Diffusion barrier property of TiN and TiN/Al/TiN films deposited with FMCVD for Cu interconnection in ULSI

Young-Hoon Shin*, Yukihiro Shimogaki

Department of Materials Engineering, Graduate School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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Abstract

Flow modulation chemical vapor deposition (FMCVD) with titanium tetrachloride (TiCl₄) and ammonia (NH₃) is effective for depositing titanium nitride (TiN) films with conformal morphology, good step coverage, low electrical resistivity, and low chlorine residual contamination. It means that FMCVD TiN film is a good candidate of diffusion barriers for copper interconnection technology in ULSI. But the diffusion barrier property of FMCVD TiN film against Cu diffusion has not been confirmed. So, firstly, we deposited Cu (100 nm)/FMCVD TiN (25 nm)/Si multilayer films and investigated the thermal stability of Cu/TiN/Si structure. Vacuum annealing was done at 400, 500, 550 and 600 °C. For films annealed for 30 min at 400 °C, Cu diffused through the TiN layer and formed copper silicides on the surface of Si substrates. Therefore, FMCVD films formed under such conditions are unsatisfactory diffusion barriers. To enhance the diffusion barrier property of FMCVD TiN films, we used sequential deposition to introduce a monolayer of Al atoms between two TiN films. Etch-pit tests showed that for TiN films with Al interlayer, Cu diffusion through the barrier occurred at 500 °C and that is 100 °C higher than TiN film without Al interlayer. Al atoms formed Al₂O₃ with oxygen atoms present in the TiN films as impurities, and fill up the grain boundaries of TiN film, thereby blocking the diffusion of Cu atoms.

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1. Introduction

Titanium nitride (TiN) films are commonly used for making wear-resistant coatings on tools [1], as a gold substitute in decorative items, for solar energy absorbers [2], IR reflectors, and for making thin-film resistors [3]. Due to its thermal stability and low electrical resistivity [4,5], TiN is widely used in the microelectronics industry as a diffusion barrier material for Al interconnects in ultra large-scale integrated devices (ULSI). TiN prevents Al atoms from diffusing into either dielectric materials or into Si substrates. At high temperatures, Al atoms diffusing into TiN films contact oxygen (O), which is present as an impurity, and form aluminum oxides, such as Al₂O₃, in the grain boundaries of TiN columnar structures. Aluminum oxides therefore act as stuffing material and restrain Al atoms from diffusing into either SiO₂ films or into Si substrates.

Because TiN is commonly used as a diffusion barrier for Al metallization, the use of TiN films for use with Cu interconnect technology has been extensively investigated [6,7]. It is difficult to use TiN films directly as diffusion barriers for Cu interconnects, because TiN has grain boundaries that act as diffusion paths for Cu atoms. Therefore, for pure TiN films, even at relatively low temperatures Cu atoms diffuse through TiN grain boundaries and into either Si substrates or into dielectric materials. Kim et al. used sputtering to insert Al interlayers into TiN films to form TiN (5 nm)/Al (2 nm)/TiN (5 nm) multilayer films. The Al at the TiN boundaries formed oxides that closed the diffusion paths for Cu atoms. They reported that TiN (5 nm)/Al (2 nm)/TiN (5 nm) multilayer films prevented Cu atoms from diffusing into Si substrates up to 650 °C [8].

For future microelectronics fabrication processes, the preferred method for depositing barrier layers is chemical vapor deposition (CVD), because the step coverage and surface uniformity possible with CVD methods is superior
to that possible with sputtering methods. CVD TiN films formed with titanium tetrachloride/ammonia (TiCl₄/NH₃) has good step coverage and low resistivity, which is needed for barrier materials. On the other hand, residual chlorine (Cl) impurities increase electrical resistance and create Cu voids during Cu deposition by electro-plating process. Hamamura et al. reported that Flow-Modulation CVD (FMCDV) can be used to form TiN films with Cl impurities less than 2%, with film electrical resistivity of about 250 μΩ cm, and step coverage greater than 90% [9]. They used gas flow modulation to create repetitive cycles of alternating deposition and reduction. Although this decreased the Cl impurities, the suitability of FMCDV TiN films for use as Cu diffusion barriers has not been evaluated. Therefore, in this report we discuss the suitability of FMCDV TiN films, with and without added Al, for use as Cu diffusion barriers. We used FMCDV to deposit TiN films (with and without Al) onto Si substrates, and then sputter-deposited Cu films onto the TiN films. We then evaluated the degree of diffusion of Cu into the TiN films.

