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Degradation of Ta_2O_5 Gate Dielectric by $TiCl_4$-Based Chemically Vapor Deposited TiN Film in W/TiN/Ta_2O_5/Si System

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Introduction

As devices are scaled down, ultra thin gate oxides less than 3.0nm are needed. Silicon dioxide (SiO_2) has its physical limit for thickness because of high leakage current due to direct tunneling. So, a thicker film with high permittivity is required to reduce leakage current. Tantalum pentoxide (Ta_2O_5) has been recommended as an alternative of SiO_2 for its high permittivity [1-3]. Ta_2O_5 can be deposited by either chemical vapor deposition (CVD) or physical vapor deposition (PVD). Penta Ethoxy Tantalum (PET: $Ta(OC_2H_5)_5$) is the most widely used tantalum precursor in CVD Ta_2O_5 process [1, 2, 4]. Reactive sputtering [5, 6] is the most common process for PVD Ta_2O_5.

There have been several studies on the reaction between TiN and Ta_2O_5 in capacitors. Diffusion of Ta into $TiCl_4$–based CVD TiN layer and void formation in the Ta_2O_5 layer were observed by H. J. Lee et al. [4] in metal/oxide/poly-silicon capacitors. J. P. Chang et al. [5] reported that excessive oxygen diffused to form a TiO_2 layer in metal/oxide/metal capacitors. However, there are few studies on the gate characteristics related to thermal stability of W/TiN/Ta_2O_5/Si devices. In this work, we show the degradation mechanism of Ta_2O_5 gate dielectric caused by $TiCl_4$–based CVD TiN or PVD TiN barrier in W/TiN/Ta_2O_5/Si system.

Experiment

10nm of tantalum pentoxide film was deposited on p-type (100) Si substrate by metal organic chemical vapor deposition (MOCVD) with the precursor of $Ta(OC_2H_5)_5$ at 450℃ using Ar as a carrier gas. Prior to film deposition, Si surface was nitrided in ammonia ambient at 800℃ for 30s to exclude oxidation of Si substrate during the Ta_2O_5 deposition. Post annealing for crystallization of Ta_2O_5 was performed at 800℃ for 5min in oxygen ambient by rapid thermal process (RTP). During the post annealing, 3.0nm of silicon oxide layer was formed under Ta_2O_5 layer. 40nm of PVD or CVD TiN film was deposited on the Ta_2O_5 layer for comparison. PVD TiN films were reactively sputtered in N_2/Ar mixture ambient with D.C power of 1kW. CVD TiN film was deposited using $TiCl_4$ and NH_3 as reactants at 680℃. Tungsten film of 100nm thickness was deposited on the TiN layer for gate electrode. After tungsten deposition, samples were annealed at 900℃ for 30s in nitrogen ambient to evaluate the thermal stability of the multi-layers. Current-voltage characteristics of the devices were measured using HP4155A with the square patterns of 1×10^{-4} cm^2 area. Transmission electron microscopy (TEM) was used to observe multi-layers. Chemical reaction and mass transport were characterized by secondary ion mass spectrometry (SIMS).

Results and Discussion

Breakdown fields measured at 1mA/cm^2 of leakage current are shown in Fig.1. In the case of as-deposited TiN barriers, PVD and CVD show similar breakdown behaviors. However, after annealing at 900℃, CVD TiN barriers show much low breakdown fields compared with PVD TiN, indicating that CVD TiN has worse barrier performance than PVD TiN.

In order to reveal the cause of the degradation of Ta_2O_5 gate devices that adopt CVD TiN barrier, TEM observations were carried out. From the cross-sectional view of PVD TiN, micro-voids are observed within the Ta_2O_5 layer along the TiN/Ta_2O_5 interface after annealing at 900℃ (Fig. 2). However, the damage of Ta_2O_5 in CVD TiN sample is much more severe than in PVD TiN. Macro-void or disconnected area is shown in CVD TiN sample. From these results, It is found that PVD TiN has better barrier property against diffusion and reaction of materials than CVD TiN.

The SIMS depth profiles confirm the origin of the void formation near the TiN/Ta_2O_5 interface. In PVD TiN sample, O and Cl profiles are kept almost constant before and after annealing. However Ta ion counts increase in the PVD TiN layer after annealing indicating that Ta diffuses into TiN layer (Fig.3). That is to say, out-diffusion of Ta from the Ta_2O_5 layer into TiN layer is conjectured to lead to void formation in the Ta_2O_5 layer. On the other hand, vigorous diffusion of O as well as Ta into TiN layer is observed in CVD TiN sample after annealing (Fig.4). We consider the degradation mechanism of CVD TiN is different from that of PVD TiN. The small amount of diffusion of Ta can be explained by the existence of excessive Ta in Ta_2O_5. However, massive movement of tantalum accompanying oxygen diffusion has to be explained in other ways. The cooperative diffusion behaviors of both elements indicate that the reduction of Ta_2O_5 is involved in the degradation of the Ta_2O_5 layer in CVD TiN sample.

It is reported that Cl_2 is the most effective dry etching chemistry for Ta_2O_5 [7]. Considering that the CVD TiN layer contains 10 times more Cl than PVD TiN, residual Cl can reduce Ta_2O_5 and generate free Ta and O atoms. Thermodynamic consideration is also consistent with this discussion. In our calculation of Gibbs free energy, gaseous tantalum pentachloride ($TaCl_5$) and oxygen can be produced by the reaction of Ta_2O_5 with Cl_2 at 900℃ (Fig.5). Or reduction of Ta_2O_5 is to occur by the corrosion behavior of Cl. Thermodynamic data for calculation is cited from Thermochemical data book [8]. Free oxygen and tantalum generated from the reduction of Ta_2O_5 can easily diffuse into TiN or Si at high temperature. All this procedures can explain the poor thermal stability of CVD TiN on Ta_2O_5 layer.

