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

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Abstract

Flow modulation chemical vapor deposition (FMCVD) with titanium tetrachloride (TiCl_4) and ammonia (NH_3) 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 AlO_x 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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Keywords: Flow modulation chemical vapour deposition; Titanium nitride; Diffusion barrier

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 Al_2O_3 , in the grain boundaries of TiN columnar structures. Aluminum oxides therefore act as stuffing material and restrain Al atoms from diffusing into either SiO_2 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

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to that possible with sputtering methods. CVD TiN films formed with titanium tetrachloride/ammonia ($\text{TiCl}_4/\text{NH}_3$) 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 (FMCVD) can be used to form TiN films with Cl impurities less than 2%, with film electrical resistivity of about $250 \mu\Omega \text{ cm}$, 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 FMCVD TiN films for use as Cu diffusion barriers has not been evaluated. Therefore, in this report we discuss the suitability of FMCVD TiN films, with and without added Al, for use as Cu diffusion barriers. We used FMCVD 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 FMCVD system used to deposit TiN and Al films. For TiN deposition onto Si(100) substrates, TiCl_4 and NH_3 were used as reactants and introduced through showerhead type inlet. TiCl_4 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 $\text{TiCl}_4 + \text{NH}_3$, 7 s purge with Ar, and 7 s reduction with NH_3 , for a total cycle time of 15 s. The deposition temperature was 410°C , which is

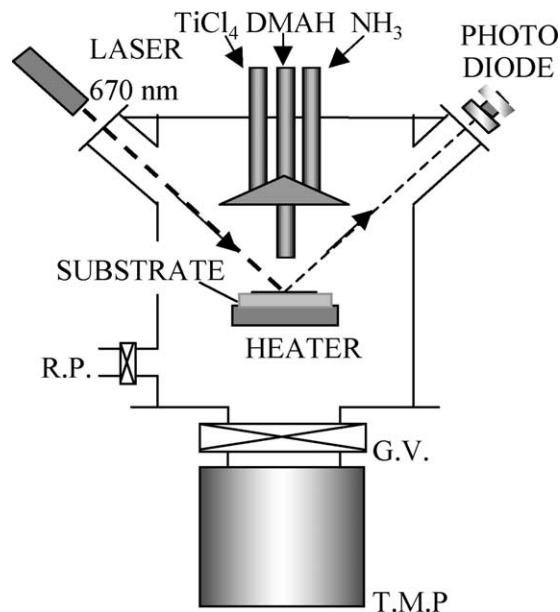


Fig. 1. Schematic diagram of the FMCVD system.

relatively low for TiN CVD with TiCl_4 and NH_3 . The total pressure, P , TiCl_4 partial pressure, P_{TiCl_4} , and NH_3 partial pressure, P_{NH_3} , 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 H_2 carrier gas through the nozzle type inlet located in the center of 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 10 mTorr.

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- Φ 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 (R_s) of Cu surfaces as a function of annealing temperature (T_a), with and without Al layers. The R_s of the Cu/TiN (50 nm)/Si substrate films decreased from $0.3 \Omega/\square$ (i.e. $0.3 \Omega/\text{square}$) (as-deposited) to $0.17 \Omega/\square$ at T_a of 500°C . Above 500°C the film R_s increased. It is well known that as T_a is increased Cu grain growth, crystallization, and agglomeration occur, causing the R_s to decrease, because layers with lower resistivity generally dominate the total electrical resistance, and Cu has a lower resistivity than TiN [10]. For T_a above 550°C , the R_s increased rapidly with increasing T_a . After annealing at 700°C , the R_s reached about $1.0 \Omega/\square$, and Fig. 2

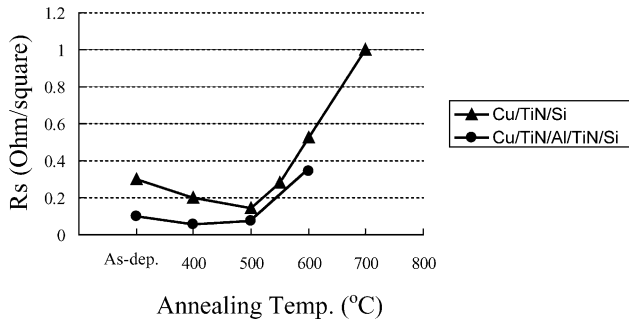


Fig. 2. Sheet resistance vs. annealing temperature for TiN and TiN/Al/TiN multilayer films.

