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Improvement of Leakage Current Property of TIT Capacitor with Compositionally Stepped HfxAlyOz Thin Films

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Compositionally stepped HfxAlyOz dielectric thin films were fabricated for application to DRAM capacitor dielectrics. Compositionally stepped HfxAlyOz dielectric thin film is composed of an Al rich bottom layer and a Hf rich top layer between top and bottom TiN electrodes. The leakage current of TIT (TiN/Insulator/TiN) capacitors with compositional stepped HfxAlyOz could be lowered by compositional stepping and accompanying post ozone treatment, respectively. The prepared TIT capacitor showed drastically reduced leakage current and highly improved break down voltage characteristics of 0.45~0.75 V, while maintaining the same equivalent oxide thickness (EOT). In the case of stepped film with Hf/Al=1/1, EOT showed a very small value of 12.8 Å while maintaining leakage current as low as 2×10^{-16}A/cell at +1.0 V.

Keywords: HfxAlyOz, TIT capacitor, ALD, ozone, leakage current

1. INTRODUCTION

It is considered that the EOT value should be less than 14 Å to obtain a 30 fF/cell for development of a 70 nm generation DRAM capacitor[1]. Therefore, high-k materials such as Ta_2O_5, HfO_2, ZrO_2, and Al_2O_3 have been studied. ALD (Atomic Layer Deposition)-processed HfO_2 thin film is considered to be the most promising candidate capacitor dielectric material for 70 nm generation DRAMs or beyond due to it's high dielectric constant (~25) and high band gap (5.6 eV) energy[2]. However, it is not easy to use a single layer itself because of poor thermal stability during post thermal processes after deposition of dielectric films such as formation of a top electrode or inter layer dielectrics (ILD). This poor stability mainly originates from easy crystallization at low temperature[3,4]. It is generally known that grain boundaries can be leakage paths along in a capacitor[5].

Consequently, most research on HfO_2 based dielectrics has concentrated on finding a means of suppressing crystallization such as through lamination or alloying with Al_2O_3[6,7] Our group recently reported that nano-mixed HfxAlyOz thin film could be formed by ALD and is much more stable than single HfO_2 in terms of thermal endurance during post thermal processing[8]. Notably, the ALD process for HfxAlyOz thin films should be carried out at 300 °C or less due to thermal decomposition of the Hf precursor itself[9]. However, previous research has found that this low temperature process results in poor electrical properties due to residual impurities such as carbon or hydrogen[10,11]. There is also concern that surface oxidation of the storage node might occur in the case of a TIT capacitor when the deposition process for dielectric films is conducted at high temperature. Under these circumstances, a low temperature process that can minimize detrimental effects arising from impurities is an attractive solution.

In this work, new dielectric film structures for a DRAM capacitor are proposed. Stepped film is/are based on nano-mixed HfxAlyOz thin films with post ozone treatment for the purpose of improving electrical properties such as leakage current and break down voltage.

2. EXPERIMENTS

Nano-mixed HfxAlyOz films were fabricated by atomic layer deposition from TEMAH (Tetrakis-Ethyl-Methyl-Amino-Hafnium) and TMA (Tri-Methyl-Aluminum) as chemical precursors for Hf and Al, respectively. The ALD process was performed by repeating a unit cycle of $[(Hf/N_2/O3/N_2)_m(Al/N_2/O3/N_2)_n]$ at 300 °C. The bubbler and delivery line for the Hf precursor were heated at 90 °C and 110 °C, respectively. Film composition was controlled by changing the feeding ratio, m/n (hereafter, m/n refers to the gas feeding ratio). More details on the experimental conditions for

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nano-mixed HfxAlyOz films can be found in our previous publication[8].

Ozone treatment was carried out at 430 °C after deposition of dielectric films. MIM (Metal/Insulator/Metal) type capacitors with a TiN layer as the top and bottom electrodes were fabricated for the evaluation of electrical properties, including leakage current and dielectric properties. Impurities such as carbon or hydrogen were analyzed by secondary ion mass spectroscopy (SIMS). Composition of the HfxAlyOz films was compared by auger electron spectroscopy (AES). Transmission electron microscopy (TEM) was used for the analysis of microstructure of HfxAlyOz itself and the interface between the dielectric and electrode.

3. RESULTS AND DISCUSSION

Many studies have reported that annealing in reactive gas ambient such as N_2O, O_2 plasma, and UV-O3 as well as pure ozone is effective for the improvement of the leakage current property of capacitor dielectrics[12,13,14,15]. Figure 1 shows the variation of leakage current and breakdown voltage of cylinder typed TIT capacitors with HfxAlyOz (61 Å, m : n=1 : 1) as a function of exposure time during post ozone treatment. While leakage current is effectively lowered for up to 60~120 seconds, it thereafter abruptly increased. From SIMS analysis, it was found that carbon content was reduced after post ozone treatment by about 25% (results not shown here). It is well known that carbon impurities can be a leakage source in dielectrics such as Ta_2O_5 or BST through the creation of defects such as traps[12, 14].

