Optimization of a Pretreatment for Copper Electroless Deposition on Ta Substrates

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We investigated pretreatment methods for Cu electroless deposition on a Ta substrate. The native oxide on the substrate was effectively etched by the addition of HNO3 to a HF diluted solution and this was confirmed though X-ray photoelectron spectroscopy and chronopotentiometry. To form the Pd catalyst for Cu electroless deposition, a two-step Sn sensitization and Pd activation was carried out. The oxide removal enhanced the adsorption of the Sn ions on the Ta substrate and led to well distributed Pd clusters through Pd activation. By measuring the resistivity of the film, the Sn sensitization time and the Pd activation time were optimized through changes in the incubation time, at which the sheet resistance abruptly decreased by the film formation via the coalescence of Cu grains. The resistivity of the Cu electroless film deposited using the optimized pretreatment conditions was 3.59 μΩ cm, which was further reduced to 2.7 μΩ cm through an annealing process.

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Experimental

The substrates used in this experiment were composed of a Ta (7.5 nm)/TaN(7.5 nm)/Si wafer. To remove the native oxide on the Ta surface, either a 1 vol % HF solution or a mixture of 1 vol % HF and 1.4 vol % HNO3 was used. The etching time was optimized by monitoring the variations of the sheet resistance as a function of etching time. Chronopotentiometry was carried out in the electrolyte which contained 0.1 M HCl using an Ag/AgCl electrode and Pt wire as a reference and a counter electrode, respectively, to confirm the existence of the oxide on the surface electrochemically. After Ta oxide etching, two Pd activation methods were applied to form the catalyst for Cu nucleation. The first was a one-step Pd activation performed by a displacement reaction in the solution containing 5 x 10^-4 M PdCl2, 0.04 M HCl, and 0.14 M HF, which was previously optimized for Ta substrates. The other, known as the two-step Sn sensitization-Pd activation method, was carried out by sequentially dipping the substrate in solutions composed of 0.01 M SnCl2·2H2O and 0.1 M HCl for 2 min and 5 x 10^-4 M PdCl2 and 0.04 M HCl for 20 s, respectively. The optimum dipping time was determined by measuring the incubation time, at which point the sheet resistance decreases dramatically as the Cu film that is being formed becomes continuous. Following the Sn sensitization step in a range of individual times (1, 2, 3, and 5 min), Pd activation was carried out on each Sn-treated samples for 20 s. Then, monitoring the abrupt decrease in sheet resistance (during Cu electroless deposition) for each sample, the optimal Sn sensitization was experimentally determined. Likewise, following the Sn sensitization for 3 min, Pd activation was performed for 5, 10, 20, and 50 s, respectively. Then, Pd activation time was optimized from the incubation time measured during Cu electroless deposition. The base electrolyte consisted of 0.025 M CuSO4·5H2O, 2.9 g/L paraformaldehyde [(HCHO)0.5], 0.054 M ethylenediaminetetraacetic acid (EDTA) and 0.49 M KOH. To reduce the incorporation of oxygen into the film, 0.1 g/L 2,2′-dipyridyl, which is a well-known stabilizer, was added in the base electrolyte and the deposition temperature was maintained at 70°C.

The sheet resistance change of the Ta substrate with respect to etching time was measured by a four-point probe. The surface analyses were carried out using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). A potentiostat/galvanostat (Versastat II, EG&G Princeton Applied Research) was used for chronopotentiometry and transmission electron microscopy (TEM) was used to examine the Pd catalysts on the Ta substrate. An optical
The microscope was used for measuring the contact angles and comparing the wetting properties. Field-emission scanning electron microscopy (FE-SEM) and Auger electron spectroscopy (AES) were employed to check the thickness and depth profile of the Cu.

**Results and Discussion**

In general, the removal of oxide is essential to form Pd catalysts on low conductive barrier layers. Because the oxide passivation layer interrupts the displacement reaction between Pd ions and the barrier layer, which makes Cu electroless deposition impossible to occur. The chemical etching of the native oxide on the surface enhances the hydrophilicity related to the adhesion of Pd catalysts.\(^{13,20}\)

Figure 1 shows the change in the sheet resistance with time before and after Ta oxide etching in the two different etching solutions. As shown in Fig. 1a, an abrupt increase in the sheet resistance difference appeared after about 7.5 min of etching in a 1 vol % HF solution. On the other hand, this was delayed by 15 min when etched in a solution with 1.4 vol % HNO\(_3\) and 1 vol % HF. This abrupt increase in the sheet resistance difference is considered to be due to the etching of the Ta layer after the oxide removal or to an increase in the surface roughness. This was clarified through XPS and AFM analyses afterward.

