Copper is deposited on TaN and WN barrier layers by electroless plating without the need for activation preprocessing when substrates are (i) pretreated by wet chemical etching to remove surface oxides, and (ii) immersed in an electroless Cu plating solution containing glyoxylic acid as a reducing agent. Electrical potential measurements indicate that the redox potentials of TaN and WN in the plating solution are lower than that of copper, driving displacement plating of Cu in the initial stage of deposition. The adhesion between electroless-plated Cu and the TaN barrier layer after annealing is 0.11 kgf/cm as determined by a peeling test, which is sufficient for reliability during chemical mechanical polishing. A damascene Cu interconnect was successfully fabricated without delamination and exhibited an electrical resistivity of 2.2 μΩ cm after annealing for a 0.42 μm wide interconnect track. These results indicate that the proposed electroless process is suitable for the formation of a Cu seed layer prior to electrodeposition for the fabrication of ultralarge scale integrated interconnects.

Copper (Cu) is used widely as an interconnect metal in ultralarge scale integrated (ULSI) circuits due to its low resistivity and superior resistance against electromigration compared to conventional aluminum (Al) and alloys. However, copper is mobile in silicon (Si) and silicon dioxide (SiO₂), resulting in appreciable current leakage and dielectric breakdown resistance. For this reason, an efficient diffusion barrier metal adjacent to the copper is required to prevent copper atoms from penetrating into dielectrics or the silicon substrate. Tantalum nitride (TaN), titanium nitride (TiN), and tungsten nitride (WN) have been used widely as barrier materials, however, the high electrical resistivity of metal nitride as a barrier layer hinders uniform electrodeposition of Cu. To overcome this problem, a Cu seed layer is often sputtered on the barrier metal in the fabrication of copper ULSI interconnects. However, sputtering provides inherently poor step coverage and results in discontinuities in the Cu film at the sidewalls of fine via holes. Copper electroless plating, which does not require a sputtered seed layer, is an efficient means of filling high aspect ratio holes and has become increasingly prominent in industry. For most standard copper electroless plating processes, a solution containing SnCl₂ and PdCl₂ is used for sensitization and activation, yet the adhesion between the copper and the barrier layer using this technique is poor. In recent years, a wet activation process called displacement deposition has been considered and developed for activating the Si substrates, or TaN or TiN diffusion barrier, using a PdCl₂/HF solution or PdCl₂/HF/HNO₃ solution. In this activation solution, two galvanic half-cell reactions including Pd deposition and removal of the substrate occur simultaneously. Nakahara et al. investigated the influence of HF concentration on the initial stages of Pd deposition on Si, and Patterson described that the single-step activation of TiN using a HF/PdCl₂ solution allowed the HF to remove the surface oxide layer followed by immediate Pd seeding on the fresh TiN surface. All activation solutions are acidic, and the process steps are complicated, involving a catalysis adsorption step followed by electroless plating. The present authors have developed a very simple, direct electroless copper plating method for TaN and WN that does not require catalysis adsorption pretreatment. The technique is evaluated through measurements of the electrical potentials of the metal nitride barrier films and Cu plate with respect to the Ag/AgCl standard electrode in the plating solution, and the deposition mechanism is discussed.

Experimental

TaN/SiO₂/Si and WN/SiO₂/Si substrates were used for electroless copper plating. The TaN films were formed by reactive sputtering using Ar and N₂, and the WN film was formed by chemical vapor deposition (CVD) using WF₆ and NH₃. Prior to electroless copper plating, all substrates were cut into 10 × 20 mm slabs. The TaN substrate was cleaned by ultrasonication in acetone at room temperature for 10 min, and then etched with HF:HNO₃:H₂O = 1:1:4(v:v) solution at 25°C for 2 ～ 5 min. The WN substrate was cleaned by ultrasonication in acetone at room temperature for 10 min.

The composition of the electroless copper plating solution used in the experiment was as follows: CuSO₄ ⋅ 5H₂O (7.6 g/L), C₁₀H₁₆N₂O₄ (EDTA; 70.0/gL), glyoxylic acid (14.0 g/L) as a reducing agent, and additional agents such as 2,2'-dipyridylamine and polyethylene glycol. The pH of the plating solution was adjusted to about 12.7 with tetramethylammonium hydroxide (TMAH). The bath temperature was maintained at 70°C for TaN substrates and 60°C for WN substrate. X-ray photoelectron spectroscopy (XPS) measurements were performed using a JPS90-MXV spectrometer from JEOI using a nonmonochromatized Mg Kα X-ray source. Elemental binding energies were corrected using the C 1s binding energy at 285.0 eV. The surface roughness of Cu films was measured using an atomic force microscope (AFM; NV-3000, Olympus) in a scan range of 120 μm.

