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Citation: Journal of Vacuum Science & Technology A **18**, 1207 (2000); doi: 10.1116/1.582326
View online: http://dx.doi.org/10.1116/1.582326
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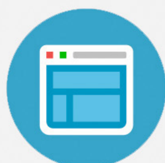

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Effects of a new combination of additives in electroplating solution on the properties of Cu films in ULSI applications

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(Received 25 October 1999; accepted 7 February 2000)

Effects of a new combination of additives in acid electroplating solution on the properties of Cu thin films have been investigated. The electroplated Cu films exhibit an excellent superfilling behavior. 0.18 μm vias with an aspect ratio exceeding 5 were filled completely without any void or seam. Strong (111) texture was found for the electroplated Cu films. The resistivity of a 450-nm-thick Cu film was measured to be 1.84 $\mu\Omega$ cm. © *2000 American Vacuum Society.*
[S0734-2101(00)08004-0]

I. INTRODUCTION

To fabricate the high performance interconnects with low resistance–capacitance delay, the integration of a low resistivity metal wiring and a low-*k* intermetal dielectric is crucial for next generation ultralarge-scale integration technology. As interconnects continue to scale down, a highly reliable interconnect system is required to allow for high current density. The practice of using copper as an advanced interconnect material becomes inevitable. Cu provides desirable high conductivity, 1.67 $\mu\Omega$ cm compared to 3.0 $\mu\Omega$ cm of Al. The introduction of Cu metallization in advanced 0.18 μm generation integrated circuits involves a revolutionary change in process architecture for multilevel interconnects. In addition, it possesses high electromigration resistance, which is one to two orders of magnitude better than that of Al. To introduce Cu into metal/via interconnections, the dual damascene process is required because Cu is difficult to etch.[1–4]

Conventional physical vapor deposition (PVD) techniques are inadequate for filling sub-0.18 μm and high-aspect-ratio trenches/vias. Accumulation of deposits at the upper corners of trenches/vias leads to pinch-off and void formation. Chemical vapor deposition (CVD) has the potential for conformal coverage, but numerous chemical and hardware issues have hampered development of the application to the filling process.[5] Recently, electroplating technology for Cu metallization has been developed to fill fine trenches/vias. It is worthwhile to note that ideally electroplating of Cu inside small-size trenches/vias should occur preferentially at the bottom, leading to void-free deposition. The special phenomenon is called superfilling, also known as bottom up.[4] In electroplating, the additives of electroplating solution play a key role in superfilling behavior. However, most additives in electroplating solution are not disclosed completely in the literature.[6–11] The additives are usually composed of leveling agent, brightening agent, and surfactant.

In the present work, effects of a new combination of additives in electroplating solution without brightening agents on Cu films were investigated. The purpose is to decrease the number of organic compounds in electroplated Cu films. The crystal orientation of the electroplated Cu films with various applied current densities was studied.

II. EXPERIMENTAL PROCEDURES

Single crystal, 15–25 Ω cm, 8 in. in diameter, *p*-type (001) oriented silicon wafers were used in this work. The blank silicon wafers were first cleaned chemically by a conventional RCA cleaning process. Following a dilute HF($HF:H_2O=1:50$) dip, a 2-μm-thick SiO_2 layer was deposited as a dielectric film by plasma-enhanced CVD on silicon. The trenches/vias were defined by photolithographic technique and reactive ion etching, 40-nm-thick TaN films as barriers and 120-nm-thick Cu films as seed layers were deposited by ionized metal plasma (IMP) PVD, consecutively. The dimensions of trench/via are 0.18–0.8 μm. For blank wafers, 40-nm-thick TaN films as barriers and 125-nm-thick Cu films as seed layers were sputtered by IMP-PVD. The electroplating solution was composed of $CuSO_4{:}5H_2O$, H_2SO_4, Cl ion, leveling agent (a kind of ester with aromatic rings (MW$<$1000 g/mol), designated as ''*L*''), polyether and silicone, which are listed in Table I. A polyether (MW $<$4000 g/mol), designated as ''*S*,'' and a small amount of

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TABLE I. Chemical compositions of electroplating Cu solution.

