Effect of NH₃/He Plasma Treatment on Electrical Reliability and Early-Stage Electromigration Behavior of Copper Interconnects

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Electromigration reliability tests of dual-damascene Cu interconnect structures with or without a NH₃/He plasma treatment have been performed in this study at 400°C under a high current density of 8 MA/cm² to clarify the effect of plasma treatment on the interface structure between Cu wires and SiCN capping layers and on the early-stage electromigration behavior and electrical reliability of the interconnects. From cumulative failure probabilities, small shape factors and large median time to failure were obtained for the interconnects with the plasma treatment, indicating an improved electromigration resistance. The oxide layer on the Cu surface was removed by plasma treatment, and an alternative CuSiN interlayer was formed at the Cu/SiCN interface, enhancing interface adhesion and reducing the diffusion paths of Cu atoms. Therefore, voids nucleated inside the Cu wires, rather than at the interface, at the early stage of the electromigration tests. The change in the Cu/SiCN interface structure varied the early-stage electromigration-induced voiding behavior and then effectively improved the electrical reliability of the Cu interconnect structures.

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Copper with a low electrical resistivity and high thermal conductivity has been adopted for interconnect metallization in ultralarge-scale integrated circuits to reduce the problem of serious resistance-capacitance delay.¹-³ However, due to the high diffusivity of Cu atoms, interconnect structures and microelectronic devices fail early.⁴⁻⁶ Among the failure modes of Cu interconnects, rapid electromigration (EM) of Cu atoms under a strong electron flow induces void formation and even wire opening especially reduces the electrical reliability of the interconnects.⁷ As the width of Cu interconnects further decreases in the generation of semiconductor manufacturing technology below 65 nm, the drastic increase in current density within Cu wires leads to a severe EM issue and accelerates the failure of microelectronic devices. Thus, in the past decades, many studies have been performed to enhance the resistance of Cu interconnect structures to EM degradation and consequently to improve the reliability of the devices.⁶⁻¹⁸

Some factors influencing the EM behaviors of Cu atoms in interconnect structures have been reported. (i) The size of the interconnects.⁴⁻⁵ Many grain boundaries and defects in large-sized wires lead to severe EM; a large difference between the sizes of wires and vias induces a high stress gradient and shortens the lifetime of the interconnects. (ii) The microstructure of the interconnects.⁹⁻¹¹ A bamboolike structure in wires with grain boundaries perpendicular to electron flow reduces the diffusion paths of Cu atoms; twin boundaries inhibit the migration of Cu atoms. (iii) Diffusion barriers:¹²⁻¹³ Barrier layers that induce the formation of a strong (111) texture in wires enhance EM resistance. (iv) Capping layers:¹³⁻¹⁵ A strong adhesion between capping layers and Cu wires retards the diffusion of atoms along interfaces, such as a CoWP capping layer exhibiting a good EM resistance.¹⁰⁻¹¹ (v) Surface plasma treatments:¹⁷⁻¹十八 Hydrogen or NH₃ plasma treatment removes the oxides on the surface of Cu wires and forms a CuSi or CuN interlayer, enhancing the interface bonding and EM resistance.

Among these factors, a good interface adhesion between Cu interconnects and capping layers is believed to reduce rapid diffusion paths of Cu atoms and therefore, most importantly, to dominate a high EM resistance of Cu interconnects.¹⁷⁻¹⁸ However, as aforementioned, Cu oxides, such as Cu₂O, CuO, or Cu(OH)₂, form on the surface of Cu wires after chemical mechanical polishing (CMP), weaken interface adhesion, and lead to a short lifetime of the Cu interconnects.¹⁷⁻²⁰ Even in accelerated EM tests under very high current densities of 5–10 MA/cm² at temperatures higher than 400°C,²¹⁻²⁵ the weak interfaces are still reported as the dominant EM failure paths. Therefore, many types of surface cleaning and plasma treatments have been extensively developed to change the interface microstructure (to remove oxides and to form a CuSi, CuN, or even CuSiN interlayer) and to improve the interface adhesion and the consequent electrical reliability.¹⁷⁻²⁰,²⁵⁻²⁷ Nevertheless, most of the previous studies focused on the reliability improvement of interconnects; how the plasma treatments influence the very early-stage EM-induced voiding behavior has not been clarified. Thus, in this study, EM reliability tests of dual-damascene Cu interconnect structures with or without applying a NH₃/He mixed plasma treatment were performed. The interface microstructure between the Cu wires and the SiCN capping layers was characterized, and the void formation in the wires under the EM tests was examined to evaluate the effect of plasma treatment on the early-stage EM behavior and electrical reliability of the Cu interconnects.

