Embedding of Copper into 30-nm-wide trench by a high-magnetic-field magnetron sputtering method with oxygen added sputtering gas

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Abstract. We successfully embedded Cu in 30-nm-wide trenches with an aspect ratio of 10 using a high-magnetic-field, medium vacuum magnetron sputtering method having high deposition speeds. We used a Ru/TaN/SiO$_2$/Si substrate featuring a Ru barrier layer and a sputtering gas formed by adding O$_2$ at 5×10$^{-5}$ Pa to 1-at.% N$_2$-Ar. The trenches could be completely filled with Cu in a sputtering time of 5 min. This result is discussed on the basis of capillary theory focusing on the wettability of Cu with the Ru barrier layer.

1. Introduction
Copper (Cu) wiring used in ultra-large-scale-integration (ULSI) devices has been patterned by methods such as electroplating and sputtering. Electroplating is currently the mainstream process for Cu embedding at wiring widths of 100 nm and narrower. Next-generation ULSIs, however, will call for even finer Cu wiring widths of 32 or 22 nm, which means that preparation of the Cu seed layer required for electroplating will be difficult as will Cu embedding by electroplating.

The sputtering method has, however, been used for Cu embedding at wiring widths greater than 100 nm. At present, it is being used for preparing the Cu seed layer and barrier layer in electroplating, but it is not being used for Cu embedding at wiring widths of 100 nm and narrower. The sputtering method, however, has features that cannot be overlooked. For example, it has been used since the time of aluminum (Al) wiring and is consequently a mature technology, and it is expected that existing sputtering equipment used for Al wiring could be appropriated for use in Cu wiring. These strong points underscore a need for developing new sputtering technology that can support Cu embedding for wiring widths of 100 nm and narrower.

We have been researching the formation of Cu wiring for ULSIs using high-vacuum planar magnetron sputtering. In this research, we found that Cu embedding characteristics can be improved by employing optimal embedding conditions in which O$_2$ is added to 1-at.% N$_2$-Ar sputtering gas[1] and by using a ruthenium (Ru) barrier layer with which Cu has excellent wettablity. We have also been successful in achieving complete Cu embedding in a Ru/TaN/SiO$_2$/Si substrate for a trench width of 30 nm and an aspect ratio (AR) = 10 by high-vacuum planar magnetron sputtering [2]. The Cu deposition speed by this sputtering method, however, is slow, as about one hour of sputtering is needed to complete Cu embedding.

Increasing the speed of Cu deposition would provide a manufacturing advantage since it would
shorten the time taken up by the Cu wiring process. With this in mind, we set out to achieve high deposition speeds and shorten sputtering time by embedding Cu using medium vacuum magnetron sputtering in a high magnetic field. We used two types of Ru/TaN/SiO$_2$/Si substrates in our experiments: one of trench width 80 nm (AR=5) and the other of trench width 30 nm (AR=10). In short, we performed Cu-embedding experiments by high-magnetic-field, medium vacuum magnetron sputtering under the optimal Cu-embedding conditions used for high-vacuum planar magnetron sputtering. In this way, we were able to embed Cu in these two types of trenches in a sputtering time of only 5 min.

2. Experiment

This experiment used a SiO$_2$/Si substrate with a trench width of 100 nm and AR = 4.5 on which a 20-nm-thick TaN barrier layer was formed. On this structure, a Ru barrier layer was also formed by high-vacuum planar magnetron sputtering equipment using an oil diffusion pump. The Ru sputtering time was varied to obtain two types of substrates: a Ru(10 nm)/TaN(20 nm)/SiO$_2$/Si substrate with a trench width of 80 nm (AR=5) and a Ru(35 nm)/TaN(20 nm)/SiO$_2$/Si substrate with a trench width of 30 nm (AR=10). The Ru barrier layer was formed under the following conditions: an arrival vacuum level of $P_0=1\times10^{-5}$ Pa, a target – substrate distance of $d = 200$ mm, an Ar sputtering gas pressure of $P_{S}=3.0\times10^{-2}$ Pa, a sputtering voltage of $V_S = 6$ kV, a sputtering current of $I_B = 7.5$ mA, a substrate temperature of $T_s = 200^\circ$C, sputtering gas consisting of pure Ar, and a target composed of Ru.

