on metal–insulator–silicon capacitors with atomic layer deposition of Al_2O_3 and multi layers of TiN film structure*

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Abstract: A metal–insulator–silicon (MIS) capacitor with hemi-spherical grained poly atomic layer deposition (ALD) deposited Al_2O_3 and multi-layered chemical vapor deposition (CVD) TiN structure is fabricated. The impact of the deposition process and post treatment condition on the MIS capacitor's time-dependent dielectric breakdown (TDDB) performance is also studied. With an optimized process, it is confirmed by Auger electron spectroscopy and secondary ion mass spectrometry analysis that the $Al(CH_3)_3/O_3$-based ALD Al_2O_3 dielectric film is carbon free and the hydrogen content is as low as 9×10^{19} cm^{-3}. The top electrode TiN is obtained by multi-layered $TiCl_4/NH_3$ CVD deposited TiN followed by 120 s post NH_3 treatment after each layer. This has higher diffusion barrier in preventing impurity diffusion through TiN into the Al_2O_3 dielectric due to its smaller grain size. As shown in energy dispersive X-ray analysis, there is no chlorine residue in the MIS capacitor structure. The leakage current of the capacitor is lower than 1×10^{-12} A/cm^2. No early failures under stress conditions are found in its TDDB test. The novel MIS capacitor is proven to have excellent reliability for advanced DRAM technology.

Key words: atomic layer deposition; Al_2O_3; multi-layer TiN; early failure; metal insulator silicon capacitors; TDDB
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1. Introduction

Higher capacitance values are necessary for long data retention times and high yields for continuous scale-down of dynamic random access memory (DRAM)[1,2]. Metal–insulator–silicon (MIS) structure capacitors with high permittivity material Al_2O_3 have been pursued for higher capacitance[3–6]. These kinds of MIS (TiN–Al_2O_3–silicon) capacitors are able to achieve low leakage below 10^{-8} A/cm^2 at 1 V[7]. However, there are still many challenges to achieve high reliability for MIS capacitors such as further reduction in the defect density and impurity content.

Atomic layer deposition (ALD) provides a unique capability for atomic-level control by alternating exposures to two or more precursor gases. Each exposure cycle involves self-limiting adsorption and reaction on the surface at low temperatures (150–500 °C) with excellent uniformity and almost 100% step coverage. ALD Al_2O_3 films grown by $Al(CH_3)_3$ and H_2O have been widely applied because of their high reaction ratio and high throughput. However, there is carbon contamination due to organic byproducts[8, 9] and at the same time hydrogen and hydroxyl impurities are found[10]. A previous study has shown that the hydrogen content can be decreased with 1050 °C spike annealing[11].

TiN film can be obtained by physical vapor deposition (PVD) or chemical vapor deposition (CVD) as barriers between capacitor top electrodes and Al_2O_3 dielectric layers to avoid inter-diffusion. CVD has been widely adopted in the MIS process due to its better step coverage and reduced damage to the Al_2O_3 dielectric film compared with PVD. But when TiN is deposited by CVD with precursors of $Ti(N(CH_3)_2)_4$ or $Ti(N(C_2H_5)_2)_4$, the carbon and oxygen contents will increase the resistivity of TiN. A post-treatment based on N_2/H_2 plasma is required to desorb carbon and oxygen to ensure a low and uniform resistivity[12, 13]. However, at the same time, the dielectric relaxation was also degraded due to nitrogen diffusing into Al_2O_3[14]. TiN deposited by CVD with precursors of $TiCl_4$ and NH_3 has no carbon and oxygen impurity content because no organic source is used, but high chlorine remaining in TiN will increase the resistivity and degrade the reliability of capacitors[15, 16]. NH_3 ambient for post treatment is more effective in removing chlorine from TiN film than N_2 ambient. However, the concentration of chlorine will still remain at 0.4% even after NH_3 ambient post treatment, and the reliability of capacitors will be affected by the remaining chlorine[17, 18].

In this paper, an MIS capacitor with a combination of hemi-spherical grained (HSG), $Al(CH_3)_3/O_3$-based ALD

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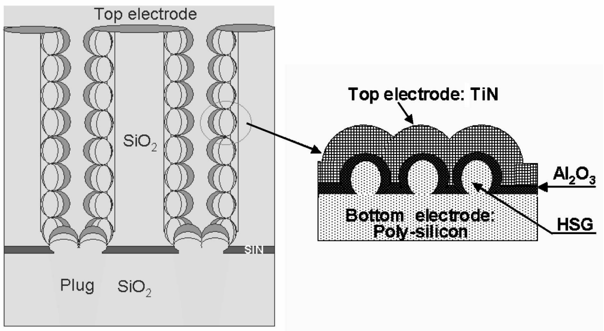

Fig. 1. Schematic view of the Al_2O_3 MIS structure capacitor.