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 HNO₃ and H₂O and TiN was removed in a 1:2:6 solution of NH₄OH, H₂O₂, and H₂O. 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

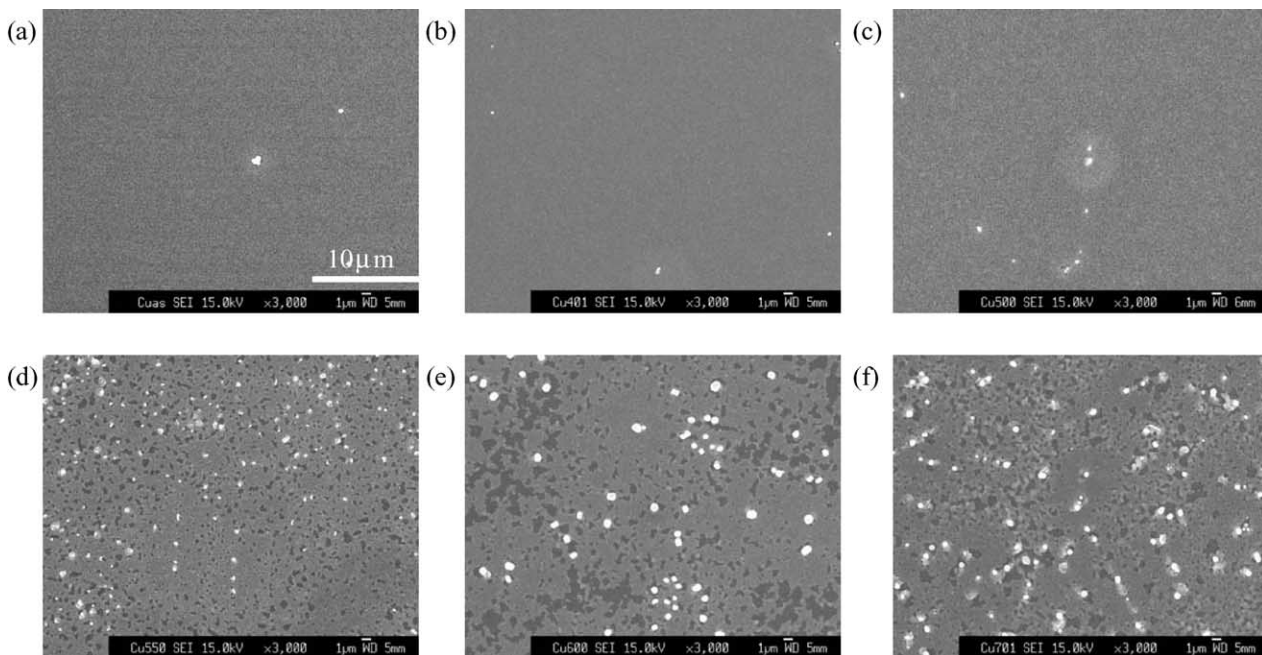


Fig. 3. Plan-view SEM images of the surface of Cu/FMCVD-TiN (50 nm)/Si-substrate. The magnification is same for all pictures. (a) as-deposited and after annealing at (b) 400, (c) 500, (d) 550, (e) 600, and (f) 700 °C.