To confirm the removal of the Ta oxide, XPS was carried out on the substrate after Ta oxide etching for the optimized time based on changes in the sheet resistance with time for the two different solutions. As shown in Fig. 2a, an abrupt increase in the sheet resistance difference appeared after about 7.5 min of etching in a 1 vol % HF solution. On the other hand, this was delayed by 15 min when etched in a solution with 1.4 vol % HNO\(_3\) and 1 vol % HF. This abrupt increase in the sheet resistance difference is considered to be due to the etching of the Ta layer after the oxide removal or to an increase in the surface roughness. This was clarified through XPS and AFM analyses afterward.

To exclude the influence by reoxidation, the coulometric reduction method (CRM)\(^{21,22}\) was adopted. When the current is applied to the Ta surface covered with Ta oxide, Ta oxide begins to reduce through the following reaction:

\[
\text{Ta}_2\text{O}_5 + 10\text{H}^+ + 10\text{e}^- \rightarrow 2\text{Ta} + 5\text{H}_2\text{O}
\]

and a sharp potential drop appears. On the basis of this, applying a constant current of 50 \(\mu\text{A}\) to 1 cm\(^2\) of the oxide-etched Ta substrates by the respective etching solutions, the electrode potentials vs an Ag/AgCl reference electrode were measured as a function of time. As shown in Fig. 3a and b, chronopotentiograms of Ta pretreated with 1 vol % HF solution displayed a transition time of 30 s in both 7.5 min and 10 min, which means Ta oxides still exist even after Ta oxide etching. On the other hand, in the sample etched Ta oxide with HNO\(_3\)-added HF solution, no transition region was observed, as shown in Fig. 3c, which proves that the oxide was completely removed by HNO\(_3\)-containing HF solution.

The surface morphologies of the substrates that were treated with the different etching methods were compared to the initial Ta substrate, as shown in Fig. 4a-c. When the Ta oxide was etched in the 1 vol % HF solution for 7.5 min, the surface roughness increased was observed through XPS, oxide peaks still existed. This is considered that the Ta surface was partially reoxidized during sample transferring. Indeed, this was confirmed that the reoxidation occurred within a few minutes of exposure to air, in the result of additional XPS analyses.

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**Figure 1.** Evolution of sheet resistance with time in two different Ta cleaning solutions: (a) 1 vol % diluted HF and (b) 1 vol % diluted HF with the addition of 1.4 vol % HNO\(_3\).

**Figure 2.** Ta 4f XPS spectra of (a) initial Ta substrate, (b) Ta substrate etched by a 1 vol % HF solution, and (c) Ta substrate etched by a mixture of 1 vol % HF and 1.4 vol % HNO\(_3\).
rapidly up to 1.1 nm, which corresponded to a 15% increase against the Ta thickness, while it slightly increased from the 0.13 nm of the initial Ta substrate to 0.2 nm in the mixture of 1 vol % HF and 1.4 vol % HNO₃. Additionally, the pitting corrosion was observed on the Ta surface etched with 1 vol % HF solution due to a partial etching of the oxide layer (Fig. 4d). Thus, it was considered that the increase in the sheet resistance after 7.5 min of etching in the 1 vol % HF solution determined by AFM and FE-SEM measurements was attributed not only to Ta oxide etching but also to an increase in the surface roughness by pitting corrosion.

Although many researchers have added HNO₃ to a diluted HF solution to remove the Ta oxide on the surface, the effect of HNO₃ is not clear. In the case of silicon (Si), mixtures of HF and HNO₃ are well-known solutions for etching Si/Si oxides through oxidization of the silicon by HNO₃ followed by the etching of the oxide by HF nearly simultaneously. The HNO₃/H₂O/HF treated Ta sample had a very smooth surface after the oxide etching at low concentrations of HNO₃ and HF, while a significant increase in the roughness was visible at higher concentrations of HNO₃ and HF. In addition, in the Pourbaix diagram of Ta in 1.0 M HF, which shows the thermodynamic stability of the species as a function of the potential and pH, TaF₇²⁻ becomes more stable than Ta₂O₅ as the pH decreases. Therefore, the addition of HNO₃ enables a more effective removal of the Ta oxides due to the decreased pH and also lowers surface roughness by acting as an oxidizing agent, controlling the removal rate of the Ta oxides.

The pretreated Ta substrate should be activated with catalysts such as palladium (Pd) to allow Cu reduction to occur heterogeneously on the surface. Although one-step Pd activation, where Pd ions are reduced by electrons generated from the oxidation of the substrate, was attempted for 20 s, as in the case of TiN substrates, it was confirmed through microscopy and XPS that Pd particles were not formed on the surface. Even though the oxide was removed, the Ta substrate was considered to be oxidized to the Ta oxide, not TaF₇²⁻, because Ta₂O₅ is thermodynamically stable in the Pd activation solution with a mixed potential of 0.214 V (vs. SCE) and pH of 0.51 (measured at 18°C). The passivation of the Ta substrate makes the formation of the Pd catalysts difficult by preventing the supply of electrons to the Pd ions.