Table 1. Experiments on three different film structures.

Experiment	ALD Al_2O_3 350 °C, 5 nm	TiN 650 °C, 30 nm
Sample 1	$Al(CH_3)_3/H_2O$	1 × 30 nm, 60 s NH_3
Sample 2	$Al(CH_3)_3/H_2O$	3 × 10 nm, 120 s/layer
Sample 3	$Al(CH_3)_3/O_3$	3 × 10 nm, 120 s/layer

Al_2O_3 and multi-layered CVD TiN is fabricated and the impact of process conditions on its performance is also studied. ALD Al_2O_3 deposition with precursors of $Al(CH_3)_3$ and O_3 by the furnace batch process is investigated. No carbon or hydrogen content is detected in the deposited Al_2O_3 film. The multi-layers of CVD TiN films are deposited with precursors of $TiCl_4$ and NH_3. With this novel multi-layer CVD TiN structure together with the increased post-treatment time in a rich NH_3 environment, the chlorine content is found to be dramatically reduced. High reliability of the MIS capacitors is achieved without any early failure of TDDB test.

2. Device structure and experiment

Figure 1 shows the structure of our MIS capacitor. It is formed by a deep contact opening with an aspect ratio of approximately 16 : 1.

The highly phosphorus doped poly-silicon plug is used as the low-resistance contact to the access transistor. The bottom electrode is formed with deposited poly-silicon with a thickness of 30 nm by decomposing SiH_4. A hemi-spherical grained (HSG) structure layer is then formed to enlarge the surface area. An Al_2O_3 dielectric film is then deposited by the ALD process with precursors of $Al(CH_3)_3$ and O_3 on top of the HSG in batch running mode. Then the top electrode is deposited by CVD using the precursors of $TiCl_4$ and NH_3 of the single wafer process.

The deposition and post treatment experiments on the MIS capacitor with ALD Al_2O_3 and CVD TiN are shown in Table 1. Three different film structures of the MIS capacitor are made to compare the remaining impurities and electrical properties.

Electrical measurement is conducted on an HP4156 and Mosaid4205 semiconductor parameter analyzer. Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) have been used to analyze the properties and impurities of ALD Al_2O_3 or TiN film with Tecnai G2F20 X-TWIN. The in-film remaining impurities are analyzed by Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS).

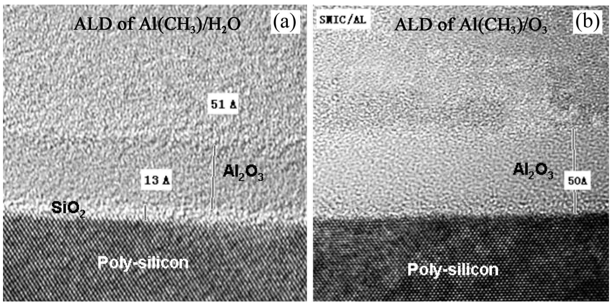

Fig. 2. TEM image of Al_2O_3/Si with different precursors.

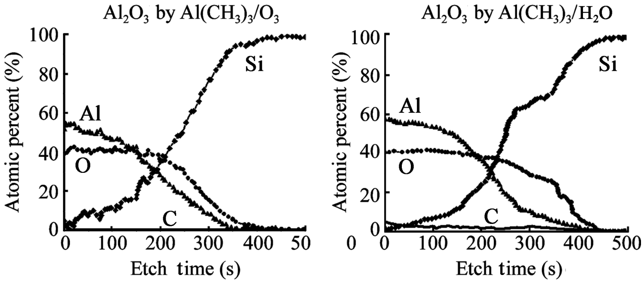

Fig. 3. AES analysis of ALD Al_2O_3 by $Al(CH_3)_3/H_2O$ and $Al(CH_3)_3/O_3$.

3. Results and discussion

3.1. Properties of ALD deposited Al_2O_3

Cross-sectional TEM images of 5 nm ALD Al_2O_3 on poly-silicon by different precursors are shown in Fig. 2. There exists an obvious SiO_2 interfacial layer between the poly-silicon and the ALD Al_2O_3 with an $Al(CH_3)_3/H_2O$ precursor as the hydroxyl diffuses through Al_2O_3 and reacts with silicon to form SiO_2, as shown in Fig. 2(a). However, there is no obvious interfacial or intermixing layer with an $Al(CH_3)_3/O_3$ precursor, as shown in Fig. 2(b). Both types of ALD Al_2O_3 are amorphous, which will reduce leakage along the grain boundaries.

