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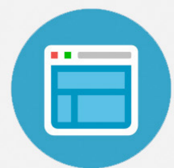

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Electroplating copper in sub-100 nm gaps by additives with low consumption and diffusion ability

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This work presents a novel leveler with low consumption and low diffusion that achieved defect-free filling in vias as small as 0.1 μm and generated as-deposited films with low resistivities. Experimental results indicate that the additive, 2-aminobenzothiazole (2-ABT), with benzyl and amino ($-NH_2$) functional groups, is a desirable leveler. It produced a highly selective concentration gradient between the opening and the bottom of the feature. This novel leveler, with weaker adsorption, also reduced the consumption during copper electroplating, and eventually deposited a film with a high conductivity. © *2002 American Vacuum Society.* [DOI: 10.1116/1.1477422]

I. INTRODUCTION

Copper electroplating has become a promising technology for producing copper interconnects in a damascene structure. In particular, a plating bath should be used to introduce a diffusion-limited leveler that results in a higher copper deposition rate at the bottom of the features than on the sidewalls, to yield excellent filling. However, not all sufficiently suppressive organic additives are effective levelers. In our previous work,[1] additives with insufficient suppression or excessive diffusion were found not to be suited to gap-filling promoters. Kobayashi *et al.*[2] found two chemistries with the approximate additive concentrations and inhibitive capacity, but one of them resulted in bottom-up filling that was free of voids or seams; and the other additive generated a conformal filling. This finding suggests that the gap-filling is more complex than can be understood by just considering the inhibition capacity of organic additives: other physical properties of organic additives in plating baths must also be considered. West[3] claimed that the surface decomposition kinetics of the additives and the additive adsorption isotherms played critical roles in leveling. According to their mathematical model,[3] a dimensionless R_{LA} ($\sim kh/DC$) was proposed as a design rule for void-free deposition, where D and k are the additive diffusion coefficient and the consumption constant of the additive, respectively. A higher rate of consumption of additives generally follows from stronger adsorption on copper surfaces, causing apparent depletion within the damascene structure. Consequently, in the damascene feature, the distribution of additives along the feature sidewalls depends on the additives' diffusion and consumption rates and determines the corresponding deposition gradient. What kind of distribution of additives within the feature is favorable? This work considers a series of compounds in the plating solution to elucidate the influence of additives on the Cu deposition behavior. Although additives in consumption reactions can enhance the efficiency of gap-filling, dilute additions of these organic components to the electrolyte led to copper deposits with impurities. The remnant organic impurities influenced the resistivity and electromigration resistance of the deposited Cu.[4] Consequently, the process window of copper electroplating was limited by the gap-filling and electrical characteristics.

In this work, defect-free filling was successfully achieved in vias as small as 0.1 μm and low resistivity films of $\sim$2.5 $\mu\Omega$ cm were generatedin as-deposited films. The common features for the thiazole derivatives additives with benzyl groups and an amino-group ($-NH_2$) were that those levelers exhibited lower diffusion and consumption, resulting in a higher gradient deposition rate along the gap sidewall. This kind of leveler was demonstrated in the author's previous study.[5] Studying the diffusion and consumption reactions of additives by cyclic voltammetric stripping (CVS) and x-ray photoelectron spectroscopy (XPS) allowed us to determine the ratio of the consumption rate to the diffusion coefficient of a leveler in order to correlate the ratio to its impact on filling capacity.