Alternatively, a two-step Sn sensitization and Pd activation method was used to form the catalytic nuclei on the Ta substrate. In this method, the electrons generated by the oxidation of Sn²⁺ to Sn⁴⁺...
angles calculated from the images were 21.8° dropping on the different types of Ta surfaces. While, the contact/H2O849

To verify the effect of the diluted HF-HNO3 solution on the hydrophilicity, contact angle measurements were carried out. Figure 6 shows optical microscope images of the water droplet of 35 μL dropping on the different types of Ta surfaces. While, the contact angles calculated from the images were 21.8° (Fig. 6a) and 16.4° (Fig. 6b) on the initial Ta and Ta substrate pretreated with 1 vol % HF solution, respectively, and that of Ta substrate etched with HF-HNO3 solutions was 8.0° (Fig. 6c), which represents the addition of HNO3 enhanced the hydrophilicity of the Ta surface and aided the Sn ions in effectively adsorbing onto the Ta substrates.

Pd activation was performed on the Ta substrates treated with Ta oxide etching and subsequent Sn sensitization. Figure 7a presents TEM images of the Pd particles with a height of 7.8 ± 1.1 nm and a diameter of 10.9 ± 2.1 nm that were formed by Pd activation. Pd was confirmed by the XPS analysis, as shown in Fig. 7b.

To optimize the Sn sensitization time and the Pd activation time, the incubation time for Cu electroless deposition, which is defined as the time at which the sheet resistance dropped abruptly, was measured as exhibited in Fig. 8. After Sn sensitization for various times at a fixed Sn concentration and subsequent Pd activation for 20 s, the incubation time was measured during Cu electroless deposition as shown in Fig. 8a. The incubation time eventually became saturated after about 3 min of Sn sensitization. This implies time is required for the Sn ions to adsorb and provide a site for Pd reduction on the surface, even though it may depend on the concentration of the Sn source. In the case of Pd activation, the incubation time was measured as differing from the activation time after evenly treating with 3 min of Sn sensitization, as shown in Fig. 8b. The incubation time was virtually the same regardless of the Pd activation time, which shows that the displacement reaction of Pd occurred rapidly compared to the adsorption of Sn.

Considering the incubation time and the resistivity of the Cu film, a Sn sensitization time of 3 min and a Pd activation time of 20 s were selected to provide optimum pretreatment conditions. Figure 9a shows the cross-sectional image of the Cu film deposited after 100 s at a temperature of 70°C using the optimized pretreatment conditions and the AES depth profiling of the as-deposited Cu film was done as shown in Fig. 9b. Although the resistivity of Cu film was 3.59 μΩ cm at 110 nm thick, which was higher than the bulk resistivity of Cu (1.7 μΩ cm), the incorporation of oxygen inside the film, which is a main factor causing increases in the resistivity, was not observed due to the use of the surfactant. Besides the resistivity could be reduced to (2.7 μΩ cm) through thermal annealing at 400°C by increasing the grain sizes.

The poor adhesion of Cu electroless film was a problem after the deposition, however it was significantly improved though the thermal annealing and passed the 3M tape test. Also the adhesion of as-deposited film of which thickness was reduced down to 50 nm by a dilution of the electrolyte could be enhanced even without the addition of surfactants. This indicates that an increase in tensile stress by an increase in the thickness is one of the main factors in degrading the adhesion property even at the same pretreatment processes.

Figure 5. XPS spectra of the Sn 3d peak on Ta samples sensitized (a) without oxide etching and (b) after oxide etching with a mixture of 1 vol % HF and 1.4 vol % HNO3.

Figure 6. (Color online) Optical images for measuring contact angles of Ta substrates (a) without oxide etching, (b) etched with a 1 vol % HF, and (c) etched with a mixture of 1 vol % HF and 1.4 vol % HNO3.
Conclusions

We performed Cu electroless deposition on a Ta substrate which had superior properties as a Cu diffusion barrier layer. As the CRM method and XPS analysis indicated, the addition of HNO₃ to a 1 vol % HF solution effectively removed the Ta oxide without increasing the surface roughness; it also assisted in the surface adsorption of Sn ions, which was an improvement from the 1 vol % HF solution alone. Sn sensitization created well-distributed and small sized Pd catalysts owing to improved wetting properties. The Sn sensitization and Pd activation time for Cu electroless deposition were optimized by measuring the incubation time and the resistivity of the film. Through the optimized conditions for Sn sensitization and Pd activation, a uniform Cu film could be deposited with a resistivity of 3.59 \( \mu \Omega \) cm, which was decreased to 2.7 \( \mu \Omega \) cm by a thermal annealing process.

Acknowledgments

This work was supported by KOSEF through the Research Center for Energy Conversion and Storage (RCECS), Dongbu Electronics, and by the Institute of Chemical Processes (ICP).

Seoul National University assisted in meeting the publication costs of this article.

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