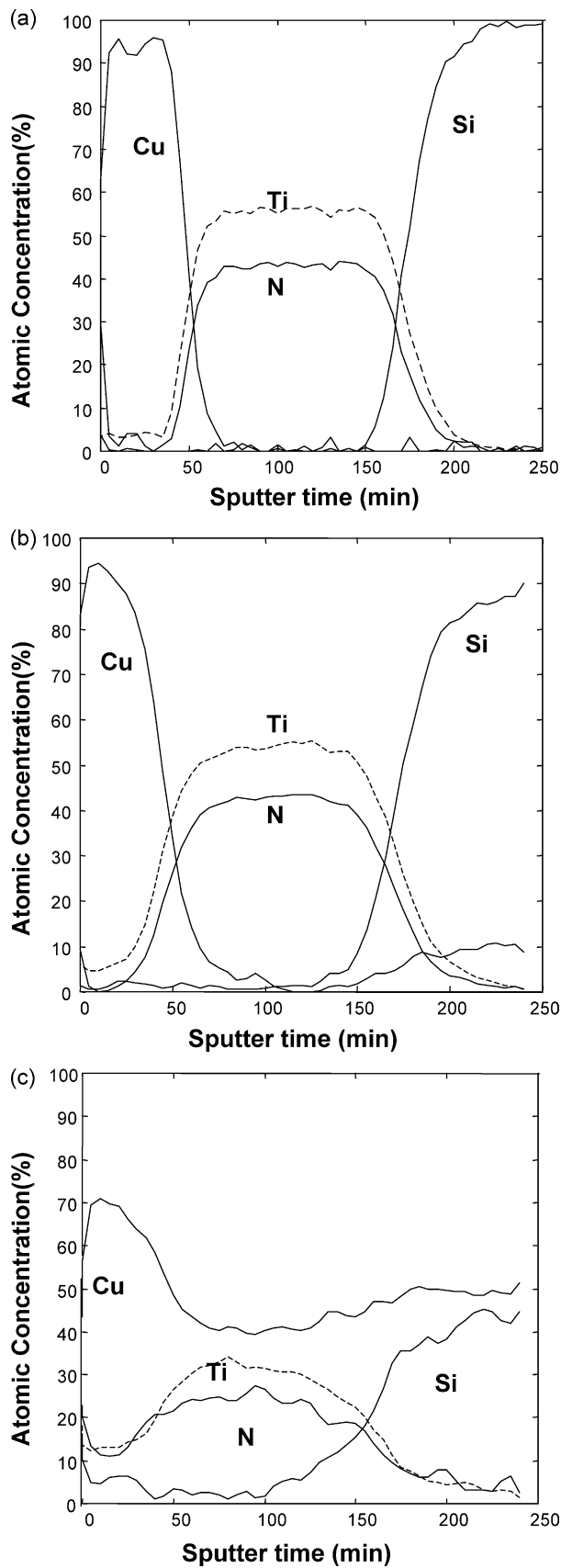


Fig. 4. XPS depth profiles of Cu/FMCVD-TiN/Si-substrate multilayer films (a) as-deposited and after annealing at (b) 400 and (c) 600 °C.

