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Electroless Copper Plating For Metallization Of Electronic Devices

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Abstract: In copper metallization, resistivity of copper seed layer is very important. Conventionally MOCVD has been used for this purpose however electroless copper plating is simple process and the resistivity of copper deposit is less than that of copper prepared by MOCVD. In this study electroless copper plating was conducted on different substrate to find optimum conditions of electroless copper plating for electronic applications. To find optimum conditions, the effects and selectivity of activation method on several substrates were investigated. The effects of copper bath composition on morphology were investigated. The effects of pH and stabilizer on deposition rate were also investigated. The optimum pH of the bath was 12 with addition of stabilizer. The resistivity of copper was decreased with addition of stabilizer and after heat treatment.

Keywords: electroless copper, plating, ULSI, resistivity, stabilizer

1. Introduction

Recently, many authors have investigated the copper as interconnection material for submicron metallization (conduction lines and contact structures), due to its low resistivity (1.7×10^{-6} Ωcm), high electromigration resistance, RC delay time, stress voiding resistance and good reliability, relative to aluminum. Copper has many advantages over aluminum in properties, however copper cannot be etched by RIE method and copper is easily diffused into silicon oxide and then diffusion barrier is required. Those are the short comings of copper in metallization[1]. However, IBM announced copper metallization FABS in 1997, many researchers has studied about copper plating[2]. Copper is manufactured by dual Damascene process. In damascene process, trench is filled by copper electroplating. And then to electroplate copper, conducting seed layer on diffusion barrier is required. Fig. 1 shows schematics of Damascene process[1]. Conducting seed layer copper can be deposited by conventional dry coating methods such as physical vapor deposition (sputtering and evaporation) and chemical vapor deposition, however it can also be deposited by wet coating methods such as electroless plating[3-6]. An electroless deposition technique has many attractive features; excellent step coverage, good via/trench filling, low tool cost and low processing temperature.

In this study the effects of pretreatment methods and characteristics of electroless copper deposition layer with varying bath conditions and substrates were investigated. And deposition rate and surface morphology were also investigated.

2. Experimental Procedure

Several substrates were used such as copper, titanium, glass and silicon wafer. Surface of copper and titanium were mechanically polished prior to pretreatment. Glass and silicon wafer were etched with HF containing etchants. TiN and Ta are conventionally used as barrier materials against copper diffusion[7,8]. TiN and Ta were deposited on silicon wafer by MOCVD and sputtering methods respectively.

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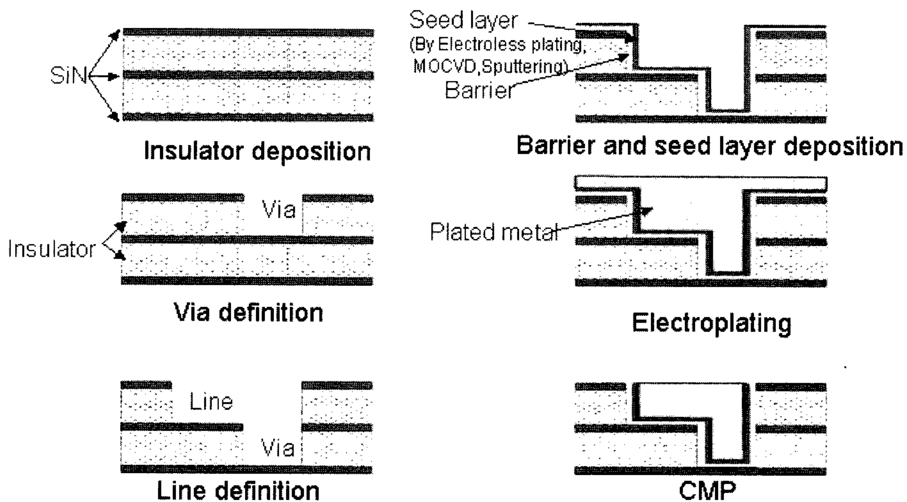


Fig. 1. Schematic diagram of Dual Damascene process.

