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Additives for Bottom-up Copper Plating from an Alkaline Complexed Electrolyte

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An alkaline, tartrate-complexed copper electrolyte containing additives that provide bottom-up fill is described. Bottom-up fill is achieved using a mixture of two additives: bis-(3-sulfopropyl) disulfide (SPS) and polyethyleneimine (PEI). Chronopotentiometric studies indicate that, unlike in conventional acidic electrolytes, SPS acts as a 'suppressor' and PEI acts as an 'anti-suppressor' in the alkaline medium. Partial-fill experiments on patterned structures confirm a SPS-PEI interaction leading to bottom-up fill from the tartrate-complexed copper electrolyte.
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Copper (Cu) electrodeposition in the presence of appropriate additives enables void-free bottom-up plating of sub-micron vias and trenches in dual-damascene metallization.[1] This process is now widely practiced for fabricating interconnects in advanced microprocessors at sub-50 nm technology nodes.[2] However, as interconnect dimensions become smaller, scaling the aforementioned interconnect metallization process to narrower geometries becomes increasingly difficult. This is primarily due to the preceding non-conformal PVD-Cu seed layer process, which develops 'overhang' at the feature opening leading to pinch-off.[3] To circumvent this, an alternative metallization process based on direct Cu electrodeposition onto conformal diffusion-barriers, such as ruthenium or cobalt, has been proposed.[4] The shift in diffusion-barrier technology requires novel electrodeposition chemistries to enable adequate Cu nucleation and uniform deposition on 300 mm resistive wafers. In this context, alkaline complexed-Cu electrolytes have been developed to achieve high Cu nucleation density and uniform plating.[5–8] In addition to their application in direct Cu plating, these electrolytes are advantageous even in conventional interconnect metallization due to the lower susceptibility for seed layer dissolution in an alkaline medium.[9]

Proposed integration schemes for direct Cu plating rely on two process steps: (i) a Cu nucleation step, utilizing an alkaline complexed-Cu electrolyte; and (ii) a bottom-up fill step, utilizing a conventional acid-Cu electrolyte with additives. However, for ease of process integration, a single-step Cu plating process providing bottom-up fill from an alkaline complexed-Cu electrolyte is highly desired. We have described earlier an alkaline tartrate-complexed Cu plating process which provides high nucleation density on ruthenium.[5] We have shown that the tartrate serves to complex the cupric ions in solution, increase the electrode polarization, enhance the plating nucleation density, as well as improve bath stability. In the present work, we identify additives that function as 'suppressors' and 'anti-suppressors' in this alkaline tartrate-complexed electrolyte. In analogy to additives in an acid-Cu electrolyte,[10] these additives interact with the copper plating process providing the sought after bottom-up fill in sub-micron features from the alkaline complexed electrolyte.

Experimental

Electrochemical characterization experiments were performed on a Cu rotating disk electrode, which provides well-defined transport. Platinized titanium mesh served as the counter electrode. The alkaline electrolyte contained 0.1 M $CuSO_4.5H_2O$ (Fisher, Certified ACS) and 0.5 M sodium potassium tartrate (Acros organics). The pH of the alkaline electrolyte was adjusted to about 12 by adding NaOH (Fisher, Certified ACS). A Cu wire electrode, immersed in acidified 0.5 M $CuSO_4$ (pH = 0.8) solution and connected to the alkaline electrolyte through an electrolyte bridge, served as the reference electrode. Electrochemical measurements were made using a VSP Bio-logic potentiostat.

Three additives were studied: bis-(3-sulfopropyl) disulfide (SPS, Raschig), polyethyleneimine (PEI, M.W. = 600, Alfa Aesar) and polyethylene glycol (PEG, M.W. = 10,000, Sigma Aldrich). Transient additives effects were examined by injecting the additives into the alkaline electrolyte under galvanostatic conditions (20 mA/cm^2) and recording the chronopotentiometric response, following the procedure described by Akolkar and Landau.[10] Partial and full-fill studies were performed on patterned test coupons mounted on the rotating disk assembly. These test coupons had relatively large trench structures, ranging from 500 nm to 1 μm in width. All test coupons were precoated with a thin PVD barrier and a Cu-seed layer. Feature fill studies were performed from the alkaline electrolyte in the presence of 15 ppm SPS and 40 ppm PEI at an average current density of 25 mA/cm^2 (calculated based on the projected wafer area). Bottom-up fill profiles were determined from SEM images of cross-sections of the plated samples, taken by a Hitachi S4500 scanning electron microscope.