The redox potentials of the barrier layers in the electroless copper plating solution were measured by a two-electrode method using Ag/AgCl as a reference electrode, and the change of the working electrode potential against time was recorded on a personal computer using LabView. The working electrode is shown in Fig. 1. The sides and back of the Si wafer were isolated from the solution, and only the barrier metal surface was exposed to the solution. Prior to electrical measurements, substrates were cut into 1.0 × 1.0 cm slabs and cleaned by ultrasonication in acetone at room temperature for 10 min. Conductive silver paste was applied to the back and sides of the substrates to form an electrical contact with barrier metal surface, and after drying in a vacuum, the substrates were mounted on the electrode for electrical potential measurements.

Results and Discussion

As barrier layers readily oxidize in air, electroless copper deposition did not proceed on TaN barrier layers without etching pretreatment. XPS spectra of TaN barrier layers taken prior to etching revealed a strong oxygen 1s peak at 531.0 eV and weak nitrogen 1s peak at 398.1 eV (Fig. 2a). The atomic ratio of oxygen to tantalum is 1.52, and nitrogen to tantalum is 0.03. After etching treatment (Fig. 2b), the oxygen/tantalum ratio decreased to 0.78, and nitrogen/
tantalum increased to 0.16. This result indicates that etching treatment effectively removed the oxygen-rich surface layer, exposing the fresh TaN layer. XPS measurements also revealed that half of the surface Ta atoms had oxidized immediately following sputter deposition. The WN barrier film was also found to oxidize in air, however, as the tungsten oxide is readily dissolved in the electroless copper plating solution, etching pretreatment was not necessary for WN barrier films.17

Osaka et al. reported that Si atoms are oxidized to SiO2 in an electroless nickel plating solution, while Ni ions in the plating solution are reduced by electrons generated by oxidation of Si and subsequently deposit on the substrate.18 Cutting the TaN and WN barrier layers into slabs for processing, as performed in this study, exposes Si atoms on the sides of the substrates. Immersing these substrates into the electroless copper plating solution therefore may lead to two mechanisms for initial Cu deposition; reduction of copper ions due to oxidation of the barrier layers, and reduction of copper ions due to oxidation of Si atoms on the side of the substrate. In order to eliminate the effect of Si atoms, the side of cut wafer was covered with chemically inert wax, effectively exposing only the metal nitride film surface to plating solution during processing.

Copper was successfully deposited on the TaN and WN barrier layers of pretreated substrates by immersion the electroless copper plating solution at 70°C. However, copper did not deposit on pretreated TiN. In the case of WN, as deposition at 70°C proceed very rapidly, the bath temperature was lowered to 60°C.

In order to understand the mechanism of Cu deposition on the TaN and WN barrier layers, the redox potentials of the TaN, WN, TiN, and Cu films were measured in the electroless plating solution (Table I). The redox potentials with respect to measurement time are shown in Fig. 3. The redox potential of Cu in the electroless plating solution at 60 and 70°C was not stable and increased with time, reflecting the decrease in the concentration of the reducing agent and pH of the plating solution with time.19 The redox potential of WN was lower than that of Cu at 60°C, indicating that the displacement reaction between WN and Cu ions can proceed. The change in the redox potential of the WN barrier layer at 60°C is classified into three stages. In the first stage, the potential increases rapidly up to the same value as for Cu. In the second stage, the potential increases in step with that of Cu, and in the third stage, the potential become lower than that of Cu. This process can be explained as follows. In the first stage, WN is oxidized, causing the Cu ions to be reduced and to deposit on the WN film. The potential of the WN electrode increases with the amount of Cu atoms on the WN surface, reaching the potential of Cu when the entire surface is covered with

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Temperature of solution (°C)</th>
<th>Initial potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>25</td>
<td>−8</td>
</tr>
<tr>
<td>Cu</td>
<td>60</td>
<td>−314</td>
</tr>
<tr>
<td>Cu</td>
<td>70</td>
<td>−383</td>
</tr>
<tr>
<td>TiN</td>
<td>70</td>
<td>−8</td>
</tr>
<tr>
<td>TaN</td>
<td>70</td>
<td>−594</td>
</tr>
<tr>
<td>WN</td>
<td>60</td>
<td>−358</td>
</tr>
</tbody>
</table>

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Cu. In the second stage, the Cu film on the WN electrode becomes thicker with time, and the potential of the electrode is maintained at the potential of a Cu electrode. In the third stage, due to poor adhesion between the WN layer and the Cu, the Cu film begins to break and delaminate as a result of internal stress. The potential of the electrode then begins to decrease to reflect that of the WN surface.

The redox potential of the TiN film in the electroless copper plating solution at 70°C is shown in Fig. 3b. The potential of the TiN barrier at 70°C was higher than that of the Cu electrode, which will prevent the displacement reaction from proceeding. This is in good agreement with the experimental results: Cu did not deposit on the TiN barrier layer when the sides of the TiN substrate were covered with chemically inert wax.

The redox potential of the TaN layer at 70°C in electroless copper plating solution changes in two discrete stages. Initially, the potential increases quickly up to that of the Cu electrode. The redox potential then increases in step with that of Cu. The initial change in redox potential is considered to occur via a mechanism similar to that for WN: the TaN layer oxidizes resulting in the reduction and deposition of Cu on the TaN until the TaN electrode is completely covered with Cu. As the adhesion between the TaN layer and the Cu film is good, the potential of the TaN electrode then remains at that of a Cu electrode. The results of electrical potential measurements clearly show that Cu is initially deposited on TaN and WN by displacement reactions with the barrier layers, after which the deposited Cu acts as an autocatalyst for the electroless deposition of Cu.