It was reported that high carbon content was found in the ALD Al_2O_3 with precursors of $Al(CH_3)_3/H_2O$[8, 9]. Likewise, as shown in Fig. 3, the concentration of carbon in the ALD Al_2O_3 with precursors of $Al(CH_3)_3/H_2O$ produced in this experiment is about 4% measured by AES analysis. However, no carbon impurity is detected in the ALD Al_2O_3 with precursors of $Al(CH_3)_3/O_3$. This is because ozone (O_3) can be easily decomposed to oxygen atoms that have high oxidizing energy to remove the carbon in the organic byproducts.

SIMS is used to analyze the hydrogen content. As shown in Fig. 4, the hydrogen content is about 9×10^{19} cm^{-3} in the bulk of Al_2O_3, with a peak of 5×10^{20} cm^{-3} at the interface of Al_2O_3/poly-silicon. It is reported that the hydrogen content can be reduced from 3×10^{20} to 1.5×10^{20} cm^{-3}

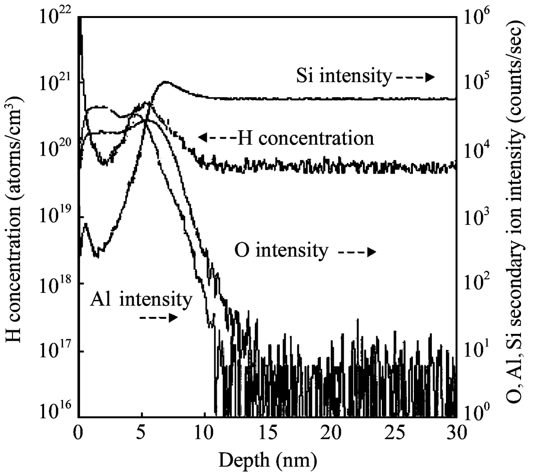

Fig. 4. SIMS analysis of ALD Al_2O_3 by $Al(CH_3)_3/O_3$.

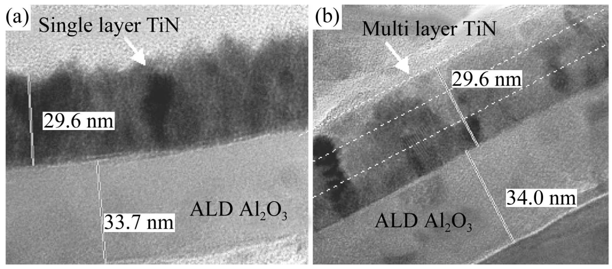

Fig. 5. TEM image of single-layer and three-layer TiN.

after 1050 °C spike annealing[11]. However, amorphous Al_2O_3 will change to single crystalline film of γ-Al_2O_3 when the annealing temperature is higher than 800 °C[8]. This will accordingly increase the leakage current along grain boundaries. At the same time, high temperatures will affect the distribution of the implanted ions in the transistor. Furthermore, significant hydrogen out-diffusion at high temperatures is not acceptable. The $Al(CH_3)_3/O_3$-based ALD Al_2O_3 film provides excellent dielectric properties with low hydrogen content and no carbon impurity (undetectable by SIMS). The precursor of H_2O produces more hydrogen and hydroxyl while the oxygen atoms decomposed from O_3 easily react with hydrogen and hydroxyl during ALD processing. Therefore, hydrogen and hydroxyl out-diffusion is reduced significantly during the ALD process by $Al(CH_3)_3/O_3$.

3.2. Properties of multi-layered TiN

In this study, the top electrode TiN film is deposited by CVD with precursors of $TiCl_4$ and NH_3 to avoid carbon and oxygen impurities[12–18]. A new solution to reduce the remaining chlorine is studied for multi-layered TiN by alternating post treatment in NH_3 ambient for each sublayer. As shown in Fig. 5(b), a three-layered TiN film is obtained with 10 nm for each sublayer. In addition, a doubled post NH_3 treatment time (120 s) has been applied after each 10 nm TiN layer deposition compared with the normal single-layer process. The grain boundary of TiN has a columnar structure. It is known that Al and Si will diffuse into TiN and some of them will punch through the columnar structure of TiN[12, 14]. As shown in Fig. 5, the height of the grain columnar boundary of TiN is shortened due to its multi-layered structure. This makes it harder for Al or Si atoms to diffuse through the multi-layered TiN than the single-layered TiN.

