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A Cu Electroplating Solution for Porous Low-*k*/Cu Damascene Interconnects

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A Cu electroplating solution applicable to porous silica ultralow-*k* films ($k = 2.1$) without pore sealing was investigated. A suppressor which causes permeation of Cu electroplating solution was replaced by polyethylene glycol (PEG) with specific molecular weight (Mw). Transmission electron microscopy observation revealed that permeation by the Cu solution into the porous silica layer can be suppressed by decreasing the molecular weight of the PEG suppressor in the electroplating solution. A Cu electroplating solution using PEG with Mw = 600 was examined for the low-*k* porous silica/Cu single-damascene integration process of 300 mm wafer. The filling characteristics in trenches and the uniformity of Cu film thickness were investigated. Interline leakage current on low-*k*/Cu damascene interconnects was successfully reduced by six orders of magnitude using this Cu plating solution compared with the conventional solution.
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Scaling of interconnects in ultralarge-scale integrated (ULSI) circuits requires interlayer materials with a low dielectric constant *k* for reducing resistance-capacitance (RC) signal delay. For achieving ultralow-*k* (ULK) of less than 2.3, introduction of pores into the dielectric film with increasing porosity is necessary. One failure mode of porous low-*k* films is voiding, which often occurs after processing. This could be attributed to reactions of permeated Cu electroplating solution with fluoride residues remaining after plasma etching.[1] Several attempts have been made to avoid this failure. A pore-sealing layer on the porous low-*k* and a defect-free barrier metal layer formed by chemical vapor deposition (CVD) were attempted to prevent such low-*k* film voiding. However, the CVD barrier material penetrated into the porous low-*k* films, resulting in the rise in *k* value of the porous low-*k* films.[2] As the thickness of the barrier metal becomes thinner and thinner on the sidewalls of trenches and vias, pinholes may not be avoided. Therefore, a new Cu solution must be developed which does not permeate into the low-*k* porous silica films through pinholes in the barrier metals.

We have investigated the effect of Cu electroplating solutions on the properties of porous silica films.[3] There was no change in leakage current of the porous silica film with hydrophobic treatment after dipping it in deionized water. However, the leakage current of the film increased significantly after dipping it in a Cu electroplating solution. In general, a Cu electroplating solution is composed of cupric sulfate solution and three component additives (suppressor, accelerator, and leveler). Thus, to identify which one of the components is responsible for the increase of leakage current, the influence of these additives was examined separately. We found that only the suppressor affects the permeation of the Cu plating solution into the porous silica films, resulting in increased leakage current.[3] In contrast, the cupric sulfate solution, containing additives other than the suppressor, does not increase the leakage current of porous silica films. Permeation characteristics of the electroplating solution were examined using polyethylene glycol (PEG) as a suppressor. It was found that the permeation of the solution into the porous silica film depends on the molecular weight (Mw) of PEG.

In this paper, the influence of Cu electroplating solutions having PEG with various molecular weights as a suppressor on the characteristics of porous silica low-*k*/Cu damascene interconnect was investigated. Performance of the Cu electroplating solution in terms of superfilling and thickness uniformity on a 300 mm wafer were examined. Interline leakage current in porous silica/Cu damascene structures was also investigated.

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Experimental

Fabrication of trench structure in porous silica dielectric film.— A single-damascene process flow is shown in Fig. 1. First, 25 nm thick SiCN was deposited by plasma chemical vapor deposition (PCVD) on a 300 mm Si(100) wafer covered with high-density plasma (HDP) SiO_2. A porous silica low-*k* film with a thickness of 140 nm was formed on the wafer by spin-coating of the precursor solution, which is derived from tetraethoxysilane (TEOS) and ethanol with water, having nonionic surfactant of triblock copolymer $(EO)_x(PO)_y(EO)_x$.[4-6] The film was calcined to burn off the surfactant and to stabilize the chemical structure of the matrix. The film was treated with 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS) for enhancing hydrophobicity. The dielectric constant of the film was 2.1. The average pore size of the film was approximately 3 nm, as measured by small-angle X-ray scattering.[5] The porosity of the film used in the present experiment was $43 \pm 5\%$.[7] A 20 nm thick SiOC or 50 nm thick SiO_2 cap was deposited by PCVD on the porous-silica low-*k* film. Next, the trench pattern was transferred using a resist mask with ArF lithography and C_5F_8/O_2-based plasma etching. After removing the resist by O_2 ashing and subsequent wet cleaning, the trench pattern was transferred to the dielectric stack.