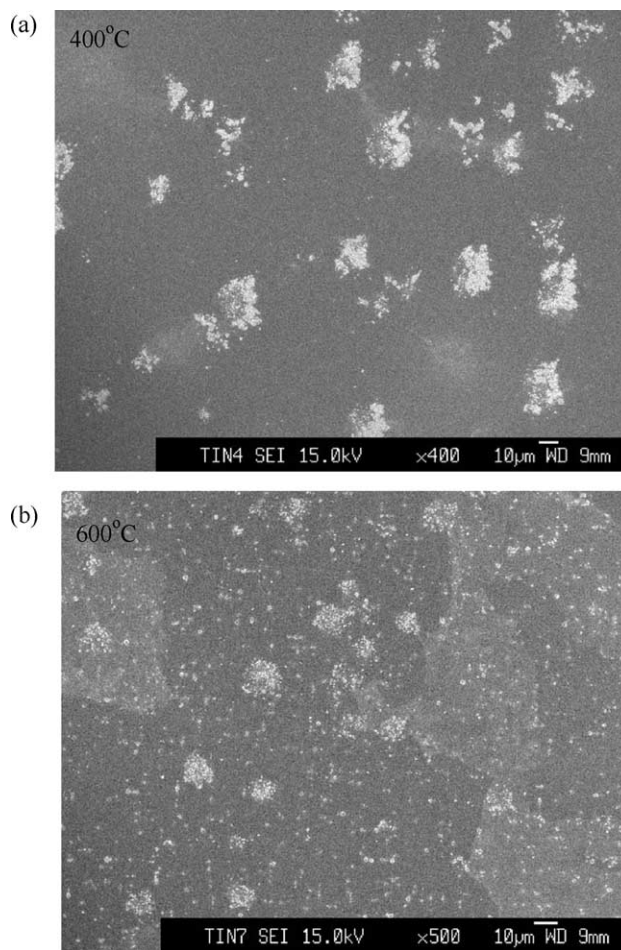


Fig. 5. SEM images of Cu_xSi on Si surfaces of Cu/FMCVD-TiN (50 nm)/Si-substrate after annealing at (a) 400 and (b) 600 °C. The Cu and FMCVD TiN were removed by wet etching before SEM observation.

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

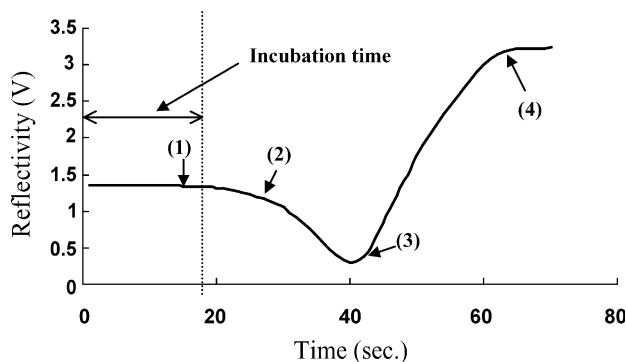


Fig. 6. Laser reflectivity vs. time during Al-CVD. The decrease and increase of reflectivity show the nucleation and growth of Al.

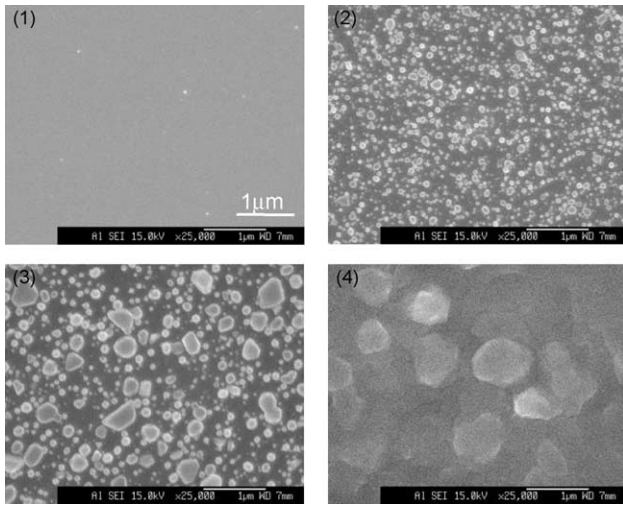


Fig. 7. SEM images during nucleation and growth of Al. The times corresponding to the SEM images are indicated in Fig. 6.

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.