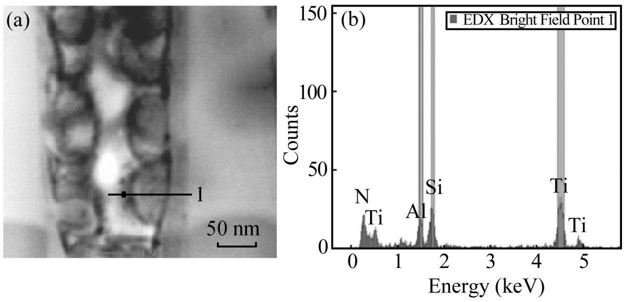

Fig. 6. TEM and EDX analysis of a real structure of the capacitor.

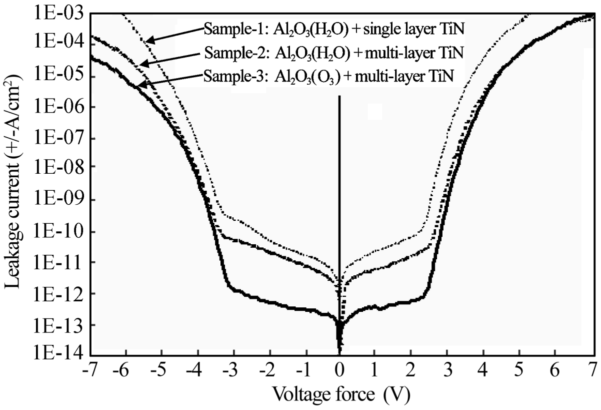

Fig. 7. *I*–*V* curve of the capacitor with three different films.

It is unavoidable that chlorine remains in the CVD deposited TiN film because of the byproduct of $TiCl_4$[15, 16]. Double time (120 s) post NH_3 treatment is found to be more effective in desorbing the chlorine residue in thin TiN film. The thinner the TiN and the longer the post NH_3 treatment, the less chlorine residue remains. As shown in Fig. 6, no chlorine is found in the three-layered TiN film with 120 s post NH_3 treatment after each sublayer of TiN deposition. The analysis is conducted by EDX in the real structure of the MIS capacitor. The dot on the short horizontal line marked in Fig. 6(a) is the location where EDX data is collected.

3.3. MIS capacitor leakage current

Electrical testing has been carried out for three types of film stack of MIS capacitor as shown in Table 1 to evaluate the influence of the remaining impurities in ALD Al_2O_3 or TiN on the capacitor leakage current. The leakage current with $Al(CH_3)_3/O_3$ based ALD Al_2O_3 and multi-layered TiN is lower than 1×10^{-12} A/cm^2 at operating conditions in the range of 0 ± 2.8 V as shown in Fig. 7. This is one order of magnitude lower than that in Bajolet's experiment[14].

Under the same testing condition, the capacitor leakage current with $Al(CH_3)_3/H_2O$-based ALD Al_2O_3 and multi-layered TiN is about two orders of magnitude lower than that with the $Al(CH_3)_3/H_2O$-based one. It also can be seen that the multi-layered TiN structure has lower leakage current com-

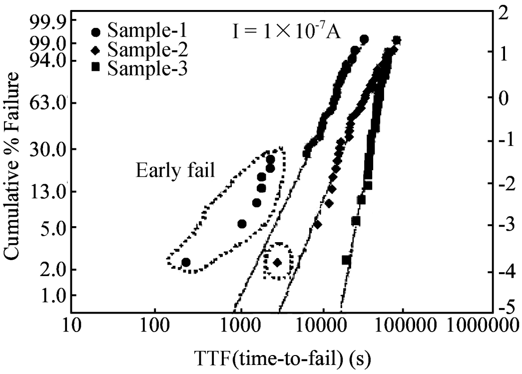

Fig. 8. TDDB Weibull distribution of three samples of the ALD Al_2O_3 MIS capacitor. T = 125 °C, E_{OX} = 8.5 MV/cm.

pared to the single-layer TiN process, which means that the impurity in the ALD Al_2O_3 dielectric plays an important role in leakage current reduction.

3.4. Early failure of capacitor TDDB

Early failures of dielectric breakdown are caused by micro defects in the silicon electrodes of SiO_2-based capacitors such as oxygen micro-precipitates and metallic contamination. The mechanism of the dielectric breakdown of these early failures is thermal breakdown. The upper limit of the early failure breakdown voltage is determined by the self-healing energy necessary for the poly-silicon electrode and is proportional to the dielectric thickness[19–22]. The Al_2O_3 capacitor (5 nm dielectric) in intrinsic failure mode has a high breakdown voltage (> 6 MV/cm). The current density varies with temperature and applied voltage on Al_2O_3 capacitor, illustrating typical phenomena of Fowler-Nordheim (FN) tunneling[23]. Based on the Wentzel-Kramer-Brillouin (WKB) approximation, extrinsic early failure will be greatly affected by defects and impurities in the Al_2O_3 MIS structure. New ALD Al_2O_3 dielectric technology is required for better reliability[24–26].