Experimental

Figure 1 schematically illustrates the dual-damascene Cu interconnect structure for the evaluations of EM behavior and electrical reliability. The height and width of the first-level metal wire (M1) were 150 and 210 nm, respectively, and the length of M1 between two first-level vias (V1) at the cathode and the anode was 250 μm. The height of V1 was 100 nm, and the width was between 90 (bottom) and 130 (top) nm. Surrounding the Cu wires, TaN was deposited as a diffusion barrier, and SiCN was deposited as a capping (etch stop) layer. Between the Cu wires, a porous SiOCH low dielectric constant material was used as the intermetal dielectric. After the CMP of each level interconnect, a NH₃/He mixed plasma treatment was applied to the surface of the Cu wires before the deposi-

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Figure 1. Illustration of dual-damascene Cu interconnect structure used for EM reliability tests. The arrows indicate the electron flow direction; M1: first-level metal wire.
tion of the SiCN capping layer. During EM reliability tests, to simulate the EM failure of interconnects under very strict stress conditions in the manufacturing generation below 65 nm,21-25 the dual-damascene Cu interconnects tested in this study were stressed with a high density current of 8 MA/cm² at 400°C until the opening of the test structures by using an HP4156C probe station. Both interconnects with or without the NH₃/He plasma treatment were tested under the same conditions to compare their electrical reliability and early-stage EM behavior under the effect of the plasma treatment.

For the analyses of electrical reliability, the original electrical resistance of the EM-tested Cu interconnect structures was defined as $R_0$, and the variation traces of resistance to test duration were recorded. Cumulative time-to-failure (TTF) probabilities as the resistance increased to different levels (including $1.1R_0$, $1.3R_0$, $1.5R_0$, and wire opening) were plotted with conventional logarithm–logarithm probability-to-lifetime axes. The experimental data were then fitted by the Weibull cumulative probability distribution function, as the following equation, to extract the best shape factors ($\gamma$), specific lifetime ($\theta$), and median time to failure (MTF)

$$F(t) = 1 - \exp\left[-\left(t/\theta\right)\right]$$

The Weibull function is appropriate for examining the distribution of failure probability and widely adopted in the analysis of lifetime and reliability. When $\gamma > 1$, the failure probability is an ascending function; the larger the $\gamma$ value, the more concentrated the failure points. To analyze the early-stage EM behavior, the cross-sectional microstructure of the test structures, the interface microstructure between Cu wires and SiCN capping layers, and the morphologies of EM-induced voids in the interconnects were examined by a focused ion beam (FIB, FEI Nova 200), a scanning electron microscope (SEM, JEOL JSM-6700F), and a high resolution transmission electron microscope (HRTEM, JEOL JEM-3000F). The samples for SEM and transmission electron microscope (TEM) observations were prepared by the FIB.

Results and Discussion

**EM-induced void formation at early stage.**—Figure 2 shows the SEM cross-sectional images around the cathodes of EM-tested Cu interconnect structures without a NH₃/He plasma treatment as the electrical resistance of the tested structures slightly increased at the early stage. Figure 2a shows that a small void formed at the M1 Cu/SiCN interface near the via bottom, associated with the appearance of some other small voids at the M2 Cu/SiCN interface, as the resistance increased to $1.003R_0$. When the resistance increased to $1.005R_0$, the void at the M1 Cu/SiCN interface grew toward the via bottom, and more voids formed at the M2 Cu/SiCN interface, as seen in Fig. 2b. These voids were expected to enlarge into pores and to connect/merge with each other, consequently raising the resistance. With extended test duration, Cu atoms migrated along with electron flow from the cathode to the anode, and more vacan-

cies were left at the cathode, leading to a further enlargement in void size, and an increase in number, and eventually to the opening of the wire.

Under a high density current, Cu atoms with sufficient momentum migrate along the direction of electron flow, leaving vacancies and subsequently inducing voids, which will then result in the gradual increase in the electrical resistance of the wires.5 As localized large pores relative to the size of the wires form, a current crowding effect further raises the local current density and accelerates the failure of the wires. In Cu interconnect structures, high tensile stresses especially concentrate at via bottoms and gather vacancies,29 inducing void formation in the region near via bottoms under a crowded current during EM tests. Cu atoms adjacent to the poorly adhered Cu/SiCN interfaces with the existence of oxides are expected to be weakly bound and to easily migrate along the interfaces as rapid diffusion paths.17-23 Therefore, the nucleation of voids, in particular at the Cu/SiCN interfaces near via bottoms, is expected,21,27 as observed in Fig. 2. Even under the strict EM test conditions with a high current density of 8 MA/cm² and at a high temperature of 400°C, the Cu/SiCN interfaces without any plasma treatment are still the dominant EM failure paths as reported.21-25