Results and Discussion

In this section, we first outline the effects due to the additives' adsorption on a flat electrode. Later, we demonstrate the effect of the additives' interactions in enabling bottom-up plating of patterned geometries.

Additives effects.— In conventional acid-Cu electrolytes, bottom-up plating of small features is achieved through the combined effects of PEG or a similar polyether which acts as a copper plating suppressor, and SPS which serves as an anti-suppressor. However, the PEG and the SPS do not function in their 'conventional capacity' as suppressor and anti-suppressor, respectively, in the alkaline complexed-Cu electrolyte. Injection of PEG into the alkaline complexed-Cu electrolyte produces only very moderate polarization (∼60 mV) even at a very high PEG concentration (1100 ppm), as shown in Figure 1a. The weak polarization was observed in the presence [Figure 1a] as well as in the absence (not shown) of chloride ions (Cl^-), which are required to enable strong polarization by PEG in an acidic copper electrolyte.[11] The lack of polarization due to the PEG in the alkaline medium is likely due to the absence of adsorbed Cl^- on the copper surface at pH∼12. At such a high pH, OH^- adsorption is likely to dominate Cl^- adsorption, similarly to observations by Lipkowski et al. on Au electrode.[12] Injection of 15 ppm SPS, on the other hand, into the alkaline electrolyte rapidly (within 10 s) produces strong suppression of about 400 mV, as shown in Figure 1b. This indicates that SPS is an effective suppressor in the alkaline copper tartrate electrolyte. The chronopotentiometric response shown in Figure 1b is observed

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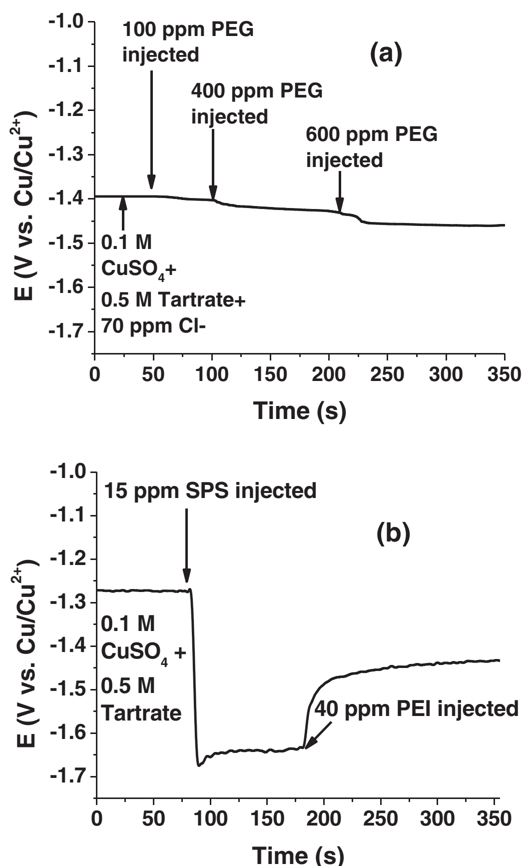

Figure 1. Potential response to the injection of additives into an alkaline, tartrate-complexed copper electrolyte from which copper is plated galvanostatically onto a rotating disk: (a) Weak suppression of Cu electrodeposition by PEG. (b) Strong suppression observed upon injection of 15 ppm SPS. The suppression effect due to SPS is partially nullified by injecting 40 ppm PEI. The SPS suppression effect is fast ($t \sim 10$ s), while the SPS deactivation by PEI is relatively slow ($t \sim 40$ s). Plating conditions: $i = 20$ mA/cm^2, pH = 12.5, [Cu] = 0.1 M, [Tartrate] = 0.5 M, rotation speed = 200 rpm.