Notably, the lowering of leakage current is more dominant at negative than at positive bias. Assuming that negative biased leakage current reflects the top interface between the top TiN and dielectric films[15], it appears that the dominant reduction at the top interface can be attributed to more effective elimination of carbon impurities from the dielectric surface. Carbon elimination from HfxAlyOz is thought to occur largely through the diffusion of activated oxygen from the surface to the bottom interface[16]. This explanation is supported by the finding that the breakdown voltage increase after treatment is much higher at negative bias than positive bias, i.e. 0.35 V and 0.2 V, respectively, as shown in inset figure. On the other hand, breakdown voltage and leakage current degraded faster at positive bias, which reflects the interface between HfxAlyOz and the storage node TiN at long time treatment. Based on our TEM analysis (results not shown here), this faster degradation at positive bias is attributed to surface oxidation of the bottom TiN electrode. Considering the general phenomenon that TiN oxidizes at a temperature of roughly 500 °C even in O_2 ambient[17], it is strongly expected that TiN oxidation can occur. This in turn has a detrimental effect on leakage current by making TiOx, which has low resistivity and band gap energy, between HfxAlyOz and TiN[18]. Considering the ozone treatment

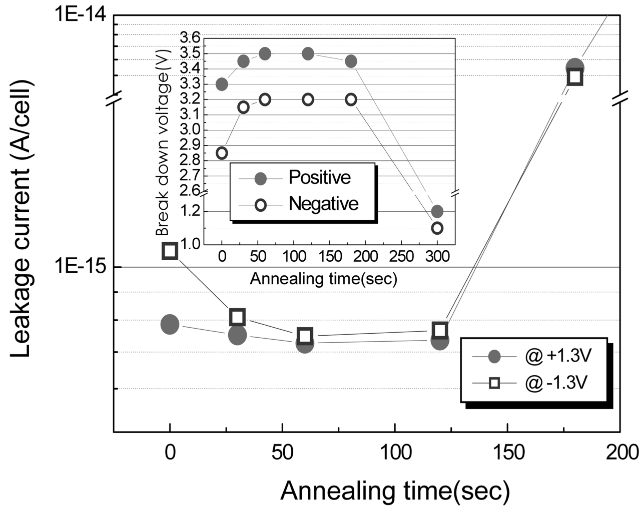

Fig. 1. Variation of leakage current and breakdown voltage of TIT capacitors with HfxAlyOz (m:n=1:1) as a function of ozone treatment time.

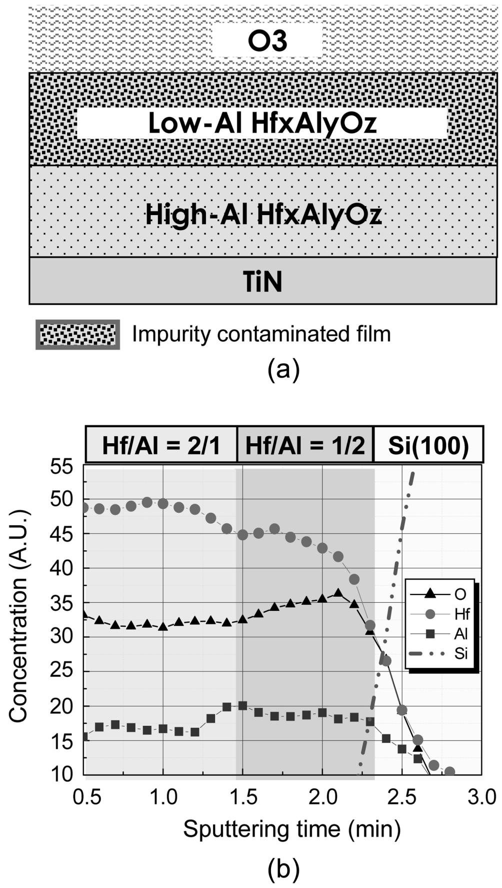

Fig. 2. Schematic illustration of compositionally stepped HfxAlyOz film (a) and depth profiles of each element within stepped films analyzed by AES (b).

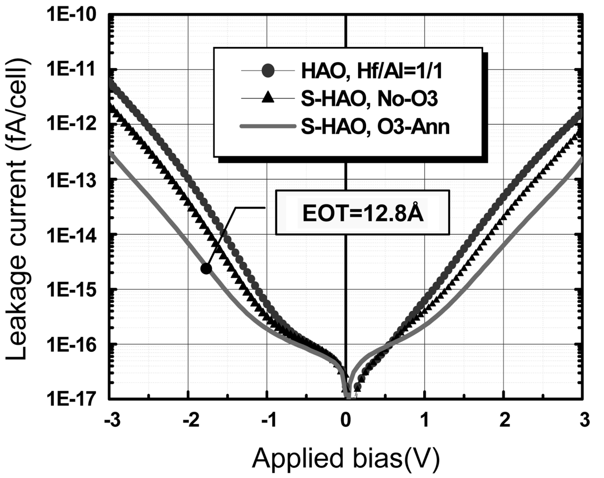

Fig. 3. IV curves of TIT capacitors with three different dielectric films. Overall Hf/Al ratio (m:n) is 1:1.