Effect of plasma treatment on EM reliability.—From the electrical resistance-to-time traces of EM reliability tests plotted in Fig. 3, the resistance of Cu interconnect structures gradually increased with test duration, as expected, when the structures were stressed
plasma treatment, the electrical resistance increased at a higher resistance of the tested structures increased to 1.18.7 with a high density current. For the interconnects without a NH3 He plasma treatment, respectively, as the electrical interconnect structures and test conditions, the only process difference, i.e., the plasma treatment, is believed to be the dominant factor for the rapid EM degradation.14 It has been reported that the EM activation energy for polycrystalline metallic films, ranging from 0.6 to 1.0 eV, is smaller than that for bulk metals31 because larger numbers of grain boundaries in the films as well as defects at the interfaces is therefore expected as an important factor for the rapid EM failure of the Cu interconnect structures. However, further EM studies at various temperatures are necessary to calculate the activation energy more exactly and also to characterize the microstructure constant, which affects the lifetime of the interconnects as well.

The flux of metallic atoms under an EM effect, $F_{\text{in}}$, is generally expressed as

$$F_{\text{in}} = \frac{ND_0}{kT} \exp(-E_a/kT)$$

where $N$ is the density of atom, $D_0$ is the diffusion coefficient, $k$ is the Boltzmann constant, $T$ is the temperature, $Z,q$ is the effective ion valence, and $E$ is the electric field. $E_a$ is the activation energy for EM. Accordingly, the MTFs of interconnects is represented as

$$\text{MTF} = \frac{A}{J^{-\alpha}} \exp(E_a/kT)$$

in which $A$ is a material constant relating to the microstructure and geometry of interconnects and $J$ is the current density applied during EM tests. The above equations show that atoms with sufficient energy higher than the EM activation energy migrate. Basically, under the same current density $J$ and a constant temperature $T$, the smaller the microstructure constant $A$ and activation energy $E_a$, the more severe the EM degradation.14 It has been reported that the EM activation energy for polycrystalline metallic films, ranging from 0.6 to 1.0 eV, is smaller than that for bulk metals31 because larger numbers of grain boundaries in the films as well as defects at the interfaces provide more vacancies for atoms to migrate.14 In the present study, a small activation energy for the diffusion of atoms through the interfaces is therefore expected as an important factor for the rapid EM failure of the Cu interconnect structures. However, further EM studies at various temperatures are necessary to calculate the activation energy more exactly and also to characterize the microstructure constant, which affects the lifetime of the interconnects as well. However, it can be simply interpreted that, with the same interconnect structures and test conditions, the only process difference, i.e., the NH3/He plasma treatment, is believed to be the dominant factor to change the Cu/SiCN interface structure, then to vary the microstructure constant or EM activation energy, and consequently to improve the electrical reliability of the interconnects.

Figure 4. Cumulative TTF probabilities of the EM-tested Cu interconnect structures (a) without and (b) with a NH3/He plasma treatment as the electrical resistance of the tested structures increased to 1.1$R_0$.

Table I. Probability distribution shape factors ($\gamma$), specific lifetime ($\theta$), and MTFs of EM-tested Cu interconnect structures with and without a NH3/He plasma treatment as the resistance of the tested structures increased to different levels, fitted by the Weibull cumulative probability distribution function.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>1.1$R_0$</th>
<th>1.3$R_0$</th>
<th>1.5$R_0$</th>
<th>Opening</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH3/He</td>
<td>2.8</td>
<td>3.1</td>
<td>3.2</td>
<td>2.8</td>
</tr>
<tr>
<td>None</td>
<td>15</td>
<td>29</td>
<td>41</td>
<td>63</td>
</tr>
<tr>
<td>$\theta$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH3/He</td>
<td>21</td>
<td>37</td>
<td>51</td>
<td>69</td>
</tr>
<tr>
<td>None</td>
<td>14</td>
<td>27</td>
<td>38</td>
<td>57</td>
</tr>
<tr>
<td>MTF (min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH3/He</td>
<td>18</td>
<td>33</td>
<td>45</td>
<td>61</td>
</tr>
</tbody>
</table>
Effect of plasma treatment on early-stage EM behavior.—How the NH₃/He plasma treatment influenced the Cu/SiCN interface structure and the early-stage EM-induced voiding behavior in Cu interconnects was further examined by TEM. Figure 5 shows the HRTEM images around the Cu/SiCN interfaces without and with the NH₃/He plasma treatment. Figure 5a clearly shows that an oxide (oxygen-rich) layer about 5 nm thick, most probably Cu₂O according to the TEM and X-ray photoelectron spectroscopy (XPS) analyses in our previous study, existed at the interface without the plasma treatment due to atmosphere exposure and surface oxidation of the Cu wire after CMP. In comparison, as seen in Fig. 5b, the oxide layer was removed, and an alternate layer of CuN of similar thickness was expected to form under the NH₃/He plasma treatment. During the subsequent deposition of the SiCN capping layer, a CuSi or even CuSiN interlayer might form due to the reaction of the SiCN precursor to the Cu surface or to the CuN layer, as reported. The formation of a CuN, CuSi, or CuSiN interlayer would enhance the adhesion of the Cu/SiCN interface, which was believed to reduce the rapid diffusion paths of Cu atoms and therefore to improve the EM resistance of Cu interconnects, consistent with the reliability results obtained in the present study.