II. EXPERIMENT

The patterned wafer consisted of a 30-nm-thick chemical-vapor deposited (CVD)-Ti/TiN layer as the diffusion barrier, and a 200-nm-thick ionized metal plasma deposited

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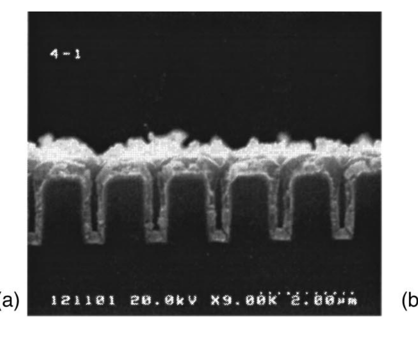

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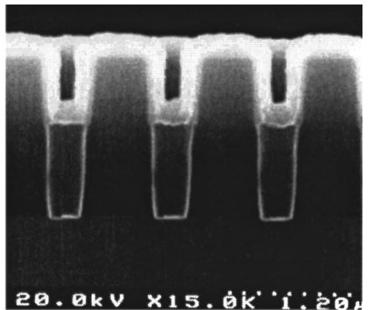

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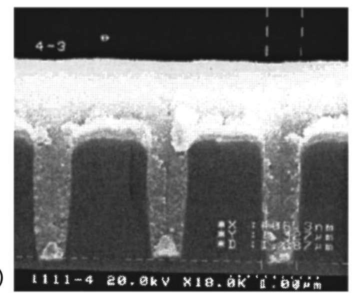

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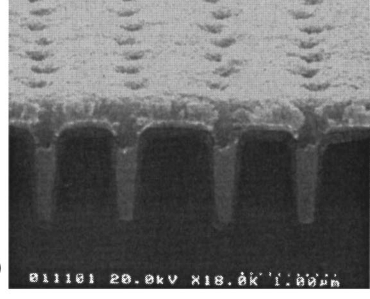

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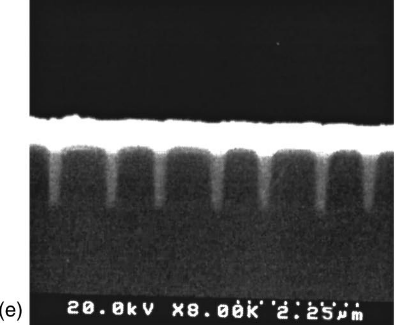

(e)

FIG. 1. Filling profiles in vias, using (a) 4-mercaptopyridine (4-MP), (b) ammonium peroxydisulfate, (c) thiourea, (d) 2-mercaptopyridine (2-MP), (e) 2-aminobenzothiazole (2-ABT) as levelers.

(IMP)-Cu film as the seed layer. In this investigation, the electrolyte was composed of copper sulfate (30 g/l), sulfuric acid (150 ml/l), chloride ion (100 ppm), and polyethylene glycol (PEG) as a suppressor (40 ppm). All leveling agents were used at a concentration of 40 ppm. All electroplating was undertaken at room temperature. The electrochemical behavior of the levelers, including the adsorption and the mass-transport dynamics, was examined with polarization measurements and cyclic voltammetric stripping (CVS) measurements. Direct current (dc) polarization analysis was performed on an EG&G Potentiostat/Galvanostat Model 273A. The CVS measurements were made at room temperature, using an EG&G PARC Model 616 RDE. The filling profiles of the deposited films were obtained using a field emission scanning electron microscope (FESEM). The sheet resistance of the deposited Cu was measured using a four-point probe station (Napson RT-80/RG-80). The chemical composition of Cu films after electroplating was determined by XPS.

III. RESULTS AND DISCUSSION

In our previous work,[1] we experimentally estimated the additive's diffusion and inhibition effects on gap-filling and concluded that a rate of diffusion that was too high and an adsorption that was too weak for the additive, caused poorer gap-filling. Furthermore, West[3] proposed the ratio of the consumption constant to the diffusion coefficient of the additive, determining the gap-filling behavior of the additives in copper electroplating.[3] Thus, the selection of an additive with optimized functionality in realistic applications requires more research. In this study, polyethylene glycol (PEG) was used as an inhibitor; and other organic additives, such as thiourea, ammonium peroxydisulfate, 4-mercaptopyridine (4-MP), 2-mercaptopyridine (2-MP), and 2-aminobenzothiazole (2-ABT), were used as levelers with various characteristics. The filling ratio $\Delta y/\Delta x$ (Ref. 1) of "bottom-up" to "side-wall shift" from the cross section of a partially filled copper profile on the SEM image was used to define the filling power of different organic additives, combined with PEG. The filling powers ($\Delta y/\Delta x$) in order, are as follows: 2-ABT (2.16) > 2-MP (1.83) > thiourea (1.69) > 4-MP (1.49) > ammonium peroxydisulfate (1.17). Figure 1 shows scanning electron microscopy (SEM) images of filling profiles for various organic additives. Ammonium peroxydisulfate, thiourea, and 4-MP were found not to be effective in defect-free filling. Only 2-ABT and 2-MP, providing not only adequate over potential but also a selective inhibi-

