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Superconformal Cu Electrodeposition on Various Substrates

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For application to Cu interconnection, superconformal electrodeposition has been performed on various substrates, including physical vapor deposited (PVD) Cu, two kinds of electroless deposited (ELD) Cu, TiN barrier, and metallorganic chemical vapor deposited Ru. ELD Cu with HCHO as the reducing agent was compatible with PVD Cu in terms of conformal characteristics and film continuity. Both PVD and ELD Cu seed layers enabled superconformal filling with distinct bumps. Superfilling was also attained on resistive substrates of TiN and Ru through Pd activation and subsequent slight seeding by electrodeposition to enhance the action of additives.
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In the Cu electrodeposition process, the substrate is important to the formation of uniform and void-free Cu films in the damascene structure.[1] There have been many investigations about the characteristics of electrodeposition on various substrate.[2,3] The most widely used substrate is a physical vapor deposited (PVD) Cu seed layer due to its low resistivity and well-oriented crystal structure. However, poor step coverage, which is the intrinsic drawback of PVD, becomes a serious problem in nano-scale devices. On the other hand, Cu seed layer grown by metallorganic chemical vapor deposition (MOCVD) has superiority in step coverage. But it also has such problems as relative high resistivity and poor adhesion,[3] among others. Recently, electroless deposition (ELD) has been proposed as a seed layer formation method.[2,4] The merits of ELD include good step coverage, low process cost, and good uniformity on an extensive area. In particular, introduction of ELD can make an interconnection process through only wet-processes of seed layer formation with subsequent electrodeposition. In addition, there are other proposals for direct Cu electrodeposition on a barrier layer without a Cu seed layer.[5,6] But the high resistivity of barrier metal does not allow the formation of a continuous Cu film. Kim *et al.*[7] achieved continuous Cu films by using Pd activation on TiN substrates. Josell *et al.*[8] conducted Cu electrodeposition on a evaporation-deposited Ru substrate.

However, the application of various substrates to damascene Cu electrodeposition is rather complicated because the additive chemistry is essentially involved in the electrodeposition. Generally, superconformal electrodeposition is achieved through the adsorption and catalytic effects of additives.[9-13] Among them, the adsorption of an accelerator which has a mercapto group (-SH) or disulfide (S-S) is well known on Cu and Au surface.[14,15] Therefore, the existence of a Cu surface is essential to the function of the additives. Consequently, some variations on electrodeposition procedures according to the substrates are demanded for superconformal electrodeposition in the damascene structure.

In this study, superconformal electrodeposition was carried out on five types of substrates prepared with several deposition methods: PVD Cu, two kinds of ELD Cu, CVD TiN, and MOCVD Ru. Superconformal electrodeposition was achieved with various electrodeposition procedures according to the type of substrate used.

Experimental

Substrate fabrication.—The substrates used in the experiments were (100) oriented p-type blanket and patterned (aspect ratio of 2 and 2.5) Si wafers that were coated with CVD TiN (100 Å)/PVD Ti(150 Å) as a diffusion barrier layer. Four types of top layer were fabricated on these wafers with optimized fabrication conditions

1. PVD Cu seed layer was deposited on the TiN surface by a hollow-cathode magnetron (HCM) PVD. The source was operated with a dc power supply with a maximum output of 36 kW and the stage was cooled in the range of −50 to −40°C.

2. HCHO-ELD Cu seed (electrolessly deposited Cu using paraformaldehyde as the reducing agent) was fabricated with the following steps: First, the TiN surface of the substrate was cleaned by HF solution composed of 200 mL deionized (DI) water and 4 mL of 50% HF by dipping the wafer for 10 min at room temperature to remove native Ti oxide formed on the TiN. After cleaning and rinsing with DI water, Pd activation on the pretreated TiN layer was performed at 40°C for 20 s in an activating solution, which was composed of $PdCl_2$ (0.1 g/L), 35% HCl (3 mL/L), and 50% HF (5 mL/L).[2,16,17] Electroless deposition of Cu seed was performed at 50°C with a solution consisting of 0.005 M $CuSO_4 \cdot 5H_2O$, 0.01 M ethylenediaminetetraacetic acid (EDTA), 0.015 M *para*-formaldehyde (HCHO) as the reducing agent, and 0.05 M KOH as the pH adjuster.[2,16]