Figure 6 shows the FIB and HRTEM images around the M1 Cu/SiCN interface of the EM-tested Cu interconnect structure without a NH₃/He plasma treatment as the electrical resistance of the tested structure increased to 1.004R₀. In Fig. 6a and b, an elongated void was clearly observed to form at the Cu/SiCN interface near the via bottom. Under detailed observations of this seamlike void at high magnifications, as shown in Fig. 6c and d, a thin region with discontinuous Cu lattices on the Cu wire surface was found at the Cu/Cu₂O interface, especially near the via bottom. This thin region indicated the migration of Cu atoms and the gathering of vacancies, i.e., the formation of void, along the weak Cu/Cu₂O interface. Though both the SiCN and Cu₂O layers looked amorphous without an obvious difference and a clear interface, the Cu₂O layer with a thickness of about 5 nm still existed at the Cu/SiCN interface according to the aforementioned TEM image (Fig. 5a) and previous XPS analyses. It was then realized that at the very early stage of EM tests, due to the existence of oxide at the Cu/SiCN interface without the plasma treatment as aforementioned, Cu atoms on the wire surface just adjacent to the weak Cu/SiCN interface (more exactly the Cu/Cu₂O interface) most probably migrated first along the interface as a rapid diffusion path and voids consequently nucleated and grew at the interface. In comparison, Fig. 7 shows the HRTEM images around the M1 Cu/SiCN interface of the EM-tested Cu interconnect structure with the NH₃/He plasma treatment as the electrical resistance of the tested structure also increased to 1.004R₀. Alternatively, either an obvious void at the via bottom or a thin region inside the Cu wire, rather than right at the Cu/SiCN interface, was observed because a formed CuSiN interlayer was expected to strengthen the interface and to reduce the rapid diffusion path after the plasma treatment.

The inhibition of a void nucleation at the Cu/SiCN interface by the strongly bonded CuSiN interlayer was further confirmed under a more detailed lattice examination, as the HRTEM images of the M1 Cu/SiCN interface with a NH₃/He plasma treatment shown in Fig. 8. As the electrical resistance of the EM-tested interconnect structure increased to 1.3R₀, a large pore was observed in the M1 Cu wire near the Cu/SiCN interface, as seen in Fig. 8a. However, this pore was found to form inside the Cu wire, and a Cu residue layer remained adjacent to the interface, indicating that at the early stage voids nucleated inside the Cu wire rather than at the Cu/SiCN interface. Between the residual Cu and SiCN capping layer, some lattice structures (as circled in Fig. 8b) with a spacing of about 0.195 nm were identified, which was just between the spacing of the Cu₂N(200) lattice plane, 0.191 nm, and the Cu₃Si(312) plane, 0.199 nm.
Figure 8. HRTEM images around the M1 Cu/SiCN interface of EM-tested Cu interconnect structure with a NH3/He plasma treatment as the electrical resistance of the tested structure increased to 1.3 R0 (a) around the M1 Cu/SiCN interface and (b) at the Cu/CuSiN interface at a high magnification. The circled region in (b) shows the lattice structure of CuSiN.

Conclusion

In this study, EM reliability tests of dual-damascene Cu interconnect structures with or without the application of NH3/He mixed plasma treatment were performed at 400°C under a current density of 8 MA/cm². The interface structure between Cu wires and SiCN capping layers and the EM-induced void formation were examined to investigate the effect of plasma treatment on the early-stage EM behavior and electrical reliability of the Cu interconnects. During the EM tests, voids formed around the Cu/SiCN interfaces near the via bottom, resulting in the increase in the electrical resistance of the wires. For the interconnects with the plasma treatment, small shape factors of cumulative failure probability distribution and large MTF indicated an improved EM resistance. After the plasma treatment, the oxide layer on the Cu wire surface was removed, and a CuSiN interlayer with a lattice spacing of 0.195 nm formed at the Cu/SiCN interface, enhancing the interface adhesion and reducing the diffusion paths of Cu atoms. Therefore, at the early stage of EM tests, voids nucleated inside the Cu wire, rather than at the interface. The change in the interface structure by the plasma treatment varied the early-stage EM-induced voiding behavior, enhanced the EM resistance, and then effectively improved the electrical reliability of the Cu interconnect structures.

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