- 300mm Si substrate
- HDP-SiO2 deposition : 1000 nm
- Etch stop layer (SiCN) deposition : 25 nm
- Porous silica layer by spin coating : 140 nm
- Low-k cap layer (SiO2 ; 50nm or SiOC; 20nm) deposition
- Trench lithography
- Trench etching
- Ashing & Wet cleaning (Resist mask removal)
- Barrier layer & Cu seed layer by PVD : 10 nm & 20 nm
- Cu electroplating & post annealing
- Chemical mechanical polishing

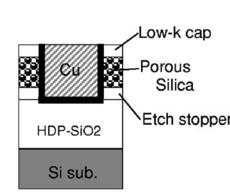

Figure 1. Single-damascene process flow using a resist mask for trench patterning.

Finally, a 10 nm thick Ta/TaN barrier layer and 20 nm thick Cu seed layer were deposited by physical vapor deposition (PVD) without pore sealing.

Cu electroplating.— A commercial Cu electroplating solution (Ebatronfill II: Ebara-Udylite Co., Ltd) based on standard cupric-sulfate aqueous solution was used together with three additives (suppressor, accelerator, and leveler). The mixing ratios of suppressor (Ebatronfill II-A), accelerator (Ebatronfill II-B), and leveler (Ebatronfill II-C) for standard cupric-sulfate aqueous solution (Ebatronfill II-KH) were 2×10^{-2}, 7×10^{-3}, and 5×10^{-3} in volume concentration, respectively, as the condition of a conventional electroplating solution. The commercial suppressor was replaced by PEG for detailed consideration in this experiment. The molecular weights of PEG were changed from 62 to 20,000. The standard concentration of each PEG was 0.3 g/L, which was the same mass concentration, in order to standardize comparatively the number of ethylene oxide (-CH_2–CH_2–O-) per unit volume of the solution, because ethylene oxide of PEG was considered to affect the adsorption of PEG onto a hydrophobic surface[8,9] and the adsorption of water molecule on PEG.[10] For accomplishing uniformity of the film thickness and integrating a Cu/low-*k* damascene structure, Cu electroplating was performed with equipment in which a porous resistive plate is inserted between anode and cathode for a 300 mm wafer.[11]

Evaluation method.— Permeation of Cu electroplating solution was evaluated by observing cross sections of the low-*k*/Cu damascene structures with transmission electron microscope (TEM) with energy-dispersive X-ray analysis (EDX). The lateral resolution of EDX was about 10 nm. To investigate the influence of additives in the electroplating solution on the permeation of the solution into the porous silica film, the contact angle of the solution to the surface of porous silica blanket film and the leakage current of the film dipped in the solution were measured by a pendant drop shape analysis and a mercury probe, respectively. Uniformity of the Cu film thickness on a 300 mm wafer was determined by sheet resistances. Leakage current was measured in N_2 atmosphere after degassing moisture for 30 min at 150°C of a single-damascene structure with the porous silica low-*k* film after chemical mechanical polishing (CMP).

Results and Discussion

Permeation of Cu electroplating in a single-damascene structure.— Figure 2 shows cross-sectional TEM images of a damascene trench with porous silica before and after the Cu electroplating process. The thickness of Ta/TaN barrier metal layer on the sidewall of trenches was 5 nm as shown in Fig. 2c. There is no voiding or defects in the porous silica layer before Cu electroplating (Fig. 2a), while after Cu electroplating with a conventional plating solution, Cu penetration was observed in the porous silica layer (Fig. 2b). The gray region in the porous silica layer was analyzed by TEM-EDX for elemental composition. The EDX energy spectra for the porous silica layer before and after electroplating are compared in Fig. 3. Only Si, O, and C were detected before electroplating (Fig. 3a). In contrast, new peaks corresponding to Cu were detected at the gray region of the porous silica layer after plating (Fig. 3b). There is no influence of electron scattering from Cu filled in trenches of the damascene structure on analysis of the middle of the layer, because the lateral resolution of TEM-EDX was about 10 nm and no Cu peak was detected for a similar structure with a dense SiOC film as interlayer dielectric.