Composition	Concentration
$CuSO_4{:}5H_2O$	60–90 g/ℓ
H_2SO_4	150–180 g/ℓ
Cl ion	60–80 ppm
Ester with aromatic ring, leveling agent *L* (MW <1000 g/mol)	200–500 ppm
Polyether, surfactant *S* (MW <4000 g/mol)	<1.0 g/ℓ
Silicone, defoaming agent	<10 ppm

silicone were used as the surfactant and defoaming agent, respectively. The applied current densities were less than 100 A/m^2.

X-ray diffractometer (XRD) was utilized to investigate crystal orientation of the electroplated Cu films. An Auger electron spectroscope (AES) was applied to determine the stoichiometry and uniformity along the depth direction. The morphology and step coverage were studied by a field emission scanning electron microscope (FESEM). Four-point probe was used to measure the sheet resistance of samples.

III. RESULTS AND DISCUSSION

To determine the effects of additives on the deposition rate, the electroplating current was measured as a function of applied potential by a potentiostat for different electroplating solutions. The results are shown in Fig. 1. According to Faraday's law of electrolysis, an appropriate amount of current–time product is required to produce a definite weight of deposit m ($m = ZQ = ZIt$, m: deposited weight of metal, Z: electrochemical equivalent, Q: charge in coulomb, I: current in ampere, t: time in s). The deposited weight of metal is therefore proportional to applied current density. The results indicate that the electrodeposition solution with additives led to a lower plating rate than that without additives.

Figure 2 shows the deposition rate as a function of the concentration of leveling agent *L*. The deposition rate was found to decrease with increasing concentration of *L*. Furthermore, the highest deposition rate occurred for electroplating solution without *L*. It is assumed that the concentration of *L* in the diffusion layer, i.e., boundary layer, is proportional to that in the bulk solution. The investigation helped to determine the appropriate concentration of leveling agent.

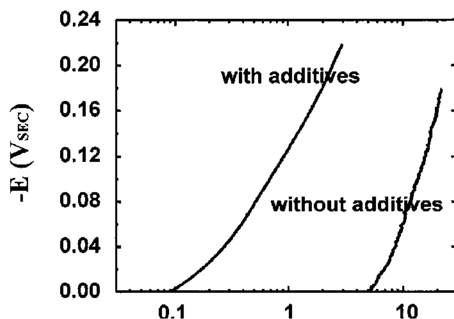

FIG. 1. Relationship of current vs potential of electroplating solutions by a potentiostat measurement (V_{SEC}: potential of calomel electrode).

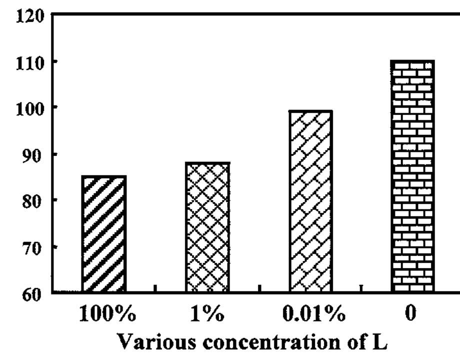

FIG. 2. Deposition rate as a function of the concentration of leveling agent *L* with 100% concentration of *L* being 200 ppm. The concentrations are 100% *L*, 1% *L*, 0.01% *L*, and 0% *L*.

Superfilling behavior can be explained by a diffusion-controlled theory of additives. It can be understood by comparing deposition rates at different points along the featured profile. Figure 3 shows possible variation of electroplating rate along the line profile. The additives are accumulated at the top of the hole (point *A*) over a short distance from the diffusion boundary because diffusion time is relatively short. In contrast, the diffusion time to the valley of the hole (point *C*) is too long to keep up with the consumption of additives. As shown in Fig. 1, the effect of additives is to decrease the deposition rate. As a result, the addition of additives leads to a higher deposition rate at the bottom of the hole than that at the top, i.e., it is superfilling. In addition, the supply of Cu^{2+} must be rapid enough to sustain a surface-reaction controlled deposition.