After being momentarily drawn into the surrounding atmosphere, the fabricated substrate was transported to ultra-high-vacuum equipment having a cryopump. This equipment was used to perform Cu embedding by the high-magnetic-field, medium vacuum magnetron sputtering method under the following conditions: $P = 1\times10^{-8}$ Pa, $d = 200$ mm, $P_S$= several Pa, $V_S = 200$ V, $I_B = 1.65$ A, $T_s = 250 – 400^\circ$C, sputtering gas: 1-at.% N$_2$-Ar, added gas: O$_2$, added O$_2$ partial pressure: $P_{O_2} = 10^{-3} – 10^{-6}$ Pa, and target: Cu.

The 1-at.% N$_2$-Ar sputtering gas was provided by a cylinder containing a mixture of these gases, and variable leak valves were used to supply the sputtering gas and added gas to the sputtering equipment. The Cu sputtering time was varied according to the objective in question.

The state of Cu embedding was observed by scanning electron microscope (SEM) after cutting away samples of the Cu-sputtered substrate with nippers. Resistivity ($\rho$) was calculated based on the Cu film thickness and the sheet resistance measured by the four probe method.

3. Results and Discussion

The embedding of Cu using the high-magnetic-field, medium vacuum magnetron sputtering method was performed using 1-at.% N$_2$-Ar sputtering gas to which O$_2$ at $5\times10^{-2}$ Pa was added. The substrate temperature was 350$^\circ$C. These conditions are the same as the Cu-embedding conditions found to be optimal for the high-vacuum planar magnetron sputtering method [2]. However, when using the high-magnetic-field, medium vacuum magnetron sputtering method, Cu deposition speed under these conditions was 80 nm/min, which is more than 20 times that of the high-vacuum planar magnetron sputtering method.

Results of embedding Cu in 80-nm-wide (AR = 5), trenches with Ru(10 nm)/TaN(20 nm) barrier layer are shown in Figure 1. The Cu sputtering time was 5 min. For comparison purposes, the case of using pure Ar sputtering gas is also shown. An SEM image of the substrate cross section before Cu embedding is shown in Figure 1(a), and the result of Cu embedding under optimal conditions is shown in Figure 1(b). As can be seen, the trenches are completely filled under optimal conditions. The result of Cu embedding using pure Ar sputtering gas is shown in Figure 1(c). In this case, some of the trenches are incompletely filled. These results demonstrate that optimal Cu embedding conditions for the high-vacuum planar magnetron sputtering method are also effective for the high-magnetic-field, medium vacuum magnetron sputtering method.

On the basis of these results, we next attempted to embed Cu in 30-nm-wide (AR = 10), trenches with Ru(35 nm)/TaN(20 nm) barrier layer under optimal embedding conditions. Results are shown in
Figure 1. Embedding of Cu in 80-nm-wide, AR = 5 trench with Ru(10 nm)/TaN(20 nm) barrier layer
(a) Before embedding of Cu, (b) after embedding of Cu under optimal Cu-embedding conditions, and (c) after embedding of Cu using pure Ar sputtering gas
Cu sputtering time: 5 min; substrate temperature: 350°C

Figure 2. Embedding of Cu in 30-nm-wide, AR = 10 trench with Ru(35 nm)/TaN(20 nm) barrier layer
(a) Before embedding of Cu, (b) after embedding of Cu under optimal Cu-embedding conditions, and (c) after embedding of Cu using pure Ar sputtering gas
Cu sputtering time: 5 min; substrate temperature: 350°C

Figure 2. The Cu sputtering time here was 5 min, and the result of using pure Ar sputtering gas is also shown for comparison purposes. An SEM image of the substrate cross section before Cu embedding is shown in Figure 2(a). The result of Cu embedding under optimal conditions is shown in Figure 2(b), where it can be seen that the trenches are completely filled. The case of Cu embedding using pure Ar sputtering gas is shown in Figure 2(c). In this case, some of the trenches are incompletely filled, as was the case with the 80-nm-wide trenches.