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TABLE I. Chemical structure of each leveling agent and their performance in gap-filling.

Additives	Structure	Filling profile
PEG+Ammonium peroxydisulfate	$(NH_4)_2S_2O_8$	Anti-conformal
PEG+thiourea	$(NH_2)_2CS$	Conformal
PEG+ 4-mercaptopyridine	SH N	Anti-conformal
PEG+ 2-mercaptopyridine	N SH	Super filling
PEG+ 2-aminobenzothiazole	N S NH_2	Super filling

tion gradient achieved superfilling. Table I shows chemical structures and filling results of various additives in PEG-containing electrolytes.

In electrochemical deposition, cathode polarization measurements usually yield comparisons of the inhibition abilities of additives. Figure 2 shows the cathode overpotential of various additives in PEG-containing electrolytes at a constant current density ($0.001\ A/cm^2$) as follows: thiourea $(-0.253\ V) > 2\text{-MP}\ (-0.186\ V) \approx 4\text{-MP}(-0.188\ V) > 2\text{-ABT}\ (-0.145\ V) >$ peroxydisulfate $(-0.132\ V)$. In spite of thiourea's having the greatest inhibition effect, its high diffusion rate results in a near-equilibrium concentration within the whole damascene structure,[1] failing to provide a selective inhibition gradient within the via. Consequently, a conformal profile with a seam for the corresponding deposit was observed. However, the inhibitive effect of ammonium peroxydisulfate with the least overpotential was too small at the opening of the feature and resulted in an anticonformal profile. The activation overpotential of 4-MP was almost equal to that of 2-MP. However, 4-MP could not form a chelate, while 2-MP could;

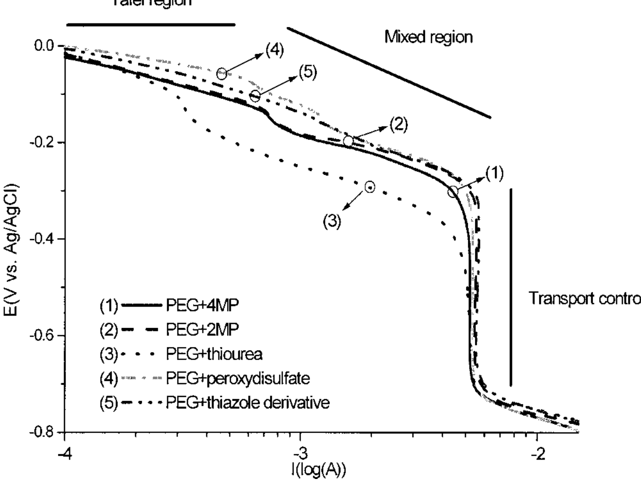

FIG. 2. Cathode polarization curves of various additives in acid-copper solutions.

the concentration gradient of 2-MP between the top and the bottom of the damascene was more than that of 4-MP, because the adsorption ability of the former exceeded that of the latter.[1]

Following the mathematical model of West,[3] a dimensionless R_{LA} ($\sim kh/DC$) was presented in a design rule for void-free deposition; where D and k are the additive diffusion coefficient and the constant rate of consumption of the additive, respectively. R_{LA} can be viewed as estimating the penetration of the leveling agent into the feature. As $R_{LA} \rightarrow \infty$, the concentration of the leveling agent quickly declines to zero at a short distance from the trench mouth, and when $R_{LA} \rightarrow 0$, the leveling agent concentration is constant, and equals the bulk value.[3] A value of R_{LA} slightly less than unity provides the most ideal leveling situation and achieves void-free metallization.[3] Void formation is predicted when R_{LA} is too large or too small. Consequently, an excessive diffusion rate or a consumption rate that is too low cannot produce a concentration gradient within the feature. This model can explain the experimental results presented here.