A rather smooth surface of the electroplated Cu film was formed with the solution listed in Table I. An example is shown in Fig. 4. Smooth deposition is particularly important since it yields good electrical contacts and ensures low porosity for the plated film. It is also very useful in the post-treatment chemical/mechanical polishing. The resistivity of the 450-nm-thick Cu film is 1.84 $\mu\Omega$ cm. The low resistivity of electroplated Cu film suggested that without a brightening agent, which is a kind of organic additive, the amount of organic impurities in electroplated Cu films is decreased. It is a peculiar metallurgical property of thin films (on the order

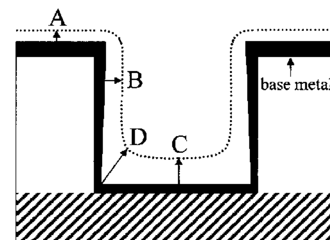

FIG. 3. Possible variation of electroplating rate along the line cross-section profile.

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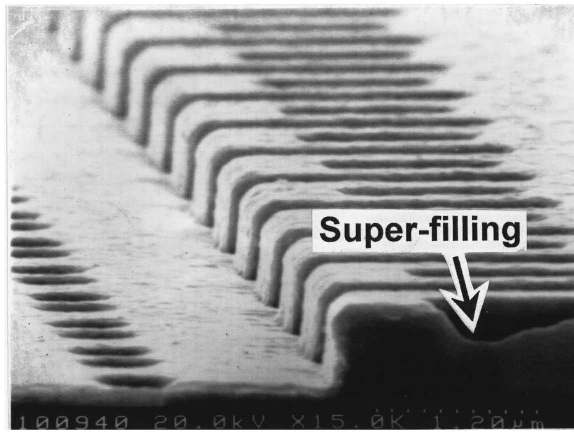

FIG. 4. SEM image of the Cu film by electroplating. Applied current density was 100 A/m^2.

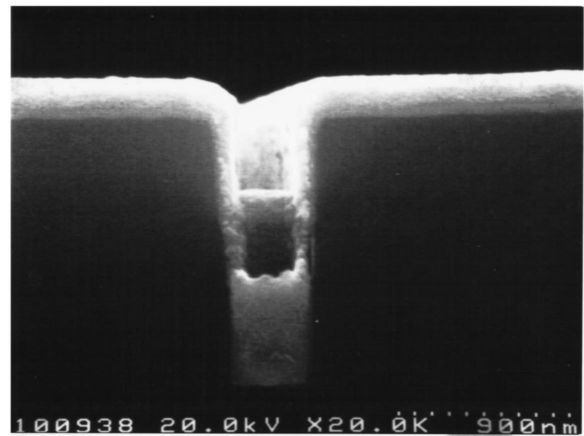

FIG. 7. SEM image of a partially filled 0.4 μm dual Damascene structure by Cu electroplating. The depth is 1.5 μm and applied current density was 60 A/m^2.

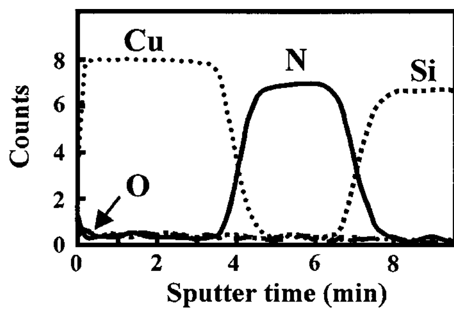

FIG. 5. AES depth profile of an electroplated Cu film. Applied current density was 60 A/m^2.

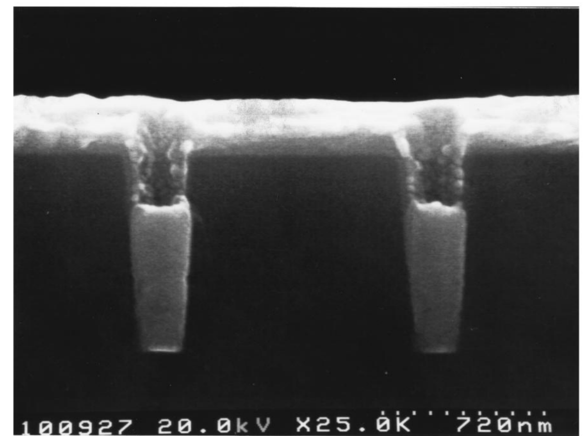

FIG. 8. SEM image of a partially filled 0.18 μm holes by Cu electroplating. The aspect ratio is 5.5. Applied current density was 60 A/m^2.