in the absence of chloride ions, indicating that chloride ions are not required for SPS functionality as a suppressor in the alkaline medium. It is known that, in the absence of Cl^- ions, SPS provides mild inhibition in an acidic medium.[13,14] In the alkaline medium, however, SPS provides strong inhibition [Figure 1b]. This might be due to the interaction of adsorbed SPS moieties with adsorbed OH^- in the alkaline system, which could lead to a surface passive film with stronger suppression characteristics for Cu electrodeposition.[15,16]

In conventional acid-Cu electrolytes, PEI strongly polarizes the Cu surface and is labeled a ‘leveler’, a term designating strong copper plating suppressors that typically contain nitrogen and which are not displaced from the copper surface (or deactivated) by SPS. However, in the alkaline copper tartrate electrolyte, PEI acts as an anti-suppressor by gradually depolarizing the suppression provided by the SPS. As seen in Figure 1b, injection of 40 ppm PEI into SPS-containing alkaline electrolyte nullifies almost half the polarization provided by the SPS. This depolarization occurs over a time period of about 40 s, similar to the time-scale observed in conventional acid-Cu electrolytes for the interaction between PEG and SPS (displacement of adsorbed PEG by SPS).[10] While the mechanistic aspects of the SPS-PEI interaction in an alkaline complexed-Cu electrolyte are not fully understood, it is believed that the PEI gradually deactivates the SPS from the Cu surface, leading to depolarization. In an acidic medium, it is known that the PEI interacts with the surface adsorbed SPS moieties, and forms a surface passivating film with markedly different polarization characteristics.[15] An analogous effect might be envisioned in our

Table I. Additives’ effects in an alkaline, tartrate-complexed Cu electrolyte and in a conventional acid-Cu electrolyte.

Electrolyte Type	Suppressor	Anti-suppressor	Leveler (Strong Suppressor)
Acid-Cu	PEG	SPS	PEI
Alkaline tartrate-complexed Cu	SPS	PEI	–

alkaline system; however, unlike the Cu(I)-MPS-PEI precipitation reported by Hai et al.[15] in the acidic medium, we have not observed precipitate formation in our alkaline system in the range of SPS and PEI concentrations (<50 ppm) studied for as long as 30 minutes of plating.

In the injection study described above, the SPS and the PEI concentrations were set at 15 ppm and 40 ppm, respectively. However, it should be noted that the SPS deactivation by the PEI was observed in a much wider concentration range (not shown). Table I highlights the key differences between the additives effects observed in an alkaline complexed-Cu electrolyte and a conventional acid-Cu electrolyte.

Patterned wafer studies.— To characterize the role of the antagonistic SPS-PEI interactions in generating the bottom-up fill, plating tests were conducted on patterned wafer coupons from electrolytes containing a single additive, i.e., SPS or PEI, and from electrolytes containing a mixture of SPS and PEI. As seen in Figure 2a and Figure 2b, electrolytes containing a single additive (SPS or PEI) do not yield bottom-up fill, but provide instead conformal plating, leading eventually to void trapping. Bottom-up fill was achieved only from an electrolyte containing both SPS and PEI [Figure 2c], indicating that SPS-PEI interactions are essential for generating bottom-up fill.

Progressive-fill studies were conducted in electrolytes containing a mixture of 15 ppm SPS and 40 ppm PEI. Figure 3 shows the partial-fill results for increasingly longer plating times: 20 s, 30 s, 45 s and 75 s. At short times (20 s), a localized acceleration at the trench bottom corners is observed. This localized corner acceleration is analogous to that reported in published literature on the Curvature Enhanced Accelerator Coverage (CEAC) effect,[17,18] and is believed to be due to accumulation of the accelerator species (here, PEI) at locations where the surface area contracts during growth. At moderate time-scales (30–45 s), a flat bottom develops, which progressively advances upwards. This flat bottom is again a known characteristic of the bottom-up fill in acidic media. At an average current density of 25 mA/cm^2 used in this experiment, complete trench fill was achieved in 75 s.