3. The same oxide cleaning step and activation step of HCHO-ELD Cu seed fabrication were done for the fabrication of Co-ELD Cu seed (electroless deposited Cu using Co(II) as a reducing agent). The electroless deposition was performed at room temperature with a deposition solution composed of 0.025 M $CuCl_2 \cdot 2H_2O$, 0.15 M $Co(NO_3)_2 \cdot 6H_2O$ as reducing agent, 0.6 M ethylenediamine as complexing agent, and HNO_3 pre-mixed in DI water at pH 6.8.[2,18,19]

4. The Ru film, one of the diffusion barrier, was deposited on TiN using the MOCVD process with a bis(ethyl-π-cyclopentadienyl) ruthenium ($Ru(EtCp)_2$) precursor. The substrate temperature for deposition was 320-360°C. The showerhead, carrier gas (Ar) line, and reaction gas (O_2) line were heated to over 110°C to avoid the condensation of the precursor. The bubbler and pre-bubbler carrier line temperature was 90°C The flow rates for carrier gas and reaction gas were 150 and 50 sccm, respectively, and the process pressure was 3 Torr.

Surface activation prior to electrodeposition.—The PVD and two kinds of electroless Cu were used as seed layers for electrodeposition without any surface activation. However, Pd activation was performed on the Ru and TiN surfaces prior to the electrodeposition to enhance the initial nucleation during the electrodeposition. Activation was performed by dipping the wafer for 40 s in activating solutions composed of 0.28 mM $PdCl_2$, 36.5 mM HCl, and 185.2 mM HF[7,16,17] for the Ru surface at room temperature and 0.56 mM $PdCl_2$, 36.5 mM HCl, and 123.5 mM HF for the TiN surface at 40°C. Displacement-deposited catalyst particles are known to be very effective in the formation of continuous, bright, and low resistivity Cu films by electrodeposition on high resistivity foreign metals.[7]

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Table I. Sample structures, fabrication methods, and experimental conditions for superconformal electrodeposition of Cu on each substrate.

Layer structure	Substrate (A)	Activation prior to electrodeposition	Electrodeposition potential (*vs.* SCE)	Electrolyte and additives
A/TiN/Ti/Si	PVD Cu	None	−250 mV	Base electrolyte (BE) + 3 additives (SPS + PEG + NaCl)
	HCHO-ELD Cu	None	−250 mV	
	Co-ELD Cu	None	−250 mV	
	None	Pd activation	Seeding: −500 mV Filling: −250 mV	Seeding: BE + PEG Filling: BE + 3 additives
	MOCVD Ru	Pd activation	Seeding and filling at −200 mV	Seeding: BE Filling: BE + 3 additives

Electrodeposition conditions and additives.—Electrodeposition on PVD and ELD seeds was performed at −250 mV [*vs.* a saturated calomel electrode (SCE)] with electrolytes composed of 1 M H_2SO_4, 0.25 M $CuSO_4 \cdot 5H_2O$ and DI water (base electrolyte). Additives used in the feature filling were 50 μM SPS bis(3-sulfopropyl)disulfide ($Na^+, {}^-O_3S(CH_2)_3S\text{-})_2$], 88 μM poly(ethylene glycol) (PEG, Mw 3400), and 1 mM NaCl.[9,11,13,20,21] From the authors' previous investigations,[13] SPS is more effective in superconformal filling on damascene structure than MPSA 3-mercapto-1-propane sulfonic acid, sodium salt, $Na^+, {}^-O_3S(CH_2)_3SH$]. This is because SPS can diffuse deeply inside the trench and adsorb on the Cu surface without any interference from the reaction involving it as SPS is already an oxidized form. Then the adsorbed SPS undergoes reductive desorption by the applied potential to form a catalytic species (*i.e.*, MPSA) able to reduce cupric ion to cuprous ion.

However, Cu electrodepostion on Pd activated Ru and TiN substrates was performed with two steps:[7] electrodeposition on the Pd-activated substrate in the base electrolyte for 40-45 s as a seeding process, and further electrodeposition with the three-additives system stated above. For Ru substrate, seeding and filling were performed at −200 mV. In the TiN substrate, seeding was carried out at −500 mV with the addition of 0.12 mM PEG into the base electrolyte as an adhesion promoter and filling was performed at −250 mV. Potentials were predetermined from linear sweep voltammetry. The reason for the two-step method is that the additive system has been developed for Cu surfaces and the reactions between the Cu surface and additives are quite important in superfilling.[9,11,22] The equipment used in applying the potential was a PAR 263 potentiostat (EG&G Princeton Applied Research Corporation), and a Cu bar was used as the anode. After electrodeposition, all samples were rinsed with DI water and dried in an N_2 stream. Experimental conditions are summarized in Table I.