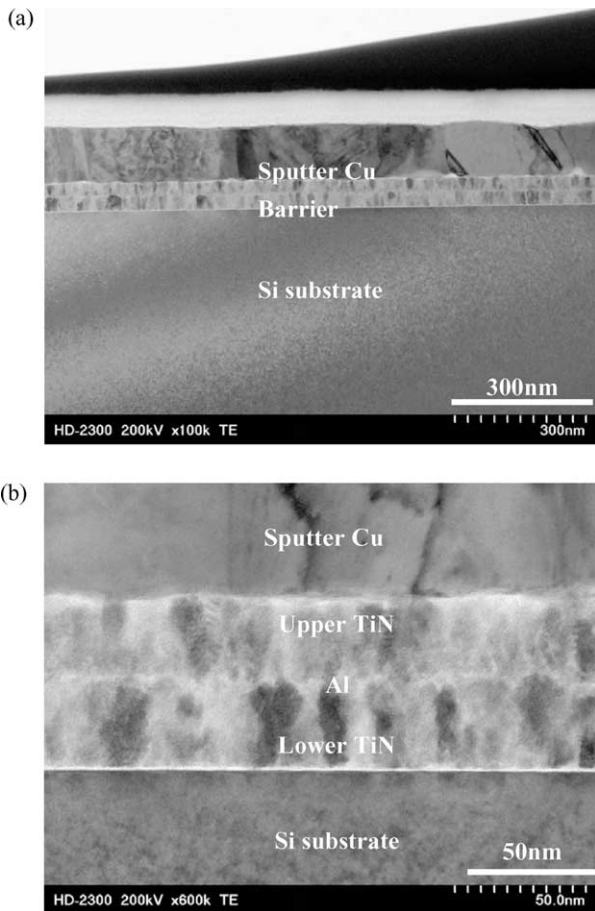


Fig. 8. Cross-sectional STEM images of Cu (100 nm)/TiN (25 nm)/Al (monolayer)/TiN (25 nm) multilayer films after annealing at 400 °C. (a) $\times 10$, (b) $\times 60$ K.

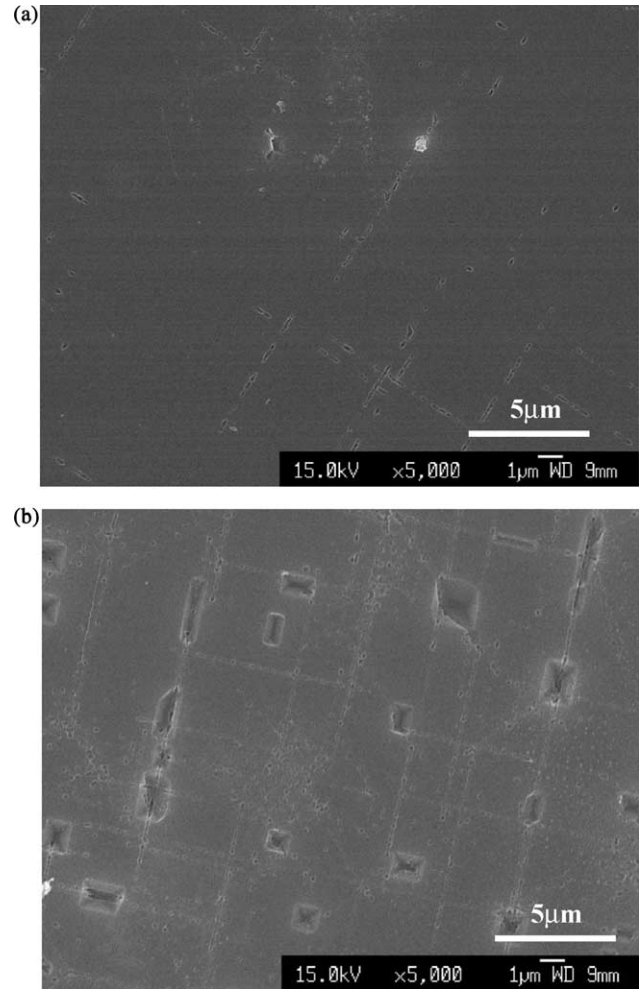


Fig. 9. Etch pits on Si substrates of Cu/TiN/Al/TiN/Si substrate after annealing at (a) 500 and (b) 600 °C. Cu/TiN/Al/TiN were removed by wet etching methods.

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 $K_2Cr_2O_7$, H_2O , 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