Effect of molecular weight of PEG as suppressor.— We have reported the influence of Cu electroplating solution on the characteristics of porous silica blanket film.[3] An increase of leakage current in the porous silica film due to permeation by the Cu plating solution was found when the porous silica film was dipped in the solution. As shown in Fig. 4a, the leakage current increased by two orders of magnitude after dipping into the Cu electroplating solution

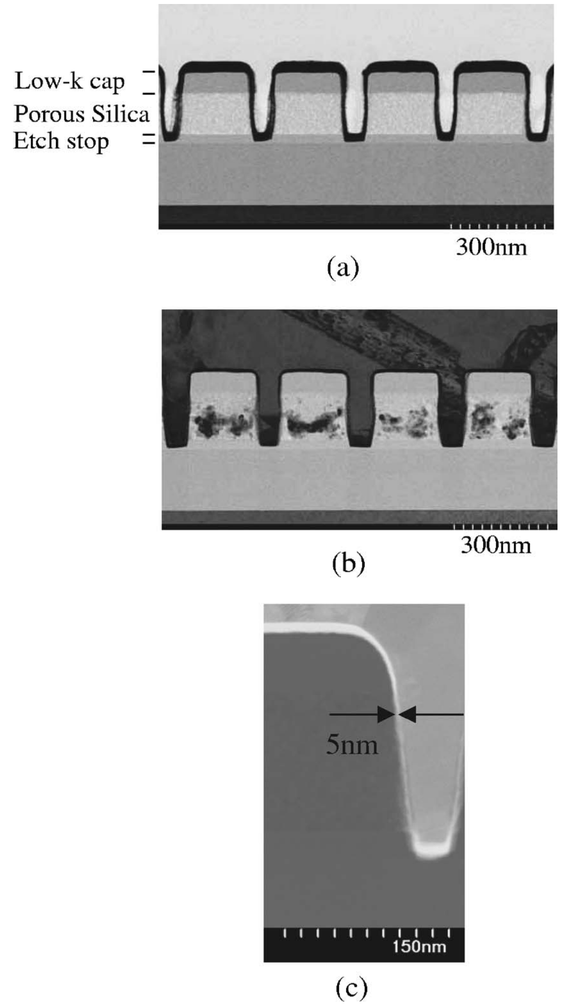

Figure 2. Cross-sectional TEM images of trenches with porous silica as interlayer dielectric: (a) before electroplating and (b) after electroplating. Note that a conventional Cu electroplating solution was used. (c) Z-contrast image of the sidewall in damascene interconnects. The Ta/TaN barrier layer appears bright.

with the suppressor, compared with electroplating solution without the suppressor. This Cu electroplating solution contained additives (accelerator and leveler) other than suppressor in conventional condition. The leakage-current characteristics of porous silica films dipped into the electroplating solution without the suppressor or deionized water (DIW) were the same as those of the control. The contact angle of these solutions on porous silica was measured. Time change of the contact angle is shown in Fig. 4b. For the Cu

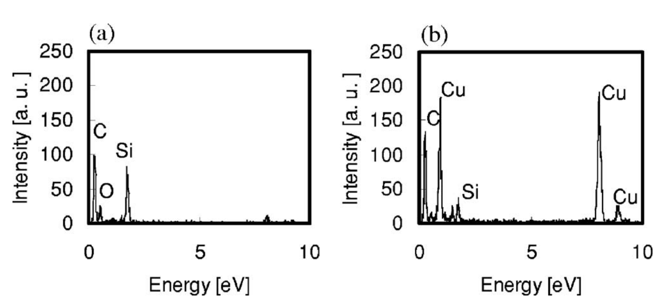

Figure 3. EDX spectra of porous silica layer (a) before electroplating, and (b) after electroplating.