A leveler generally adsorbs on the metal surface, primarily through the sulfur or nitrogen atom and forms a chelate with the metal surface, causing a stronger chemical inhibition.[6] Table II presents the consumption effect of different levelers in copper deposits, elucidated by XPS. The consumption on copper surfaces for different levelers is $2\text{-MP}\ (40.15\%) >$ thiourea $(36.78\%) > 4\text{-MP}\ (26.82\%) > 2\text{-ABT}\ (18.58\%)$. The content of remnant organic impurities (only calculating amounts of S atoms and N atoms, since other atoms do not participate in leveling) for 2-MP (40.15%) were actually exceeded that for 4-MP (26.82%) and the higher rate of consumption (adsorption capacity) of 2-MP was proven. However, diffusion rates of these two additives (2-MP, 4-MP) are approximate because their molecular weights (111) and chemical organizations were similar.[1] Consequently, 4-MP, with a smaller R_{LA}, led to a lower inhibition gradient because the rate of consumption of 4-MP was less than that of 2-MP. Finally, 4-MP produced an anticonformal profile with a void, as shown in Fig. 1(a). Figure 3(a) schematically explains the situation. Although the rate of consumption of thiourea $(S+N=36.78\%)$ was close to that of 2-MP $(S+N=40.15\%)$, the diffusion rate of thiourea largely exceeded that of 2-MP, because the molecular weight of thiourea (76) is less than that of 2-MP (111).[1] CVS measurements in our previous work[1] indicated that thiourea exhibited superior mass-transport characteristics (diffusion capacity) than other additives. Consequently, thiourea produced a conformal profile with a seam, as shown in Fig. 1(c).

2-ABT provides excellent gap-filling performance in a sub-130 nm damascene process,[5] although its inhibitive ability was poorer than that of the 2-MP additive. Figure 4 presents the CVS measurement obtained from 2-ABT baths. When the electrode rotation rate increased from 0 to 1500 rpm; the inhibition effect decreased, because of an observed increase in the copper stripping area. These data suggest that the mass-transport characteristics of 2-ABT are similar to those of 2-MP or 4-MP but differ from those of thiourea.[1] The diffusion rate of 2-ABT is smaller than that of 2-MP

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TABLE II. XPS analysis: chemical composition calculated from peak area (at %). $S+N$ denotes the consumed amounts of additive impurities for leveling; the order is 2-MP>thiourea>4-MP >2-ABT. R: electrical resistance of copper films f: a factor which is related to the effects of impurities on resistivity. $f=C*4+N*7+O*5.5+S*9$, (where C, N, O, S represent the concentration of containment atoms trapped in copper films, as percentages of atoms).

	PEG + 2-ABT	PEG + 4-MP	PEG + 2-MP	PEG + thiourea	PEG
XPS ANALYSIS					
C	43.20 %	34.74 %	14.02 %	23.02 %	0.46 %
N	18.08 %	18.55 %	34.26 %	30.83 %	0 %
O	32.04 %	24.83 %	33.46 %	29.52 %	14.31 %
S	0.5 %	8.27 %	5.89 %	5.95 %	2.66 %
S+N	18.58 %	26.82 %	40.15 %	36.78 %	
f	4.76	4.79805	5.32940	5.23800	1.04485
R	2.5 μΩ-cm	3.433 μΩ-cm	8.7 μΩ-cm	5.4 μΩ-cm	2.3 μΩ-cm