The deposition rates for electroless copper plating on the TaN and WN barrier layers were measured by cross-sectional scanning electron microscopy (SEM). The thickness of the films with respect to plating time is shown in Fig. 4. The results show that copper was deposited on the surface of the TaN and WN substrates. Although the bath temperature for WN was lower than that for TaN, both processes produce the same initial deposition rates. The AFM mea-
measurements indicated that the surface roughness ($R_s$) of 1.4 µm thick Cu films was 10.4 nm for TaN and 14.6 nm for WN, which is comparable with electroless-plated Cu films activated using $\text{PdCl}_2$/SnCl$_2$. The crystallography of the Cu film on TaN was measured by X-ray diffraction. The peak intensity ratio $I_{(111)}/I_{(200)}$ was 2.8, and the full-width at half-maximum (fwhm) of (111) for the 1.4 µm thick Cu film was 0.26°. After annealing at 400°C in an N$_2$ atmosphere at 1.0 mTorr, the peak intensity ratio $I_{(111)}/I_{(200)}$ increased to 4.30, and the fwhm of (111) decreased to 0.20°, indicating that the Cu(111) texture was enhanced by annealing.

The adhesion between the Cu film and the barrier layer is a very important factor of the reliability of interconnects. Two methods, an adhesive tape test and peeling test, were used to determine the adhesion strength between the Cu film and the TaN barrier layer. The Cu film did not delaminate in the adhesive tape test regardless of annealing, indicating that the adhesive strength is sufficient to endure chemical mechanical polishing (CMP). For the peeling test, the Cu film was thickened by electroplating at a current density of 0.03 A/cm$^2$ for 1 h at room temperature, resulting in a copper thickness of 20 µm. The peeling strength between electroless-plated Cu and TaN film was 0.11 kgf/cm after annealing (see Table II), which is less than that for the electroplated Cu/sputtered Cu structure, indicating that further improvement of this technique with respect to adhesion is required. The peeling interface for the electroless-plated copper sample is the interface between the TaN and copper, whereas peeling occurs between TaN and SiO$_2$ for the sputtered copper seed sample.

The resistivity of electroless-plated copper was determined by a four-probe technique in order to obtain accurate measurements. Electroless-plated copper was deposited on the TaN barrier layer with trench patterns fabricated by dry etching and then the Cu interconnects were fabricated after CMP processing. The resistivity of 0.42 µm wide interconnect tracks was 2.3 µΩ cm, and improved to 2.2 µΩ cm after annealing. A cross-sectional transmission electron microscopy (XTEM) micrograph of a Cu damascene interconnect with TaN barrier is shown in Fig. 5. After annealing at 400°C for 30 min in 0.1 mTorr N$_2$ ambient, no voids were observed in the Cu interconnects, and the grain size was in the range 70 to 300 nm. These results indicate that Cu electroless plating is suitable for application to ULSI multilevel interconnection.

### Conclusions

Cu was successfully deposited on TaN and WN barrier layers by electroless plating without activation treatment. The substrates were pretreated by wet chemical etching to remove surface oxides and then immersed into the electroless Cu plating solution. The redox potentials of TaN and WN in the electroless Cu plating solution were lower than that of copper, driving the reduction and deposition of Cu ions from the solution. The surface roughness of 1.4 µm thick plated Cu films was 10.4 nm for TaN and 14.6 nm for WN, and so uniform and smooth Cu films were obtained. The adhesion of this film to the TaN barrier layer was measured by an adhesive tape test and peeling test. After annealing, the sample exhibited an adhesion strength of 0.11 kgf/cm, which is sufficient for reliable CMP processing. The electrical resistivity of a 0.42 µm wide damascene Cu interconnect on TaN after annealing was 2.2 µΩ cm. These results indicate that the proposed electroless process is suitable for the formation of a Cu seed layer prior to electrodeposition for the fabrication of ULSI interconnects.

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### References


### Table II. Peel strength of electroless-plated Cu on TaN.

<table>
<thead>
<tr>
<th>Treatment condition</th>
<th>TaN/EPL-Cu/EP-Cu, annealed at 400°C for 30 min</th>
<th>TaN/Sputtered Cu/EP-Cu, unannealed</th>
<th>TaN/Sputtered Cu/EP-Cu, annealed at 400°C for 30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesion (kg f/cm) Peeled interface</td>
<td>TaN/EPL-Cu</td>
<td>TaN/SiO$_2$</td>
<td>TaN/SiO$_2$</td>
</tr>
<tr>
<td>----------------------------</td>
<td>------------------------------------------------</td>
<td>-----------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td></td>
<td>0.11</td>
<td>0.25</td>
<td>0.35</td>
</tr>
</tbody>
</table>

*Figure 5.* TEM micrograph of electroless-plated Cu trench in 15 nm TaN film after annealing.