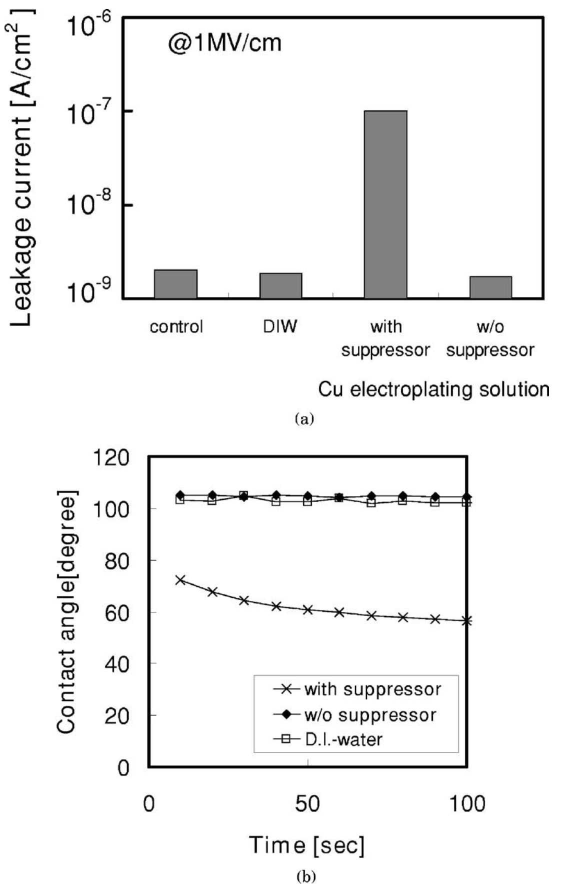

Figure 4. (a) Leakage current of porous silica film after dipping into the Cu electroplating solution with or without suppressor. (b) Contact angle of the Cu electroplating solution with or without suppressor. The results of DIW are included for comparison.

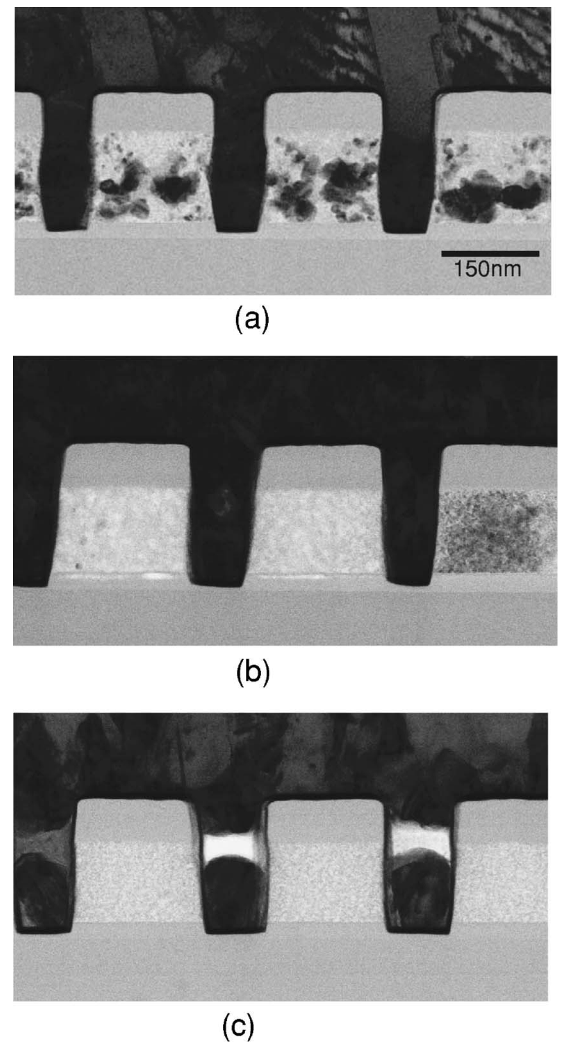

Figure 6. Cross sections of trenches with porous silica as interlayer dielectric after Cu electroplating using PEG with various Mws: (a) 3400, (b) 1000, and (c) 600.

electroplating solution with suppressor, the contact angles were smaller than 90°, and decreased with time. In contrast, the contact angles of the solution without suppressor were greater than 100° which was equivalent to DIW, and did not change with time. These results of leakage current and contact angle indicate that the suppressor in the Cu electroplating solution caused permeation into the porous silica film. Next, the permeation characteristics of the electroplating solution were examined using PEG as a suppressor. It was found that the permeation of the solution into the porous silica film depends on the molecular weight of PEG. Figure 5 shows the relationship between the leakage current of porous silica films and Mw

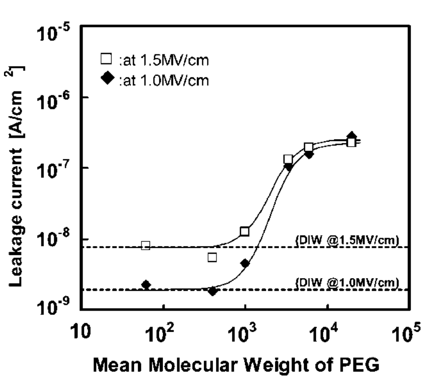

Figure 5. Leakage current as a function of mean molecular weight of PEG in Cu plating solutions.

