Development of TiSiN CVD process using TiCl$_4$/SiH$_4$/NH$_3$ chemistry for ULSI anti-oxidation barrier applications

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Abstract

CVD-TiSiN may be promising material for O$_2$ diffusion-barrier films in ultra-large scale integrated (ULSI) circuit applications, especially for dynamic random-access memory (DRAM) capacitors. We developed a method for introducing Si into TiN, which is a common material used for diffusion-barrier films. TiSiN films were deposited by reacting TiCl$_4$, SiH$_4$, and NH$_3$ in a hot-wall CVD reactor. We measured TiSiN film deposition rates, composition, crystal structure, and resistivity as a function of SiH$_4$ partial pressure. Adding Si to TiN converts the TiN film structure from columnar grains to columnar-free structure films, thereby effectively removing the diffusion paths for O$_2$. The resistivity of TiSiN films was increased by adding SiH$_4$ to the reactant gas. With an increase in SiH$_4$ partial pressure up to $P_{SiH_4} = 0.8$ Torr, the resistivity gradually increased, but for $P_{SiH_4} = 1.2$ Torr, the phase present in the film was almost SiN and its resistivity jumped up. TiSiN film rapid thermal annealing was performed to evaluate the anti-oxidation performance at the temperature range from 400 to 600 $^\circ$C in 100 Torr of O$_2$. For an increase the Si concentration up to 4.4 at.% improved anti-oxidation performance of TiSiN films. Flow modulation chemical vapor deposition (FMCVD) was used to create TiSiN films with low Cl concentration and improved anti-oxidation performance.

Keywords: TiSiN; Barrier metal; TiCl$_4$; SiH$_4$; NH$_3$; CVD; Partial pressure; Anti-oxidation

1. Introduction

To achieve the integration required for dynamic random access memory (DRAM) devices larger than 256 Mbits requires advanced dielectric materials and complicated capacitor structures. Currently, Ta$_2$O$_5$ formed by using chemical vapor deposition (CVD) is a promising dielectric material for making DRAM storage capacitors, because of its high dielectric constant and excellent step coverage over crown-shaped capacitor [1]. To achieve uniform step coverage, the deposition of Ta$_2$O$_5$ is done in the temperature range of 350–450 $^\circ$C by using Ta(OC$_2$H$_5$)$_5$ as the source precursor [2]. The as-deposited films formed under these conditions have carbon impurities and void, which results in high leakage current and low dielectric constant. The leakage current can be reduced by repairing oxygen vacancies, by removal of carbon, by densification and by increasing the overall oxide thickness. Several post-annealing methods were evaluated for improving the electric characteristics of Ta$_2$O$_5$ [3–9]. O$_2$ annealing at 600–750 $^\circ$C is effective for reducing the leakage current and crystallization of Ta$_2$O$_5$ [5–8], however, at these relatively high temperatures O$_2$ diffuses into the bottom electrode, resulting in oxidation of the plug electrode that is made of poly-silicon (poly-Si) [9]. Once poly-Si is oxidized with the thickness of over several nanometers, the total capacitance of memory cell is substantially reduced, due to the lower dielectric constant of silicon oxides. Therefore, an O$_2$ diffusion barrier metal is required between Ta$_2$O$_5$ layers and poly-Si plugs. The requirements for O$_2$ diffusion barrier metal are as follows, (1) the film resistivity should be as low as that of poly-Si of 1000 $\mu$cm, (2) barrier metal is hardly oxidized for keeping its low resistivity, and (3) barrier metal should prevent oxygen diffusion into underlying poly-Si to protect it against oxidation.

Titanium nitride (TiN) films are commonly used as diffusion-barrier layers in ultra-large-scale integrated (ULSI) circuits for aluminum/tungsten interconnect technology [10,11]. TiN films are also used for copper [12] and O$_2$ [13] diffusion-barrier layers, but TiN films tend to form columnar structures, which can form paths of rapid diffusion...
and therefore, degrade the barrier properties. It has been also reported that TiN layers are easily oxidized above a temperature of 450°C [14,15]. To overcome these disadvantages, TiN/SiN-nanocomposites have been synthesized by using CVD [14–17] and physical vapor deposition (PVD) [15,18,19] methods. These nanocomposite films are stable above a temperature of 1000°C due to the superior thermal properties of SiN matrices against oxygen diffusion [17]. Because these films were developed for mechanical coatings, their electrical properties have not been reported.