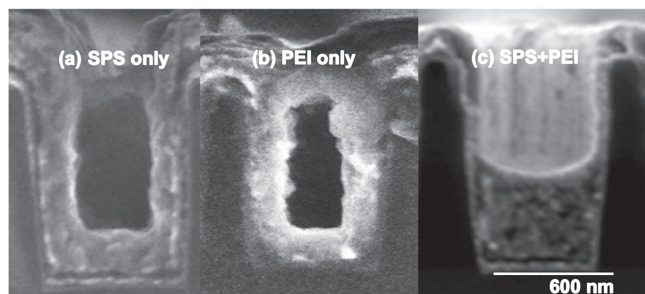

Figure 2. Partial-fill profiles after Cu electrodeposition within 600 nm wide trenches from an alkaline, tartrate-complexed Cu electrolyte at 25 mA/cm^2 for 45 s. The electrolyte contained (a) 15 ppm SPS; (b) 40 ppm PEI; and (c) 15 ppm SPS and 40 ppm PEI. Conformal fill is observed in electrolytes containing a single additive, leading to void formation. Bottom-up fill is observed in electrolyte containing both SPS and PEI, indicating the role of antagonistic interactions between these additives. Plating conditions: $i = 25$ mA/cm^2, pH = 12.5, [Cu] = 0.1 M, [Tartrate] = 0.5 M, rotation speed = 200 rpm.

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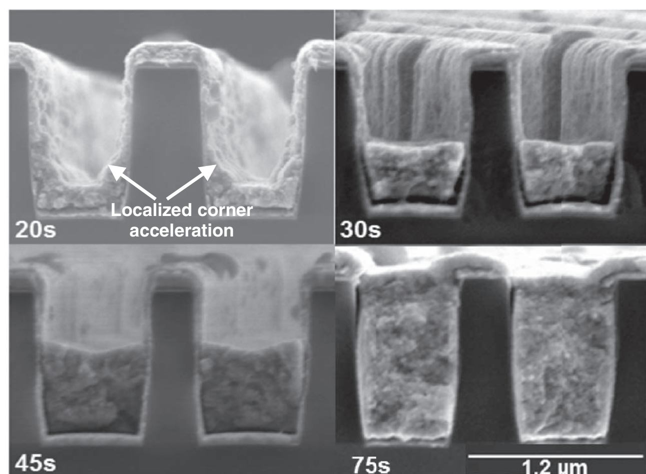

Figure 3. Partial-fill profiles for Cu electrodeposition from an alkaline, tartrate-complexed Cu electrolyte containing 15 ppm SPS and 40 ppm PEI. The plating current density (on the flat region of the wafer segment) is 25 mA/cm^2 and the plating times are 20 s, 30 s, 45 s and 75 s. Note the accelerated growth at the trench bottom corners at short times (20 s), progression of flat bottom-up fill at 30–45 s, and complete fill after 75 s of plating. Plating conditions are the same as in Figure 2.

During the plating process, trench sidewalls and the wafer coupon ‘field’ regions remained completely suppressed.

In conventional acidic electrolytes, a transient diffusion-adsorption mechanism is known to play a critical role in the bottom-up fill.[10,19] This diffusion-adsorption mechanism is aided by the slow diffusion of the suppressor (PEG) in comparison to the rapid diffusion of the anti-suppressor (SPS). However, in the alkaline medium discussed herein, the suppressor (SPS) diffusion is as fast, if not faster than the anti-suppressor (PEI). While this may be deleterious to the bottom-up fill particularly in narrow sub-100 nm features, we do not observe its ill effects in the feature-fill studies reported above owing to the large feature widths of 500 nm. In future studies involving more aggressive structures, we believe that optimizing the suppressor diffusion and adsorption rates in our alkaline system will be important. This may be accomplished either by lowering the suppressor concentration, or by designing higher molecular weight ‘SPS-like’ suppressors with lower diffusion coefficients.