of PEG used as a suppressor in the electroplating solution. The leakage current increased from 10^{-9} to 10^{-7} A/cm^2 when the mean Mw of PEG was larger than 1000. In other words, the leakage current was suppressed when the Mw of PEG was less than 1000. From the experimental result using the porous silica blanket films, three kinds of PEG with different molecular weights, 600, 1000, and 3400, were selected as suppressors of the electroplating solution because of the expected difference of the permeation characteristics into the porous silica. After Cu plating was carried out in trench structure in porous silica using electroplating solutions with different Mws of PEG, the cross-sectional TEM of the trenches were observed, as shown in Fig. 6. In the case of Mw = 3400 (Fig. 6a), Cu penetration occurred, resulting from the permeation of the electroplating solution into the porous silica layer. The appearance of Cu in the porous silica film was similar to that in the case of a conventional plating solution. In the case of Mw = 1000 (Fig. 6b), the permeation of the solution was improved in comparison with the case of Mw = 3400. The Cu penetration could not be suppressed completely. In contrast, for Mw = 600 (Fig. 6c), the permeation was suppressed completely. These results support our study on blanket films of porous silica. However, there is a remaining issue; the plating solution with PEG of Mw = 600 is inadequate for Cu filling because some voids were observed in the Cu interconnects in the trenches (Fig. 6c).

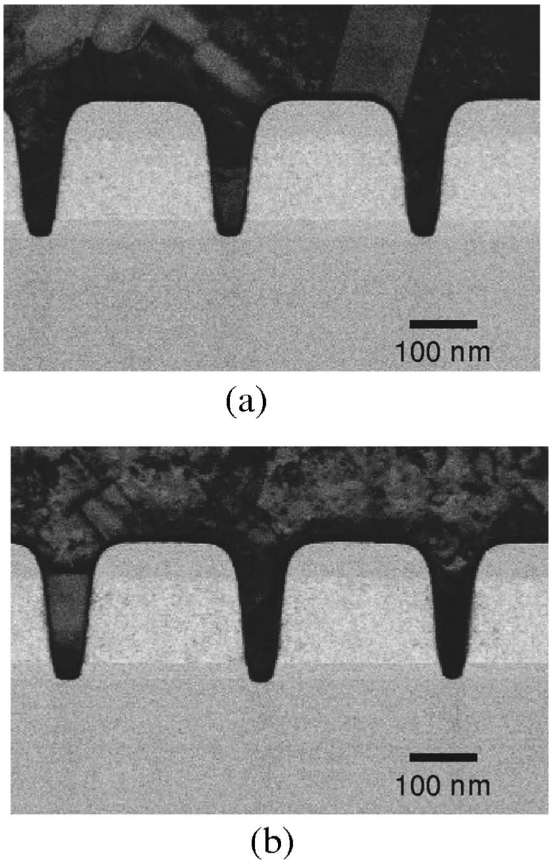

Figure 7. Cross sections of trenches with porous silica as interlayer dielectric after Cu electroplating using PEG (Mw = 600) in 0.6 g/L.

Improvement of Cu-filling performance and uniformity of film thickness.— A suppressor plays an important role in the electroplating process. The suppressor affects the Cu filling of trenches and the field-thickness uniformity of Cu film on the wafer. Because the ability of suppressing Cu deposition on the planar field substrate is weakened with decreasing molecular weight of PEG,[12] the failure of Cu filling occurred in deep trenches due to overhanging when the electroplating solution contained PEG with Mw = 600 as a suppressor. One of the methods to suppress the deposition of Cu is to increase the concentration of PEG.[12] Cu electroplating was carried out using a solution containing PEG whose concentration was two times (0.6 g/L) and eight times (2.4 g/L) higher than the standard condition (0.3 g/L). Figure 7 shows cross-sectional TEM images of Cu damascene trenches [linewidth = 60 nm, analytical reagent (AR) = 3.4] in porous silica after Cu electroplating using an electroplating solution containing higher concentrations of PEG. No penetration of Cu in the porous silica layer or failure of Cu filling inside the trenches were observed in either condition.

At the same time, the in-plane uniformity of Cu thickness on the 300 mm wafer was measured. No noticeable terminal effect was observed in both cases in spite of the ultrathin seed layer of 20 nm. When the conventional electroplating solution was used with a commercial suppressor, the uniformity across 300 mm wafers was 1.53%. In contrast, the uniformities were 2.33% for electroplating solution with 0.6 g/L PEG and 1.93% for electroplating solution with 2.4 g/L PEG, respectively. Little difference of thickness uniformity across 300 mm wafers was found among these three conditions. The thickness distribution of Cu plating film from the electroplating solution with 0.6 g/L PEG is shown in Fig. 8.