Nicolet et al. [20] suggested using amorphous layers for diffusion barriers in ULSI applications. The addition of Si into refractory metal nitrides, such as TiN [21] and (Mo, Ta, W)–N [22,23] made these nitride materials as amorphous thin layer without columnar grains that prevent Cu diffusion in ULSI Cu interconnects. TiSiN films deposited by using PVD exhibited superior barrier properties against Cu diffusion [24–26]. However, uniform step coverage over high-aspect-ratio trenches and holes is required in ULSI device fabrication, and because CVD processes provide better step coverage compared to PVD, CVD processes should be developed for depositing TiSiN films [21,27–29].

TiN films deposited from TiCl4/NH3 reactants can achieve excellent step coverage and low resistivity [30,31]. In this work, we tried to develop TiSiN CVD process by adding SiH4 into TiCl4/NH3 chemistry. Main efforts were made to determine best SiH4 concentration that could convert TiN columnar structure into TiSiN columnar-free structure for better anti-diffusion properties with low resistivity. We measured the electrical resistivity and anti-oxidation performance of TiSiN films as a function of SiH4 partial pressure, and we developed a TiSiN-CVD process for O2 diffusion-barrier applications.

2. Experimental

For TiSiN deposition, TiCl4, SiH4, and NH3 were used for titanium, silicon, and nitrogen sources, respectively. The total pressure was maintained at 2.0 Torr and the total gas flow rate was 25 sccm. Ar was used as a balance gas to control the total pressure of the reactants. Deposition was done in a hot-wall, quartz, tube reactor, which is shown in Fig. 1. The inner diameter of the reactor was 8.5 mm and a uniform temperature zone existed over 40 cm of the reactor. To avoid TiCl4–NH3 adduct formation in the gas feeding system, a coaxial nozzle was used to introduce TiCl4 and SiH4/NH3 separately. Film deposition was done at 600°C on Si substrates with 100-nm-thick thermally grown SiO2 films. The substrates were placed 18, 28, and 38 cm from the inlet to the reactor, which corresponds to 10, 20, and 30 cm from the end of the gas-inlet nozzle, respectively. Field-emission scanning electron microscopy (FE-SEM, JEOL 6340F) was used to measure film thickness. X-ray diffraction (XRD, MAC M18XHF) was used to determine the crystal structure, and film compositions were analyzed by using X-ray photoelectron spectroscopy (XPS, ULVAC-phi 1600C). A four-point probe method was used to measure the electrical resistivity of the films. For the anti-oxidation performance, the deposited films with the thickness of 50–150 nm were annealed in an O2 ambient (total pressure...
of 100 Torr) by rapid thermal annealing (RTA) chamber at 400–650 °C for 2 min. The sheet resistivity was measured after annealing and the same sample was annealed again at a temperature 50 °C higher than the previous annealing cycle. This procedure was repeated until the TiSiN film resistivity became infinite.

3. Results and Discussion

3.1. TiSiN film-deposition with TiCl₄–SiH₄–NH₃

Preliminary deposition was done to form TiSiN films from a TiCl₄/SiH₄/NH₃ mixture. The initial concept in determining the deposition conditions was a linear combination model, that the overall deposition rate could be represented as a linear combination of deposition rates of component processes. We first tested whether the deposition rate of TiSiN films could be represented as the sum of the TiN deposition rate from TiCl₄/NH₃ and the Si deposition rate from SiH₄. Fig. 2 shows the deposition rate of Si from SiH₄ and the deposition rate of TiN from TiCl₄/NH₃. The partial pressure of SiH₄, NH₃, and TiCl₄ was $P_{\text{SiH}_4} = 0.4$, $P_{\text{NH}_3} = 0.08$, and $P_{\text{TiCl}_4} = 0.024$ Torr, respectively. The film deposition rate of a mixture from SiH₄, NH₃, and TiCl₄ was lower than that from SiH₄ alone or from a mixture of TiCl₄ and NH₃. These experimental results suggest that our initial concept to estimate Si content in TiSiN film from the linear combination of TiN deposition rate and Si deposition rate, does not work for this reaction chemistry. Thus, we investigated the detail of this deposition chemistry as shown below.

The growth rate of Si films increased with increasing distance from the reactor inlet, which suggests that film deposition is strongly affected by the deposition of SiH₄ active intermediates. The active intermediates formed by SiH₄ decomposition include SiH₃, H₂SiH₂, and Si₂H₃, which readily react with each other and with other reactants [32]. These active intermediates contribute to the surface reactions to enhance the film growth rate, and enhance the gas-phase reactions. The active intermediates therefore, significantly affect the film deposition rate.