Results and Discussion

Figure 1 shows the cross-sectional field-emission scanning electron microscopy (FESEM) images of PVD Cu seed, HCHO-ELD Cu seed, Co-ELD Cu seed, and electrodeposited Cu films on each seed layer. As shown in Fig. 1a, PVD Cu seed has a uniform and conformal profile without formation of neck or seed agglomeration. Electrodeposited Cu film on PVD seed (Fig. 1b) exhibits a model image of superconformal filling. No voids or seams were observed either at the center or at the seed/electrodeposited Cu interface. In the fabrication of HCHO-ELD seed, the electroless deposition temperature was increased compared to the authors' previous method[2] to reduce the surface roughness, an inveterate problem of electroless Cu seed, by enhancing the lateral diffusion of Cu adatoms. As presented in Fig. 1c, smooth, conformal, and thin Cu seed is evident. In the fill test, superconformal electrodeposition and formation of bumps were evidently observed (Fig. 1d). Like the case of PVD seed, the filled Cu had no internal defects, which shows a strong potential of the electroless Cu seed for Cu electrodeposition. However, Co-ELD seed showed a little different characteristic. Lee *et al.*[23] have found that the Co-ELD seed underwent self-annealing phenomena resulting in large clusters. Similar results are presented in Fig. 1e. As clearly shown in the figure, the Co-ELD Cu seed had a conformal contour similarly to the other two seeds, while the surface was rough with a higher thickness due to the large clusters of the film. Note that the thickness control of Co-ELD Cu was difficult. In spite of the relatively undesirable seed appearance, fill-test on Co-ELD seed (Fig. 1f) showed a good profile with bumps on top. Anyway, sparse sidewall voids were noticed due to the discontinuous points of seed where the clusters met together and boundaries are formed.

Figure 2 shows the cross-sectional FESEM images of electrodeposited Cu on Ru and TiN substrates. MOCVD was found to be very effective in the formation of smooth and conformal Ru thin films compared to other methods, such as e-beam evaporation,[8] as shown in the small figure in Fig. 2a. However, direct Cu electrodeposition on the Ru substrate resulted in a cluster-type deposit rather than a continuous film type in our experiments, though Josell *et al.*[8] reported achievement of superfilling on an e-beam evaporation deposited Ru substrate. Therefore, two kinds of modulation of electrodeposition were introduced here to enhance the initial nucleation

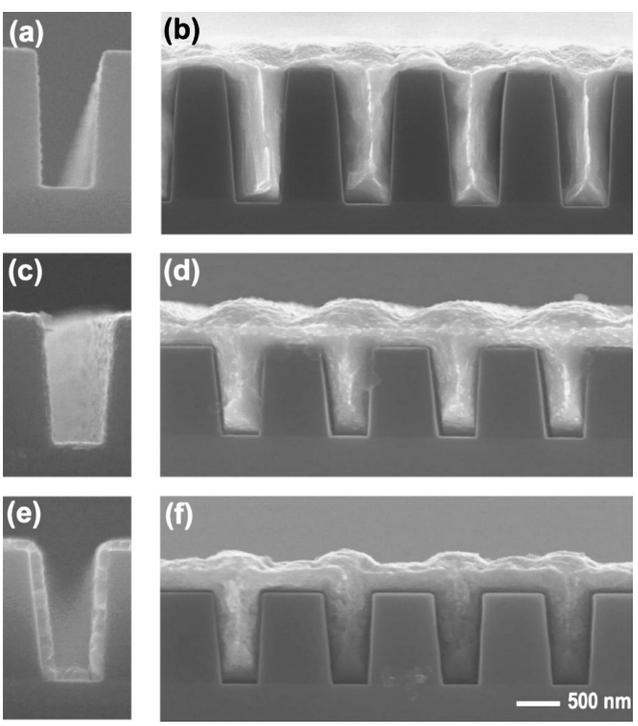

Figure 1. Cross-sectional FESEM images of (a) PVD Cu seed, (b) electrodeposited Cu on PVD seed, (c) HCHO-ELD Cu seed, (d) electrodeposited Cu on HCHO-ELD seed, (e) Co-ELD Cu seed, and (f) electrodeposited Cu on Co-ELD seed. Electrolyte for electrodeposition was composed of 88 μM PEG, 1 mM NaCl, and 50 μM SPS and the electrodeposition was performed at −250 mV *vs.* SCE.