Conclusion

We have shown the gate characteristics of W/TiN/Ta_2O_5/Si devices related to the thermal stability of TiN barriers. Breakdown characteristics of PVD TiN samples at elevated temperature are much better than CVD TiN samples. Micro-voids within the Ta_2O_5 layer are observed in PVD TiN sample after annealing at 900℃. The small amount of diffusion of Ta into TiN layer is observed and is considered to cause void formation in the PVD TiN sample. Ta_2O_5 is severely damaged in CVD TiN sample after annealing. High content of residual chlorine in CVD TiN is considered to reduce Ta_2O_5 and generate free Ta and O atoms. Free oxygen and tantalum generated from the reduction of Ta_2O_5 diffuse into TiN layer. As a result, macro void or disconnected area is formed degrading devices significantly.

References

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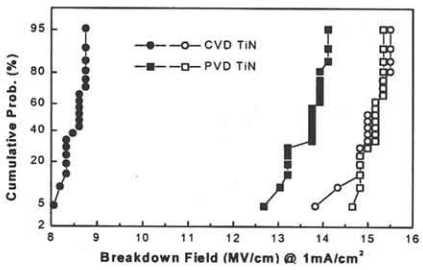

Fig.1. Breakdown characteristics of W/TiN/Ta_2O_5/Si devices at the current density of 1mA/cm^2. The open symbols indicate as deposited condition and the solid symbols indicate that samples are annealed at 900℃.

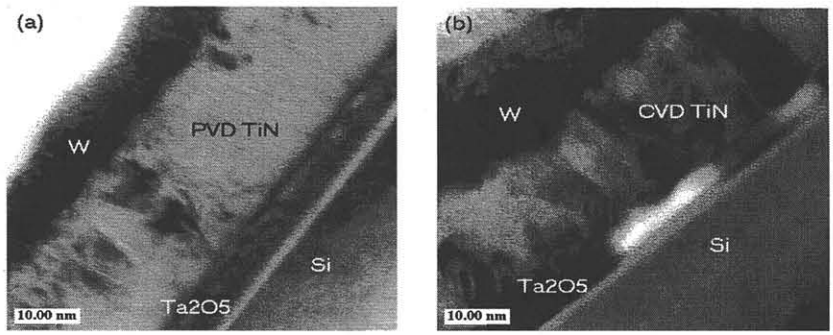

Fig.2. Cross-sectional TEM images showing damage of Ta_2O_5 layer after annealing at 900℃ for 30s in N_2 ambient (a) PVD TiN barrier and (b) CVD TiN barrier. SiO_2 layers that were formed during the post annealing of Ta_2O_5 are shown.

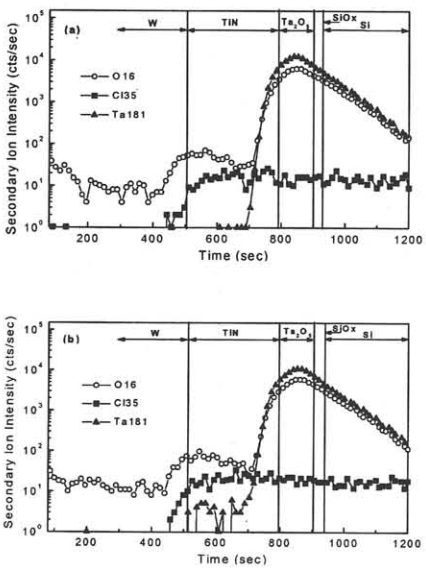

Fig.3. SIMS depth profiles of Ta, O and Cl in the samples with PVD TiN barrier. (a) as-deposited and (b) after annealing at 900℃.

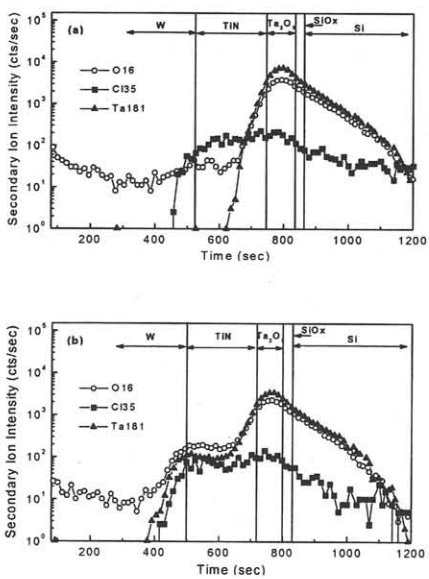

Fig.4. SIMS depth profiles of Ta, O and Cl in the samples with CVD TiN barrier (a) as-deposited and (b) after annealing at 900℃.

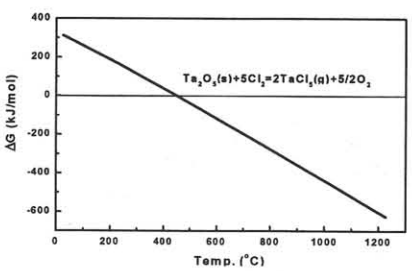

Fig.5. Gibbs free energy of the reaction between Ta_2O_5 and Cl_2 as a function of temperature. The forward reaction is possible at the temperature ranges where the reaction line lies below the horizon.