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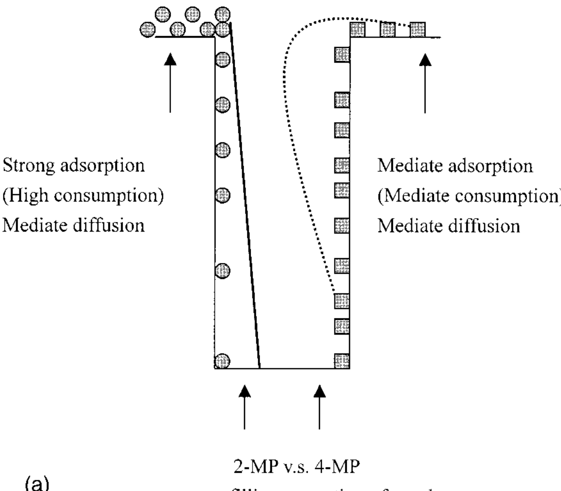

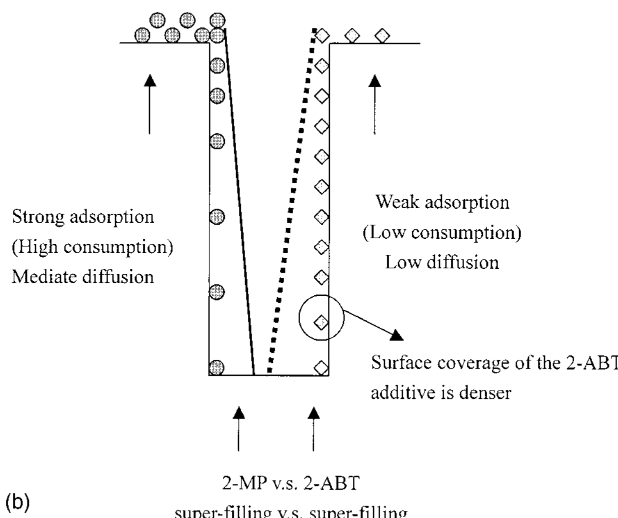

FIG. 3. Schematic figures for electrolyte in several conditions of levelers, with different diffusion rates D and a consumption rate k.

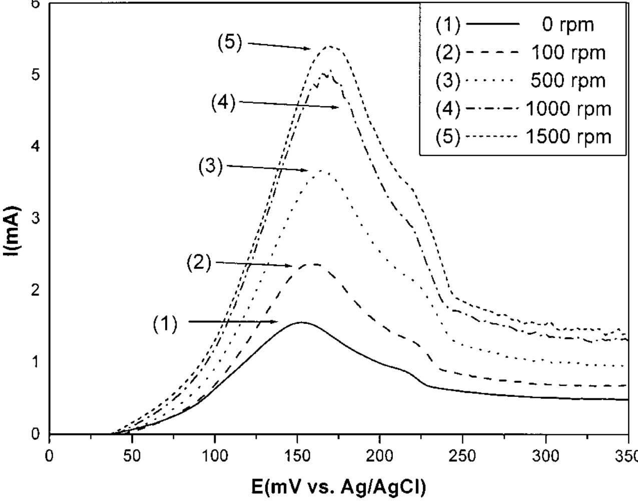

FIG. 4. Cyclic voltammetric stripping (CVS) measurements were taken in 2-ABT baths (40 ppm). The sweep rate was 50 mV/s.