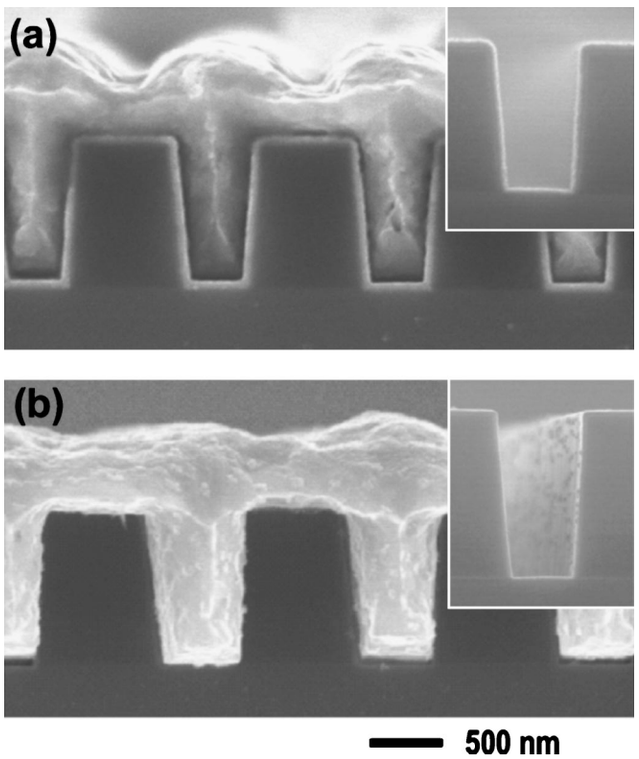

Figure 2. Cross-sectional FESEM images of electrodeposited Cu on (a) MOCVD Ru and (b) TiN. Small figures in (a) and (b) are MOCVD-grown Ru film and Pd-activated TiN, respectively. Prior to the electrodeposition, Pd activation for 40 s and subsequent seeding by electrodeposition at −200 mV for 45 s for (a) and at −500 mV for 40 s for (b) were performed. Filling with additives was carried out at −200 mV for (a) and at −250 mV for (b). Electrolyte for electrodeposition was composed of 88 μM PEG, 1 mM NaCl, and 50 μM SPS.

density essential to continuous film formation on high resistivity substrates and to facilitate the function of additives because the mechanism was strongly based on the chemical reaction among additives, Cu ions, and Cu surface. The first change was activation of the Ru surface using Pd nano particles which would act as additional nucleation sites. The second one was Cu seeding on the Pd-activated Ru surface using electrodeposition to supply a Cu surface for additive because the reaction of additives with Cu surface, *i.e.*, competitive adsorption between additives and reductive desoprtion of accelerator, seemed to be the most important. After introducing electrodeposited seed on the Pd-activated Ru substrate, the fill-test resulted in superconformal profile with bumps on the top surface (Fig. 2a). Similar modulations were done on the TiN substrate: Pd activation on TiN substrate (box figure in Fig. 2b) and subsequent seeding by electrodeposition. The consequent Cu fills (Fig. 2b) also show superfilling shape without any internal defects. These attempts to fill sub-micrometer trenches without a separate Cu seed fabrication step allow process margin of barrier deposition or electrodeposition. However, a further optimization in activation and electrodeposition is needed to improve the filling reproducibility on these high resistivity substrates.

Conclusions

PVD Cu, HCHO-ELD Cu, Co-ELD Cu, TiN barrier, and MOCVD Ru substrates were tested as substrates for damascene superconformal Cu electrodeposition. Despite the large clusters of Co-ELD Cu, electroless deposition showed very conformal characteristics, which is important in fabrication of the seed layer. The PVD and two ELD Cu seed layers enabled superfilling with distinct bumps on the top. However, superfilling was attained on the resistive substrates of TiN and Ru through modification of the surface by Pd activation and subsequent slight seeding by electrodeposition to enhance the action of additives. These accomplishments may contribute to the diversity of approaches to the interconnection process and material.

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