2. Experimental

Fig. 1 shows a schematic diagram of the FMCDV system used to deposit TiN and Al films. For TiN deposition onto Si(100) substrates, TiCl₄ and NH₃ were used as reactants and introduced through showerhead type inlet. TiCl₄ was carried by Ar gas through a bubbler held at a fixed temperature of 60 °C. The gas-flow sequence of a single cycle was 1 s deposition with TiCl₄, 7 s purge with Ar, and 7 s reduction with NH₃, for a total cycle time of 15 s. The deposition temperature was 410 °C, which is relatively low for TiN CVD with TiCl₄ and NH₃. The total pressure, P, TiCl₄ partial pressure, P₀TiCl₄, and NH₃ partial pressure, P₀NH₃, were 2, 0.01, and 0.25 Torr, respectively. The deposition rate was about 1 nm/cycle. To deposit TiN (25 nm)/Al (monolayers)/TiN (25 nm) structure, dimethylaluminum hydride (DMAH) was introduced with an H₂ carrier gas through the nozzle type inlet located in the center of the showerhead after deposition of lower TiN (25 nm) film. When DMAH is supplied onto TiN surface, nucleation of Al occurs after the incubation period. The size of Al nuclei is over several nanometers. If Al nuclei are formed on lower TiN surface, they will degrade the surface smoothness of TiN/Al/TiN structure. Thus, we should avoid Al nucleation and to monitor the nucleation of Al on lower TiN surfaces, the substrates were irradiated with a 5 mW semiconductor laser operating at a wavelength of 670 nm. The intensity of the reflected laser beam decreased when Al nuclei were formed on the TiN surface. Therefore, we could easily determine the incubation period during which no nuclei were formed. After Al deposition, TiN (25 nm) was deposited on the top of the sample again.

To evaluate Cu diffusion temperature through barrier materials, 100-nm-thick Cu films were deposited on top of the TiN (50 nm)/Si substrate and TiN (25 nm)/Al/TiN (25 nm)/Si substrate multilayer films. We used DC magnetron sputtering in an Ar atmosphere to deposit the Cu films, with a DC power of 150 W and a total pressure of 0.17 Torr. After Cu deposition, the samples were annealed in a vacuum by using rapid thermal annealing (RTA) for 30 min, at a pressure of 5 × 10⁻⁷ Torr and at either 400, 500, 550 or 600 °C. The as-deposited film thickness and film morphology were measured by using field-emission scanning electron microscopy (FE-SEM: JEOL JSM6340F). Depth profiles and the chemical composition of the films were analyzed by using X-ray photoelectron microscopy (XPS: ULVAC-Phi Model 1600C). Cross-sectional analysis of the film composition was done by using FE-STEM (Hitachi HD-2300) together with energy dispersive X-ray analysis (EDX).