Early failure is not only a function of the dielectric material for the extrinsic failures of the ALD Al_2O_3 capacitor but is also related to the forcing voltage[27]. The in-film remaining impurities enhance electron hole recombination in the MIS capacitor by the forcing voltage which will cause early failure at some high impurity density area.

Table 2. TDDB characteristics of the three samples.

Experiment	Ea	β	Slope	Life time ($T_{0.1\%}$ sec)
Sample 1	1.09	4.78	1.96	1.26×10^{11}
Sample 2	1.09	4.78	2.07	2.19×10^{12}
Sample 3	1.09	4.78	4.36	4.87×10^{13}

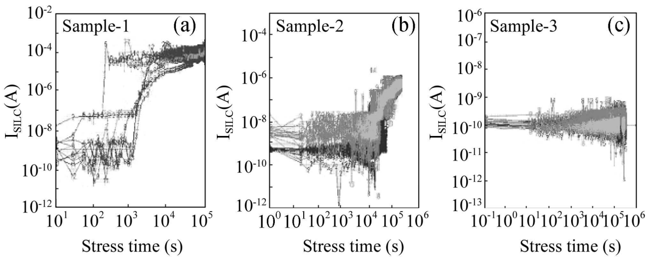

Fig. 9. I–t curve of SILC absolute degradation versus time for three samples of the ALD Al_2O_3 capacitor. T = 250 °C, E_{OX} = 7.5 MV/cm.

Three capacitor samples shown in Table 1 were prepared with different deposition processes and structures and their TDDB performance was measured and compared. Sample 3 of the MIS capacitor with $Al(CH_3)_3/O_3$-based ALD Al_2O_3 and multi-layered TiN has superior TDDB distribution and its predicted $T_{0.1\%}$ of 4.87×10^{13} s (lifetime after 0.1% failure) at operation conditions is significantly longer than the lifetime criteria of 10 years (3.15×10^8 s) as shown in Fig. 8 and Table 2. Sample 1 with $Al(CH_3)_3/H_2O$-based ALD Al_2O_3 and single-layer TiN shows serious early failures. This is attributed to its high impurities in Al_2O_3 dielectric and TiN films. Sample 2 with $Al(CH_3)_3/O_3$-based ALD Al_2O_3 and single-layer TiN shows significant improvement over sample 1 with $Al(CH_3)_3/H_2O$-based ALD Al_2O_3. Only one early failure is found and at the same time the whole distribution of sample 2 is much better than that of sample 1.

Figure 9 is the measured current–time (I–t) curve. These are the original raw data used to construct the lifetime distribution in Fig. 8. Figure 9(a) shows that there is a large variation in the initial leakage on sample 1, which reflects the early failure. However, there is no up trend till 300 000 s on sample 3 under the same stress conditions (T = 250 °C, E_{OX} = 7.5 MV/cm) as shown in Fig. 9(c). The above TDDB test results prove that an MIS capacitor with excellent reliability characteristics can be obtained by $Al(CH_3)_3/O_3$-based ALD deposition of an Al_2O_3 insulator and a multi-layered TiN conducting electrode.

4. Conclusions

We have investigated the influence of impurity residues in ALD Al_2O_3 and CVD TiN on MIS capacitor performance by both chemical and electrical analysis. No carbon and very low hydrogen are found in $Al(CH_3)_3/O_3$-based ALD Al_2O_3. There is also no chlorine residue in the multi-layered $TiCl_4/NH_3$-based CVD TiN film with 120 s post NH_3 treatment after each TiN sublayer deposition. The height of the columnar grains of TiN is reduced for a better barrier property, to prevent impurity diffusion and accordingly degradation of the ALD Al_2O_3 dielectric.

The leakage current of the MIS capacitor with $Al(CH_3)_3/O_3$-based ALD Al_2O_3 and multi-layered TiN is about 1×10^{-13} A/cm^2 at the operation voltage range of 0 ± 2.8 V. No early failure is found in the TDDB Weibull distribution. The predicted TDDB lifetime $T_{0.1\%}$ is much higher than the 10 year criterion and the initial leakage of the I–t curve shows no up trend till 300 000 s under the testing stress conditions. This new-type HSG–Al_2O_3–TiN MIS capacitor is proven to have low impurities and excellent reliability for advanced DRAM applications.

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