By controlling the concentration of PEG with Mw = 600 in the Cu electroplating solution, we have achieved efficient filling for aggressive geometries of a trench width of 60 nm (AR = 3.4) while maintaining a good uniformity across 300 mm wafers using PVD Cu seed layers with a thickness of 20 nm.

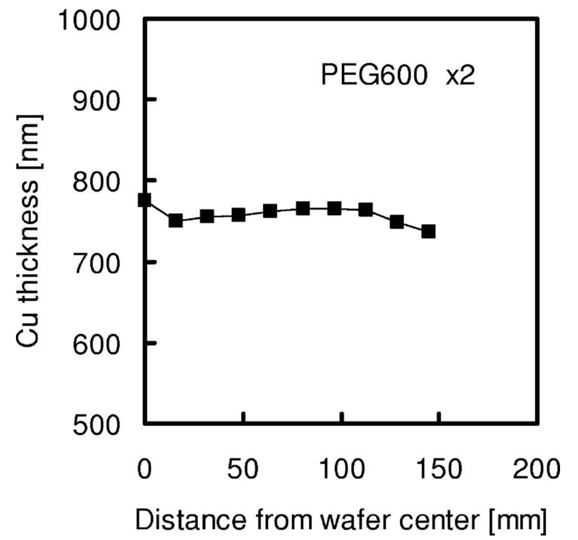

Figure 8. Distribution of Cu thickness across 300 mm wafer using PEG (Mw = 600) in 0.6 g/L.

Evaluation of line-to-line leakage current.— Cu electroplating, using the plating solution containing 0.6 g/L PEG (Mw = 600), was performed on 300 mm wafers. After Cu electroplating, a single-damascene structure was fabricated by CMP. The line-to-line leakage current without passivation was measured under nitrogen ambient after 150°C annealing for degassing of moisture. Figure 9 shows the leakage current of the comb pattern with lines and spaces of 160 and 300 nm, respectively. In the case of the conventional Cu plating solution with the commercial suppressor, the leakage current increased up to 10^{-3} A/cm^2. In contrast, in the case of the new electroplating solution with 0.6 g/L PEG (Mw = 600) as a suppressor, the leakage current was suppressed to the order of 10^{-9} A/cm^2. Therefore, the new Cu electroplating solution improved the leakage current by six orders of magnitude.

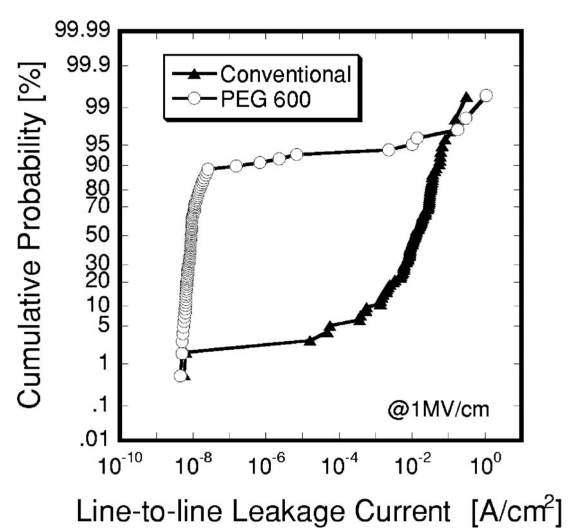

Figure 9. Leakage current of a single-damascene interconnect fabricated using the resist mask scheme. Open circle and filled triangle designate the case of the electroplating solution using 0.6 g/L PEG (Mw = 600) as suppressor and the case using conventional suppressor, respectively.

Conclusion

The influence of Cu plating solution containing PEG as a suppressor on porous silica low-*k*/Cu damascene interconnects without pore sealing was investigated. Cross-sectional TEM images of damascene interconnects revealed that Cu penetration occurs in the porous-silica-interlayer dielectric film when the thicknesses of PVD barrier metal layer at the sidewall of the trench is less than 5 nm. As a result of permeation of the Cu electroplating solution, the line-to-line leakage current increases. The permeation of the Cu electroplating solution into the porous silica layer can be mitigated by decreasing the molecular weight of PEG to less than 1000. Consequently, the characteristic of line-to-line leakage current was improved by using a new suppressor with a molecular weight of 600. The Cu filling inside trenches and the uniformity of film thickness across a 300 mm wafer were acceptable. These results suggest that this Cu electroplating solution can be applicable to future 45 nm technology node interconnects.

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