3. Results and discussion

Fig. 2 shows the sheet resistance (Rₛ) of Cu surfaces as a function of annealing temperature (Tₐ), with and without Al layers. The Rₛ of the Cu/TiN (50 nm)/Si substrate films decreased from 0.3Ω/□ (i.e. 0.3Ω/square) (as-deposited) to 0.17Ω/□ at Tₐ of 500 °C. Above 500 °C the film Rₛ increased. It is well known that as Tₐ is increased Cu grain growth, crystallization, and agglomeration occur, causing the Rₛ to decrease, because layers with lower resistivity generally dominate the total electrical resistance, and Cu has a lower resistivity than TiN [10]. For Tₐ above 550 °C, the Rₛ increased rapidly with increasing Tₐ. After annealing at 700 °C, the Rₛ reached about 1.0Ω/□, and Fig. 2
indicates that above $T_a$ of 500 °C, there is a linear relationship between $R_s$ and $T_a$. This indicates that at about 500 °C, thermally activated Cu atoms begin to diffuse into the substrate through the TiN barrier. With increasing $T_a$, Cu atoms create larger concentrations of defects, causing the electrical resistance to increase. These results agree with SEM analysis of Cu surface morphology. Fig. 3 shows plan-view SEM images of the Cu surface after annealing. Up to $T_a$ of 500 °C, the surface of Cu films remained clean and there were no visible defects. Above 550 °C, however, many defects appeared, visible as black spots. The black spots represent voids where Cu atoms were removed. However, XPS depth profiles indicated different behavior. Fig. 4 shows XPS depth profiles as a function of $T_a$. For the as-deposited samples, the profiles near the Cu/TiN and TiN/Si interfaces are steep, indicating that interlayer diffusion is negligible. Annealing at 400 °C does not significantly alter the profiles near the interfaces, but for $T_a$ of 600 °C, the profiles near the interfaces become indistinct. At $T_a$ of 400 °C, about 10 at.% of Cu atoms were detected in the Si substrate, indicating the onset of Cu diffusion. From the fact that the Cu concentration in the TiN film is lower than in the Si substrate, we conclude that pinhole and grain-boundary diffusion paths exist in the TiN film. The Cu concentration reached about 50 at.% in both the TiN film and in the Si substrate after annealing at 600 °C. At this temperature the interfaces were also destroyed. Fig. 5 shows SEM images of Si surfaces after Cu was removed in a 1:10 solution of HNO$_3$ and H$_2$O and TiN was removed in a 1:2:6 solution of NH$_4$OH, H$_2$O$_2$, and H$_2$O. Copper silicides appeared on Si surfaces at a $T_a$ of 400 °C, and continued to increase with increasing $T_a$.

TiN (25 nm)/Al (monolayers)/TiN (25 nm) structures were deposited by sequential processing in the same chamber. As we mentioned above, we should avoid Al nucleation to realize smooth surface morphology of TiN/Al/TiN structure. We introduced a 5 mW semiconductor laser operating at a wavelength of 670 nm to detect Al nuclei on the TiN surface. The reflectivity of the laser was altered by the surface morphology. Fig. 6 shows the laser reflectivity vs. time during Al deposition. The incubation time is defined as the time from the beginning of Al deposition to the appearance of Al nuclei [11]. Figs. 6 and 7 show that the reflectivity decreased with the onset of Al nucleation, and then increased as Al nuclei agglomerated. This behavior permits the incubation time and nucleation state to be uniquely correlated to the reflectivity. Because Al nuclei are several tens of nanometers in diameter and are randomly distributed on the TiN films, to ensure conformal Al atoms’ distribution over the TiN film under several nanosize for future thin barrier structure, we stopped...
the DMAH flow before Al nucleation occurred. To improve the reproducibility of the Al deposition pattern shown in Figs. 6 and 7, the incubation time was intentionally lengthened by reducing the DMAH partial pressure and deposition temperature [11,12]. FMCVD was used to deposit 25-nm-thick TiN films onto the Al film, and DC magnetron sputtering was used to deposit 100-nm-thick Cu.

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Fig. 4. XPS depth profiles of Cu/FMCVD-TiN/Si-substrate multilayer films (a) as-deposited and after annealing at (b) 400 and (c) 600 °C.

Fig. 5. SEM images of Cu/\textit{Si} surfaces of Cu/FMCVD-TiN (50 nm/\textit{Si}-substrate after annealing at (a) 400 and (b) 600 °C. The Cu and FMCVD TiN were removed by wet etching before SEM observation.

Fig. 6. Laser reflectivity vs. time during Al-CVD. The decrease and increase of reflectivity show the nucleation and growth of Al.
films onto the second TiN layer. This permitted the thermal stability of TiN/Al/TiN and TiN films to be compared. Fig. 8 shows Cu (100 nm)/TiN (25 nm)/Al (monolayer)/TiN (25 nm)/Si substrate structures after annealing at 400 °C.