We discuss the reason for these results on the basis of capillary theory focusing on the wettability of Cu with the Ru barrier layer [3, 4].

According to capillary theory, the critical free-energy barrier for nucleation $\Delta G^*$ is given by the following equation:

$$\Delta G^* \propto \frac{(2 - 3 \cos \theta + \cos^3 \theta)}{4},$$

Here, $\theta$ denotes the contact angle. Now, $\Delta G^*$ can be used to express nuclei density $N^*$ as in the following equation:
Here, \( n \) denotes nucleation-site density.

The results of observing the wettability of Cu with the Ru barrier layer are shown in Figure 3. The Cu sputtering time was 2 sec, and the case of using pure Ar sputtering gas is shown for comparison purposes. When performing Cu embedding under optimal conditions as shown in Figure 3(a), the average contact angle \( \theta_{av} \) was found to be 39.7°, but when performing Cu embedding with pure Ar sputtering gas (Figure 3(b)), it was found to be 41.5°. In other words, the average contact angle when embedding Cu under optimal conditions is about 2° less compared to that when using pure Ar sputtering gas. The standard deviation of the average nuclei angle under optimal Cu-embedding conditions was 4.7°, and 6.3° for using pure Ar sputtering gas. Next, the results of observing the nuclei density of Cu on the substrate surface is shown in Figure 4. These SEM images were used to determine average Cu nuclei density per 1 \( \mu m^2 \). Under optimal Cu-embedding conditions, average Cu nuclei density was 9/\( \mu m^2 \) as shown in Figure 4(a), and when using pure Ar sputtering gas, average Cu nuclei density was 6/\( \mu m^2 \) as shown in Figure 4(b). In short, average Cu nuclei density under optimal Cu-embedding conditions was found to be about 1.5 times that when using only pure Ar sputtering gas. From Equations (1) and (2), this increase in nuclei density \( N^* \) means a decrease in the critical free-energy barrier for nucleation \( \Delta G^* \), which supports the decrease observed in the contact angle. This result shows that Cu wettability improves under optimal Cu-embedding conditions.
Finally, the Cu surface shape when extending the Cu sputtering time is shown in Figure 5. Sputtering time was 1 min, and the case of using pure Ar sputtering gas is also shown for comparison purposes. Under optimal Cu-embedding conditions, agglomeration of Cu on the Ru barrier layer is suppressed and a Cu film is beginning to form as shown in Figure 5(a). However, when using pure Ar sputtering gas, Cu agglomerates on the Ru barrier layer and undergoes crystal growth as shown in Figure 5(b). Under optimal Cu-embedding conditions, the surface of Cu sputtered on the Ru barrier layer enters a flowing-like state and Cu wettability improves. This suggests that improvement in Cu wettability is associated with improvement in Cu-embedding characteristics.

The resistivity ($\rho$) of embedded Cu was 2.0 $\mu\Omega \cdot$ cm under optimal Cu-embedding conditions. The surface of Cu sputtered on the Ru barrier layer under optimal Cu-embedding conditions was smooth. From this and data obtained from previous measurements by secondary ion mass spectrometry (SIMS), we estimated that the density of O$_2$ in the Cu film was less than 2% [5].

4. Conclusion
We demonstrated that Cu embedding can be performed in a relatively short time using a high-magnetic-field, medium vacuum magnetron sputtering method having high deposition speeds. This method required the use of optimal Cu embedding conditions as used in high-vacuum planar magnetron sputtering. Under these conditions, Cu deposition speed and Cu resistivity ($\rho$) were 80 nm/min and 2.0 $\mu\Omega \cdot$ cm, respectively. We were able to completely embed Cu in 30-nm-wide, AR = 10 trenches in a sputtering time of 5 min. The improvement in Cu wettability at this time was observed from a drop in contact angle $\theta$, increase in Cu nuclei density, and shape of the Cu surface. These results suggest that improvement in Cu wettability is associated with improvement in Cu embedding characteristics.

References
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