The SiN deposition rate achieved by using the gas mixtures of SiH₄/NH₃ was greater than the deposition rate of Si from SiH₄ alone. This indicates that the reaction of SiH₄/NH₃ was faster than for SiH₄ alone. SiN film-deposition rates also increased with increasing axial position, possibly due to active intermediates formed in the gas phase. At 18 cm the ratio between growth rate of SiN and Si films was 2:1, and increased with increasing axial distance to a maximum of 3:1. This suggests that Si deposition from SiH₄ and the gas-phase reactions that form active intermediate species is accelerated by NH₃ addition [33,34]. However, the addition of TiCl₄ into SiN deposition chemistry significantly suppressed the growth rate. The growth rate at the inlet decreased and we did not observe higher growth rates further downstream in the reactor. This suggests that TiCl₄ and its related intermediate species significantly suppress Si/SiN deposition directly from gas phase and also suppress gas-phase reactions to form active intermediate species.

Fig. 3 shows XPS measurements of the TiSiN film composition vs. distance from the inlet. TiSiN films including 1.9 at.% of Si were obtained at 18 cm, however, SiNₓ was the major component from 28 cm and beyond. Several percentage of O, C, and Cl were contained as impurities in the film, but they totaled to less than 10%. The TiSiN film deposited at 18 cm had a relatively low electrical resistivity of 500 μΩ cm due to the small amount of Si incorporation.

Figs. 2 and 3 show that the process window to obtain acceptable TiSiN films may be narrow. Here after we investigated the effect of $P_{\text{SiH}_4}$ on the TiSiN-CVD process to

Fig. 2. Deposition rate of films using TiCl₄, SiH₄, and NH₃ as a source for Ti, Si, and N, respectively.

Fig. 3. Film composition as a function of distance from inlet, for $P_{\text{SiH}_4} = 0.4$ Torr, $P_{\text{NH}_3} = 0.08$ Torr, and $P_{\text{TiCl}_4} = 0.024$ Torr.
find the optimum condition to make TiSiN film with low resistivity with good anti-oxidation characteristics.

3.2. Effect of SiH₄ partial pressure on the film properties

As mentioned in Section 3.1, TiSiN films were successfully deposited from TiCl₄, SiH₄, and NH₃ at an axial position 18 cm from inlet. We investigated the film deposition rate of specimen at 18 cm using TiCl₄, SiH₄, and NH₃ as a function of P_{SiH₄}. Fig. 4 shows the deposition rate vs. P_{SiH₄}, and indicates that up to P_{SiH₄} = 0.8 Torr, the film deposition rate was nearly constant at about 10 nm/min, and at P_{SiH₄} = 1.2 Torr increased to about 180 nm/min. For this different deposition rate, the film composition of specimen at 18 cm was also investigated. Fig. 5 shows XPS measurements of the film composition vs. P_{SiH₄}. The film Si concentration increased gradually with increasing P_{SiH₄} up to P_{SiH₄} = 0.8 Torr. For P_{SiH₄} = 0.4, 0.6, and 0.8 Torr, the Si concentration was 1.9, 2.7, and 4.4 at.%, respectively. However, the Si concentration increased 33.8 at.% when P_{SiH₄} = 1.2 Torr. SiN films with low Ti concentration were obtained at this condition. Fig. 5 also shows that the film resistivity increased with increasing Si concentration, caused by increased P_{SiH₄}.

The effect of TiCl₄ on the deposition chemistry of SiH₄ or SiH₂/NH₃ was dominant up to P_{SiH₄} = 0.8 Torr. When P_{SiH₄} = 1.2 Torr, TiCl₄ and its related components, that suppress the SiH₄ based chemistry, might be totally consumed at the upstream of the reactor due to higher P_{SiH₄}. Thus, SiH₂/NH₃ chemistry dominated at P_{SiH₄} = 1.2 Torr. The deposition rate of 180 nm/min is reasonable for SiN deposition rate, because SiN deposition rate may be linear against P_{SiH₄} and we obtained SiN deposition rate of 65 nm/min at 18 cm from inlet when P_{SiH₄} = 0.4 Torr.