As shown in Fig. 8, the desired structure and layer thicknesses were achieved. The surface morphology of TiN/Al/TiN was conformal, and was not degraded by the insertion of an Al interlayer and no Al nuclei were observed. The upper and lower TiN films lost their continuous columnar structure. All interfaces were distinct, and no evidence of Cu diffusion was observed for annealing at 400 °C.

Etch-pit tests are one of the most sensitive tests for detecting Cu diffusion into Si substrates [13,14]. Fig. 9 indicates that after Secco etching, etch pits on the Si surface appeared. Cu/TiN/Al/TiN were etched in wet etchant. Then copper silicides on the Si substrate were also etched by dipping the structures into a 1:10:11 solution of K$_2$Cr$_2$O$_7$, H$_2$O, and HF (Secco etchant) for 5 s. Up to $T_a$ of 400 °C, no etch pits were observed. At $T_a$ of 500 °C, etch pits appeared at a surface concentration of $4.9 \times 10^9$/cm$^2$, and at $T_a$ of 600 °C, the surface concentration increased to $1.07 \times 10^{10}$/cm$^2$. From the XPS depth profile tests after annealing at 500 °C (Fig. 10a), no copper diffusion was detected into the Si substrates and 10 at.% of Cu atoms appeared after $T_a$ of
$T_a$ of 600 °C (Fig. 10b). $R_s$ also increased after $T_a$ of 600 °C (Fig. 2). Fig. 9 indicates that for $T_a$ of 500 °C, the density of Cu atoms on Si substrates was below the detection limit of either XPS depth-profile or $R_s$ measurements.

Fig. 11 shows a Cu/TiN/Al/TiN/Si multilayer film after annealing at 600 °C and imaged with FE-STEM coupled with EDX. No significant structural changes were observed, and the Al concentration at location seven is approximately 7 at.%, and that Al atoms diffused slightly into both the upper and lower TiN films. The Cu concentration was about 4–7 at.% in the upper TiN layer, and about 2 at.% in the lower TiN layer. This indicates that the Al layer prevented Cu diffusion through the TiN films. O-atoms concentration at location two (about 16 at.%) is owing to the vacuum breaking between TiN deposition and Cu deposition. The highest O concentration at location seven implies that AlO is formed at Al interlayer. This might occur because the Gibbs free energy change of Al$_2$O$_3$ is lower than that of TiO$_x$ ($2\text{Al} + 3/2\text{O}_2 \rightarrow \text{Al}_2\text{O}_3$, $\Delta G = -1581$ kJ/mol, $2\text{Ti} + 1/2\text{O}_2 \rightarrow \text{Ti}_2\text{O}$, $\Delta G = -192$ kJ/mol at 300 K), causing Al atoms to attract O impurities from TiN films, resulting in higher O concentrations at the Al interlayer.

Etch-pit tests of films indicated that Cu diffusion occurred annealed at 500 °C (Fig. 9). This Cu diffusion might occur through the grain boundaries of TiN films, although evidence of this diffusion was not observed in the STEM image range. Therefore, etch-pit tests indicated TiN/Al/TiN barrier failure at 500 °C, which is higher than the 400 °C point at which the TiN barrier failed. The reason for the TiN/Al/TiN multilayer film provides diffusion barrier up to a higher temperature is because (1) FMCVD TiN contains O-atom impurities, which react with Al to form aluminum oxides, and these aluminum oxides block the diffusion paths, such as grain boundaries of TiN. (2) Insertion of an Al layer creates a multilayer structure and grain boundaries mismatch, which means the diffusion paths of Cu atoms are...
disrupted, slowing the diffusion of Cu atoms through TiN grain boundaries.

4. Conclusions

Cu diffusion barrier properties of TiN and TiN/Al/TiN films deposited by FMCVD were investigated. Although the failure temperature (i.e. point at which substantial interlayer Cu diffusion occurred) was 400 °C for TiN films, by adding an Al layer between two TiN layers, the failure temperature was increased to 500 °C for the TiN/Al/TiN multilayer film.

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