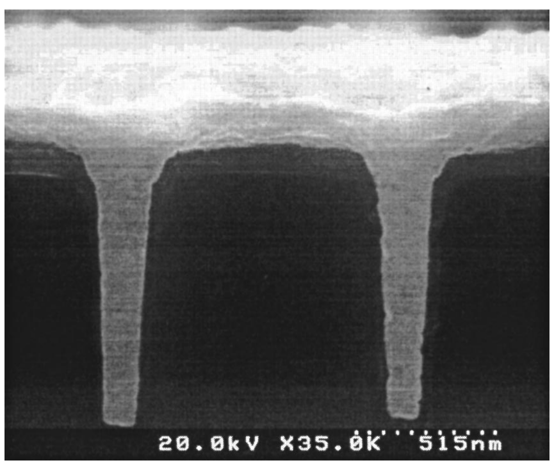

FIG. 5. SEM profile of a 0.1 μm via with an aspect ratio of 10:1 was achieved using 2-ABT as the leveler.

because 2-ABT has a higher molecular weight. Although the consumption of 2-ABT (18.58%) is lower than that of 2-MP (40.15%), the lower diffusion rate of 2-ABT compensates for the lower consumption to yield a selective inhibition gradient. Another benefit of the 2-ABT leveler, with a lower consumption rate and lower diffusion rate, was that more 2-ABT additives were present within the feature and formed a dense surface coverage along the sidewall surface. Figure 3(b) schematically depicts this observation. The lower consumption of 2-ABT at the opening of the feature is such that more 2-ABT additives can adsorb onto the sidewall's surface than can 2-MP additives, leading to a slower deposition of copper in the horizontal direction, relatively enhancing deposition in the vertical direction (bottom-up deposition). This result produces a higher filling power ($\Delta y/\Delta x$) for 2-ABT. Deligianni and co-workers[7] also claimed an improvement in superfilling that was related to lower inhibition and a lower additive flux. Consequently, an additive with a lower consumption rate and a lower diffusion rate can excellently fill high-aspect ratio trenches and vias. Figure 5 shows that a void-free deposit was achieved in vias as small as 0.1 μm, using 2-ABT as a leveler.

The XPS data show that incorporating these remnant organic impurities in the deposited metals cannot be prevented because of their leveling mechanisms. Some papers[6,8] have reported that additives decomposed into sulfide ions that combined with cupric ions to form CuS compounds on the cathode. Such a compound would become a second-phase particle and increase the magnitude of the grain boundary pinning pressure, estimated by Zenner's model.[9] The film resistance naturally increased due to greater number of such sites. Actually, most additives for electroplating applications face the same problem. The resistance of copper films normally depends on the incorporated impurity atoms and their concentrations in copper films. XPS was used to determine which elements were present on the copper films with various electrolytes. The presence of sulfur and nitrogen atoms in the copper deposits indicates that additives are chemisorbed on deposited copper. Following Cunningham,[10] one

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factor is proposed to describe the influence of the characteristic remnant organic impurities on the resistivity of the deposited films. This impacting factor, f, is expressed as $f = 4*C + 5.5*O + 7*N + 9*S$ (C, O, N, S denote the normalized peak areas of C, O, N, S atoms in the deposits). The calculated f values of various added organic additives are in the following order: 2-MP (5.329 40) > thiourea (5.238 00) > 4-MP (4.798 05) > 2-ABT (4.76), and are given in Table II. This trend coincides with the order of the film resistances, 2-MP (8.7 $\mu\Omega$ cm) > thiourea (5.4 $\mu\Omega$ cm) > 4-MP (3.433 $\mu\Omega$ cm) > 2-ABT (2.5 $\mu\Omega$ cm). In this experiment, 2-aminobenzothiazole (2-ABT), with low consumption and diffusion capacity, was found to be a desirable leveler.

IV. CONCLUSIONS

Approaches of copper electroplating in trenches or vias as small as 0.1 μm, 10:1 AR have been developed by a typical acid-copper electrolyte with a 2-ABT leveler. This leveling agent consists primarily of thiazole derivatives, which meet the requirements of gap-filling promoters because of their low consumption and diffusion capacity in forming deposition gradient along the damascene sidewalls. The low consumption capacity of thiazole derivatives leads to the introduction of fewer compound formations in the deposits, reducing the electrical resistance of the deposited copper films to below 2.5 $\mu\Omega$ cm. In this experiment, 2-aminobenzothiazole (2-ABT), with low consumption and diffusion capacity, was found to be a desirable leveler.

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