Substrates were immersed in sensitization and activation solution prior to electroless copper deposition. After pretreatment, substrates were immersed in the electroless copper solution containing cupric sulfate, EDTA (complexing agent), formaldehyde (reducing agent). The pH of the solution was adjusted by NaOH, LiOH or TMAH. TMAH were used to replace NaOH to obtain a sodium free copper coating. Stabilizer was added to the solution to increase the solution stability and to decrease the surface tension or residual stress. The compositions of the electroless copper deposition solution and pretreatment solution is shown in Table 1. After electroless copper plating, specimens were examined by XRD, four point probe, SEM, AFM, scratch test, AES and α-step analysis.

Table 1. Composition of electroless copper deposition solutions

	Chemicals	Concentration
Copper Source	$CuSO_4 \cdot 5H_2O$	5-15 g/l
Complexing agent	EDTA	30-45 g/l
Reducing agent	HCHO	5-15 ml/l
pH adjuster	NaOH, LiOH, TMAH	pH 11-13
Stabilizer	2,2'-dipyridyl	0-5 ppm
Sensitization	10 g/l $SnCl_2$+30 ml HCl	
Activation	0.4 g/l $PdCl_2$+10 ml HCl	
Temperature	30-70°C	

3. Result and Discussion

3.1 Effects of pretreatment

Copper was electroless deposited on copper and titanium substrates after activation pretreatment and copper was plated on alumina substrate after sensitization and activation pretreatment. However copper was partially and poorly deposited silicon wafer and glass surface after activation and sensitization pretreatment. Generally copper is easily deposited on metallic surface after activation pretreatment. To improve uniform adhesion of copper on glass and silicon wafer, mechanical and chemical etching of substrates were applied. After silicon wafer and glass were etched, copper was successfully deposited. Fig. 2, 3 and 4 shows surface morphologies of copper deposits on different substrates.

The effects of pretreatments on coating were tabulated in Table 2. Copper can be selectively coated on metal substrate. And sensitization or etching is required pretreatment process to coat copper on ceramic or glass substrates.

3.2 Effects of pH

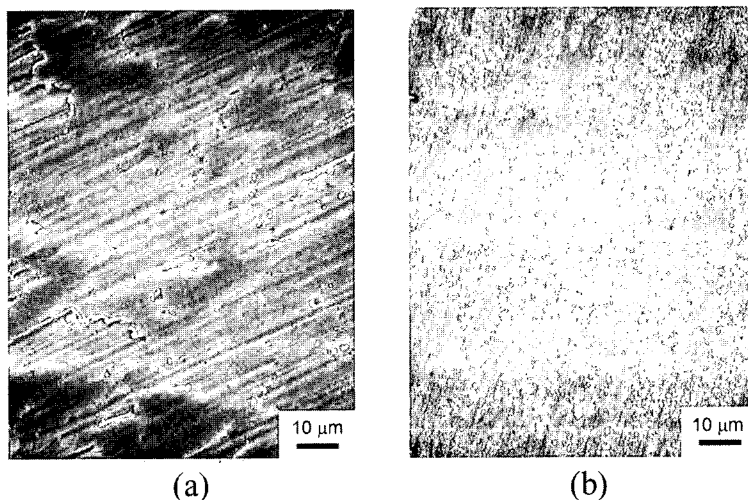


Fig. 2. SEM images of copper on titanium substrate (a) bare substrate (b) activation.