Conclusions

An alkaline, tartrate-complexed Cu electrolyte containing SPS and PEI as additives, which provides bottom-up fill in submicron features is described. In contrast to their role in acidic electrolytes, in alkaline medium, SPS acts as a suppressor and PEI acts as an anti-suppressor. The interactive behavior of these additives is characterized using injection studies. While the SPS suppresses the electrode surface rapidly, the PEI deactivates the SPS slowly – antagonistic effects quite similar to the PEG-SPS interactions which are known to provide bottom-up fill in conventional acid-Cu electrolytes. Bottom-up fill is uniquely observed in the presence of both SPS and PEI, further indicating the critical role of the SPS-PEI interactions in the fill process in alkaline complexed electrolytes.

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References

1. P. C. Andricacos, C. Uzoh, J. O. Dukovic, J. Horkans, and H. Deligianni, *IBM J. of Res. and Dev.*, **42**, 567 (1998).
2. International Technology Roadmap for Semiconductors, 2011 edition: http://www.itrs.net/Links/2011ITRS/2011Chapters/2011ExecSum.pdf.
3. V. M. Dubin, R. Akolkar, C. C. Cheng, R. Chebiam, A. Fajardo, and F. Gstrein, *Electrochim. Acta*, **52**, 2891 (2007).
4. O. Chyan, T. N. Arunagiri, and T. Ponnuswamy, *J. Electrochem. Soc.*, **150**, C347 (2003).
5. A. Joi and U. Landau, “An Alkaline Copper Plating Process Providing High Nucleation Density on Ru and Bottom-up Fill”, Abstract #1944, 220th ECS Meeting, 9–14 October 2011, Boston, MA.
6. R. Akolkar, T. Indukuri, J. Clarke, T. Ponnuswamy, J. Reid, A. J. McKerrow, and S. Varadarajan, “Direct seed electroplating of copper on ruthenium liners”, *Interconnect Technology Conference and 2011 Materials for Advanced Metallization (IITC/MAM)*, 2011 IEEE International, pp. 1–3, 8–12 May 2011.
7. S. Armini, Z. El-Mekki, K. Vandersmissen, H. Philipsen, S. Rodet, M. Honore, A. Radisic, Y. Civale, E. Beyne, and L. Leunissen, *J. Electrochem. Soc.*, **158**, H160 (2011).
8. S. Armini, *J. Electrochem. Soc.*, **158**, D390 (2011).
9. L. Boehme, J. Wu, X. Kang, R. Preisser, and U. Landau, “The Impact of Electrolyte Acidity on Bottom-up Metallization of Copper Interconnects”, Abstract #2734, 222nd ECS Meeting, 7–12 October 2012, Honolulu, HI.
10. R. Akolkar and U. Landau, *J. Electrochem. Soc.*, **151**, C702 (2004).
11. J. J. Kelly and A. C. West, *J. Electrochem. Soc.*, **145**, 3477 (1998).
12. A. Chen and J. Lipkowski, *J. Phys. Chem. B*, **103**, 682 (1999).
13. W. P. Dow, H. S. Huang, M. Y. Yen, and H. H. Chen, *J. Electrochem. Soc.*, **152**, C77 (2005).
14. P. Broekmann, A. Fluegel, C. Emnet, M. Arnold, C. Roger-Goepfert, A. Wagner, N. T. M. Hai, and D. Mayer, *Electrochim. Acta*, **56**, 4724 (2011).
15. N. T. M. Hai, T. T. M. Huynh, A. Fluegel, M. Arnold, D. Mayer, W. Reckien, T. Bredow, and P. Broekmann, *Electrochim. Acta*, **70**, 286 (2012).
16. T. T. M. Huynh, F. Weiss, N. T. M. Hai, W. Reckien, T. Bredow, A. Fluegel, M. Arnold, D. Mayer, H. Keller, and P. Broekmann, *Electrochim. Acta*, **89**, 537 (2013).
17. T. P. Moffat, J. E. Bonevich, W. H. Huber, A. Stanishevsky, D. R. Kelly, G. R. Stafford, and D. Josell, *J. Electrochem. Soc.*, **147**, 4524 (2000).
18. A. C. West, S. Mayer, and J. Reid, *Electrochem. Solid-State Lett.*, **4**, C50 (2001).
19. R. Akolkar and U. Landau, *J. Electrochem. Soc.*, **156**, D351 (2009).

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