Fig. 6 shows XRD measurements of the crystal structure of the films. The TiN (200) peaks broadened with increasing P_{SiH₄}, because the concentration of amorphous Si₃N₄ increased in the crystalline TiN matrix. TiN (200) peaks disappeared for P_{SiH₄} = 0.8 Torr, and Si,N₄, TiSi₃ peaks appeared for P_{SiH₄} = 1.2 Torr. Fig. 7 shows cross-sectional SEM images of the TiSiN structures. Fig. 7a shows a cross-sectional SEM image of a TiN film deposited from a mixture of TiCl₄ and NH₃ (no SiH₄), which has a columnar structure. Fig. 7b shows a cross-sectional SEM image for P_{SiH₄} = 0.8 Torr, and indicates that the columnar structure disappeared. This indicates that adding Si into TiN can remove the columnar structure that acts as a fast diffusion path.

3.3. Anti-oxidation test

TiSiN films should have excellent anti-oxidation characteristics. First, electrical resistivity of the sample was measured by using a four-point probe method. Then, the anti-oxidation test was done by using RTA, and the resistivity measured after each annealing temperature. To determine the anti-oxidation characteristics of the films, we
did RTA for 2 min. at $P_{O_2} = 100$ Torr and the temperature from 400 to 600 °C. Fig. 8 shows the temperature profile during the anti-oxidation tests. This procedure was repeated until the resistivity became infinite. Fig. 9 shows the resistivity as a function of annealing temperature. TiSiN films with larger Si concentration had good anti-oxidation characteristics. For $P_{SiH_4} = 0.8$ Torr, TiSiN films had good anti-oxidation characteristics up to 550 °C.

The TiSiN films had relatively high Cl content, which was present as a residual impurity. The Cl impurities create a diffusion path for O$_2$ when Cl desorbs from TiSiN films during RTA O$_2$ annealing. To improve the anti-oxidation characteristics of TiSiN films, the Cl impurities must be removed. To reduce the residual Cl from TiN films, we used flow modulation chemical vapor deposition (FMCVD) [33], and we successfully formed TiN films with low residual Cl. The FMCVD sequence consists of a 1 min. TiSiN deposition period (TiCl$_4$/SiH$_4$/NH$_3$), and 1 min. Cl reduction period (SiH$_4$/NH$_3$). This cycle was repeated 10 times. Compared to TiSiN films deposited with normal CVD, FMCVD TiSiN films had larger Si concentration (32%) and low Cl concentration (~1%). This is because with FMCVD it was possible to make SiN during the reduction period. The resistivity of FMCVD TiSiN films was almost the same as that of CVD-TiSiN films grown at $P_{SiH_4} = 0.8$ Torr. The Si content of FMCVD TiSiN films was almost the same as for CVD-TiSiN films grown at $P_{SiH_4} = 1.2$ Torr, but the resistivity was lowered by 75% lower. Fig. 9 indicates that TiSiN films deposited by using FMCVD have good anti-oxidation performance up to 600 °C. Finally, TiSiN films with relatively high Si concentration have improved the anti-oxidation performance at temperatures above 600 °C.

Fig. 7. Cross-sectional SEM images of TiN and TiSiN films formed on SiO$_2$ substrates: (a) TiN film with columnar structure for $P_{TiCl_4} = 0.024$ Torr and $P_{NH_3} = 0.08$ Torr, (b) TiSiN film without columnar structure for $P_{TiCl_4} = 0.024$ Torr, $P_{NH_3} = 0.08$ Torr, and $P_{SiH_4} = 0.8$ Torr.

Target temperature

R.T.

![Graph](image)

Fig. 8. Temperature profile during RTA anti-oxidation test with $P_{O_2} = 100$ Torr.

![Graph](image)

Fig. 9. Sheet resistivity of TiSiN films after O$_2$ annealing at a temperature range of 400–600 °C.
4. Conclusions

A CVD process for making TiSiN films was developed for use as anti-oxidation barriers. TiSiN films were deposited by using CVD with a gas mixture of TiCl₄, NH₃ and SiH₄. We found that TiCl₄ did not significantly react with SiH₄/NH₃. The Si concentration of TiSiN films increased with increasing PSiH₄, and anti-oxidation performance were determined by the film Si concentration. Higher Si concentrations increased the Si₃N₄ phase in the crystalline TiN matrix, causing the anti-oxidation performance to be improved. However, higher Si concentrations also increased the resistivity of the films. Because TiSiN layers must have anti-oxidation performance as well as low resistivity, for our experimental conditions PSiH₄ must be kept below 0.8 Torr. In addition, CVD-TiSiN films had relatively high Cl concentrations, which could be reduced by using FMCVD. Because FMCVD decreased the Cl concentration in TiSiN films to about 1%, FMCVD TiSiN films were stable against oxidation up to 600 °C.

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