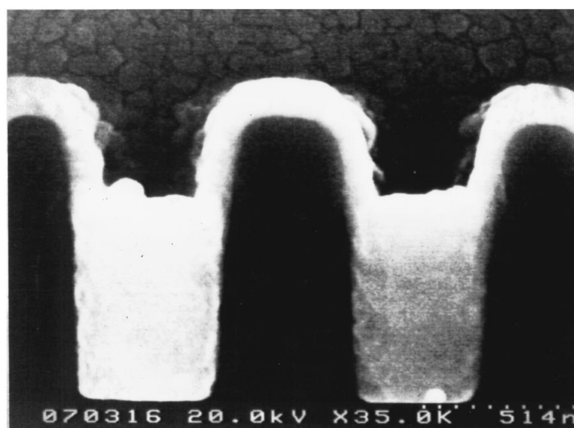

FIG. 6. SEM image of the partially filled 0.45 μm holes by Cu electroplating. The aspect ratio is 2.3. Applied current density was 60 A/m^2.

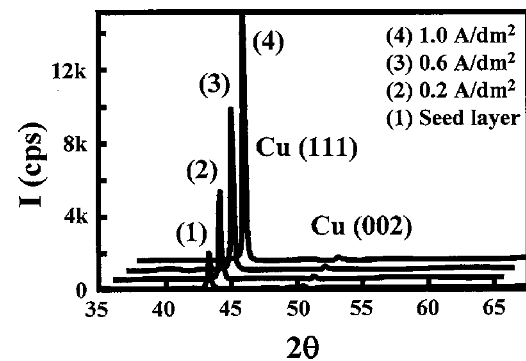

FIG. 9. XRD peaks of electroplated Cu films. The deposition time is 5 min and applied electrical current densities were 20, 60, and 100 A/m^2, respectively.

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of 1 μm) of electroplated Cu that the resistivity after plating is about 20%–25% higher than the expected resistivity of the metal (about 1.67 μm cm).[4]

From AES measurement, the concentration of oxygen in samples with an applied current density of 60 A/m^2 was found to be rather low, as shown in Fig. 5. It indicates that the oxidation of Cu in the samples was minimal. Figure 6 shows a SEM image of partially filled 0.45 μm holes by Cu electroplating. The aspect ratio is 2.3 and applied current density was 60 A/m^2. It exhibits an excellent superfilling behavior. Excellent filling behaviors were also found for a dual Damascene structure with a depth as high as 1.5 μm, as shown in Fig. 7. Moreover, 0.18 μm vias with an aspect ratio exceeding 5 were filled completely without void or seam. An example is shown in Fig. 8.

Figure 9 shows XRD θ–2θ scan peaks of electroplated Cu films on IMP-Cu(125 nm)/IMP–TaN(30 nm) substrates with various applied current densities. The deposition time was 5 min. From XRD analysis, samples deposited with higher current density exhibited stronger (111) texture. Although higher current density leads to faster deposition rate by Faraday's law, it reduces the ability of superfilling. Usually, the applied current is less than 100 A/m^2.

IV. CONCLUSIONS

Effects of a new combination of additives in electroplating solution on the properties of Cu thin films have been investigated. The electroplated Cu films exhibit an excellent superfilling behavior. 0.18 μm vias with an aspect ratio exceeding 5 were filled completely without any void or seam. The electrodeposition solution with additives exhibited a lower plating rate. Low resistivity, low porosity, and highly uniform electroplated Cu films were obtained. Strong (111) texture was found for the electroplated Cu films. The resistivity of a 450-nm-thick Cu film is 1.84 $\mu\Omega$ cm.

ACKNOWLEDGMENT

The work was supported by the Republic of China National Science Council through Grant Nos. NSC89-2215-E007-006 and NSC89-2215-E110-001.

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