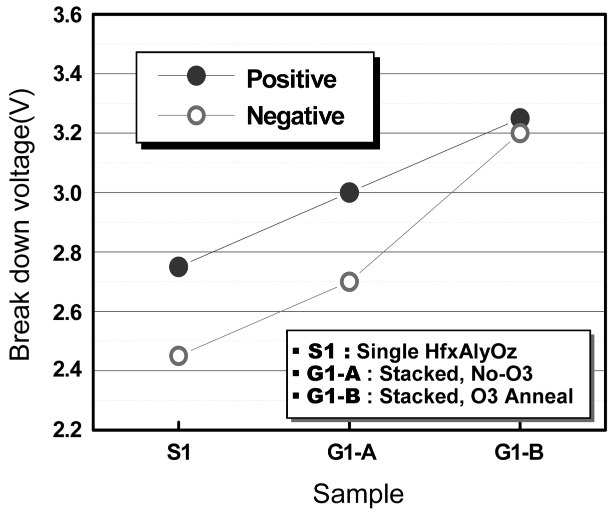

Fig. 4. Variation of breakdown voltages of TIT capacitors with three different dielectric films. Overall Hf/Al ratio (m:n) is 1:1.

temperature of 430 °C, this explanation appears to be reasonable. This result implies that post ozone treatment can be very effective in terms of lowering leakage current by reducing carbon impurities, but should be accurately controlled in order to avoid TiN oxidation.

According to our previous results concerning HfxAlyOz dielectrics[8], leakage current is reduced and the dielectric constant decreases when Al concentration increases. These results imply that both leakage current and dielectric property can be controlled by regulating composition. In addition, it was also found that carbon impurity level can also be lowered by increasing Al content in HfxAlyOz films. This trend in carbon level shows that the main carbon source originates from HfO_2 rather than Al_2O_3, more specifically, from TEMAH rather than TMA. In the case of TEMAH for HfO_2, the residual carbon may be higher due to the lack of reactivity with ozone at the same temperature in comparison with TMA.

Upon consideration of the above experimental results, we designed a new dielectric film structure from HfxAlyOz, as shown in Fig. 2(a). This new film structure is compositionally stepped and accompanied by post ozone treatment. Regarding dielectric films, the bottom layer is designed to be rich in Al content for the purpose of lowering leakage current without any treatment for carbon elimination and the top layer is relatively Hf rich for overall modulation of the dielectric constant. Final post ozone treatment is applied in order to reduce carbon contents in the Hf rich region. In this type of film structure, post ozone treatment can be concentrated only on the dielectric surface in order not to oxidize the bottom TiN layer via long time exposure. The designed film structure was confirmed by AES analysis, as can be seen in Fig. 2(b).

It is generally known that the leakage current of a capacitor is required to be less than 0.2 fA/cell at 1.0V for practical application to the DRAM industry. Figure 3 shows I-V curves of TIT capacitors with single HfxAlyOz film and stepped films applied to an 80 nm scale cylinder typed storage node. In this experiment, ozone treatment was conducted for only 90 seconds in order to prevent surface oxidation of bottom TiN from the result of Fig. 1. In the case of stepped film with post ozone treatment, leakage current was significantly lowered from 6×10^{-16}A/cell to 2×10^{-16}A/cell while maintaining almost the same EOT values of 12.8 Å. This data confirms that the proposed structure fulfils its designed role. Besides leakage current, breakdown voltages are significantly increased, as shown in Fig. 4. In the case of G1-B with final ozone treatment, unlike G1-A, the breakdown voltage at negative bias displayed a greater increase than at positive bias after ozone treatment. This dominant increase in breakdown voltage at negative bias is mainly attributed to preferential improvement of the top interface, i.e., carbon reduction, in accordance with the result shown in Fig. 1. This data reveals that enhanced electrical properties can be achieved by compositionally stepped HfxAlyOz film structure at a real DRAM cell structure.

4. CONCLUSIONS

We have proposed a new concept for a dielectric film structure, a compositionally stepped HfxAlyOz film applicable to a 70 nm scale DRAM capacitor. The stepped film structure is composed of dual layers having different Hf/Al composition accompanied by post ozone treatment. It was found that compositional stepping and ozone treatment made a vital contribution to the reduction of leakage current while maintaining the same equivalent oxide thickness. The

TIT capacitor with stepped HfxAlyOz film showed drastically reduced leakage current of 2×10^{-16}A/cell at +1.0 V and highly improved break down voltage of 0.45~0.75 V.

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