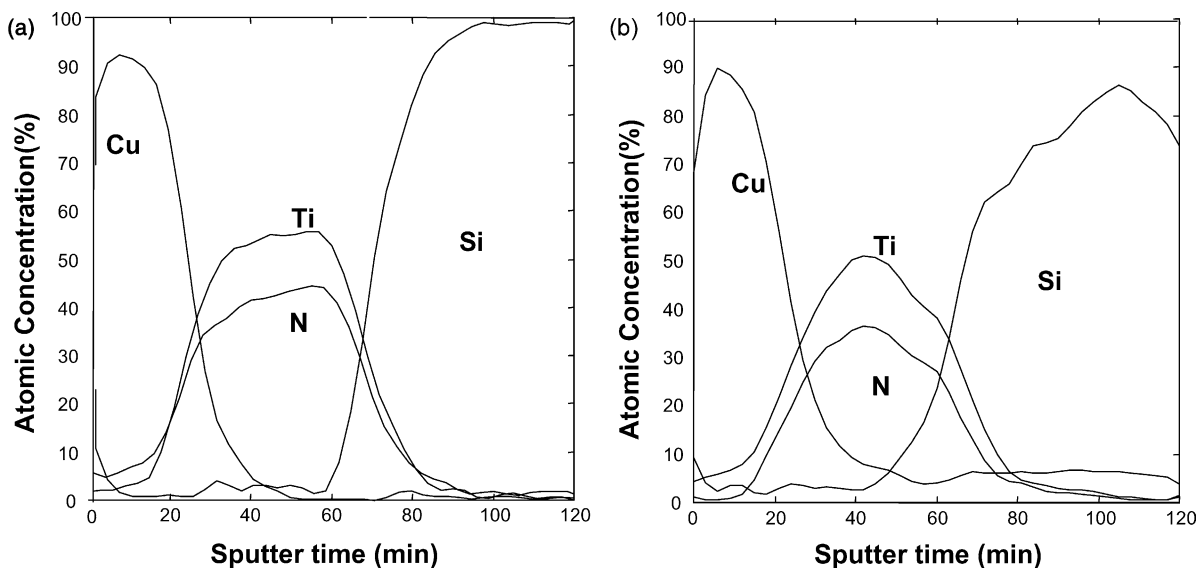


Fig. 10. XPS depth profiles of Cu/TiN/Al/TiN/Si multilayer films after annealing at (a) 500 and (b) 600 °C.

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 was 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_x is formed at Al interlayer. This might occur because the Gibbs free energy change of Al_2O_3 is lower than that of

TiO_x ($2Al + 3/2O_2 \rightarrow Al_2O_3$, $\Delta G = -1581$ kJ/mol, $2Ti + 1/2O_2 \rightarrow Ti_2O$, $\Delta G = -192$ 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

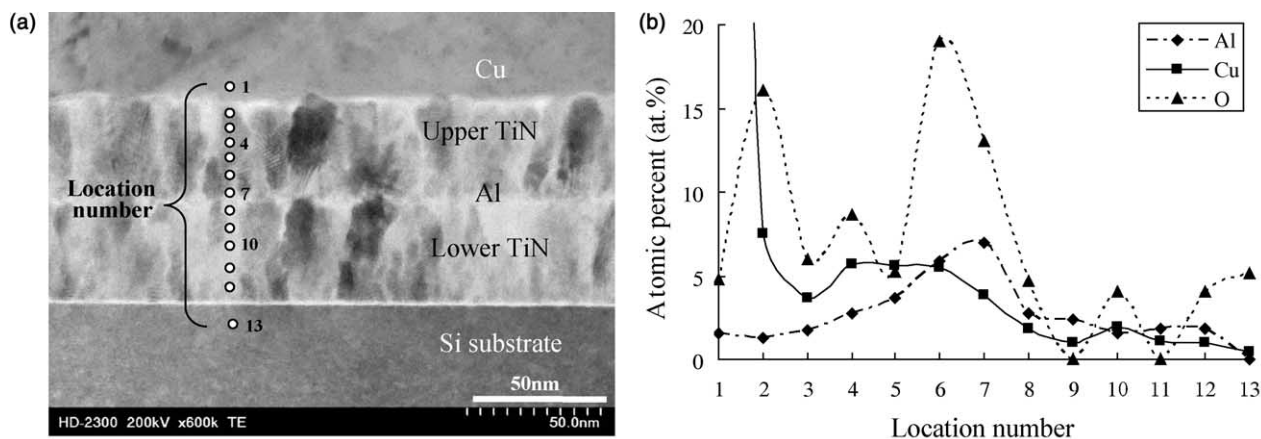


Fig. 11. (a) Cross-sectional STEM image and (b) EDX measurement results after annealing at 600 °C.

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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