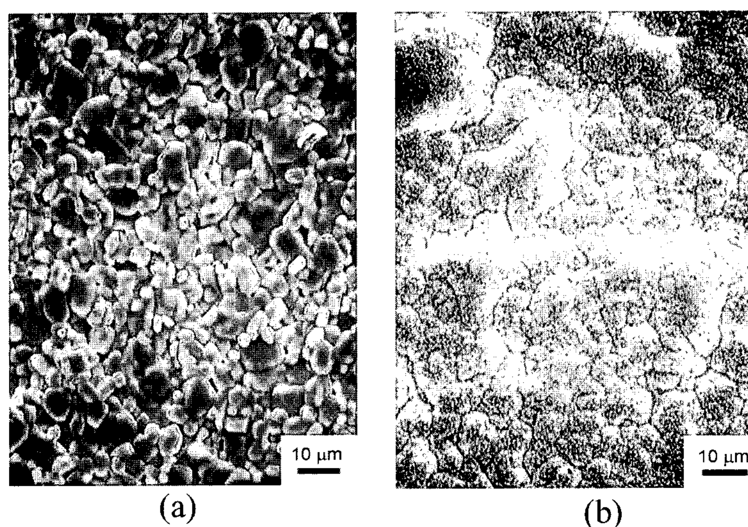


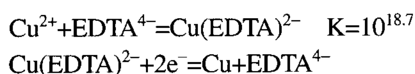
Fig. 3. SEM images of copper on alumina (a) bare substrate (b) sensitization and activation.

The reduction and oxidation reactions are presented below[9].

Anodic reaction (oxidation of formaldehyde)

$$2HCHO+4OH^- = 2HCOO^-+2H_2O+H_2+2e^-$$

Cathodic reaction (reduction of copper)



$$Cu^{2+}+EDTA^{4-}=Cu(EDTA)^{2-} \quad K=10^{18.7}$$
$$Cu(EDTA)^{2-}+2e^-=Cu+EDTA^{4-}$$

Overall reaction

$$2HCHO+4OH^-+Cu(EDTA)^{2-}=Cu+2HCOO^- +2H_2O+H_2+EDTA^{4-}$$

If copper is existed as ions (cuprous or cupric) in alkaline solution, it will form hydroxide and be precipitated[10]. And then formation of stable complex is very important. There are many copper organic complexes and among them copper formed very stable complex with EDTA[11]. From above reactions, copper was reduced from EDTA complexed solution by oxidation of formaldehyde

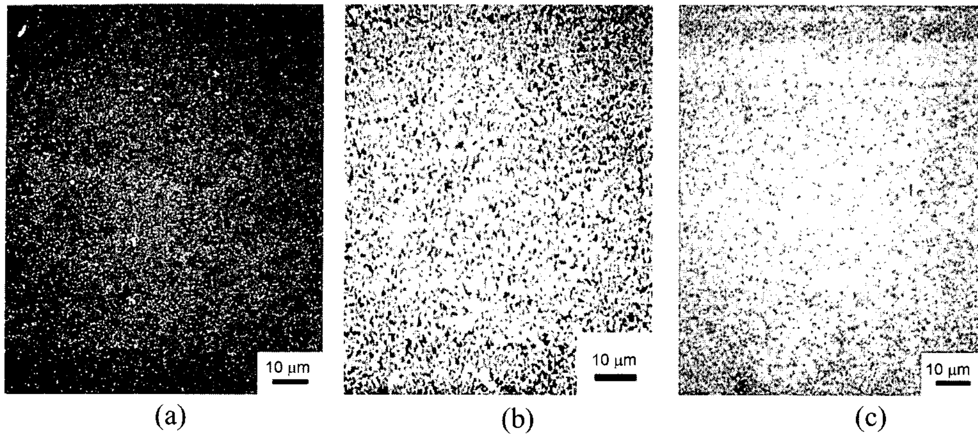


Fig. 4. SEM images of copper on glass, silicon wafer and TiN substrate. (a) silicon wafer (b) glass (C) TiN.

Table 2. Selectivity of pretreatments on different substrates.

Method \ Substrate	Cu	Ti	Alumina	Si-wafer	Glass	TiN	Ta
Activation	O	O	X	X	X	X	Δ
Sensitization/Activation	O	O	O	Δ	Δ	Δ	O
Etching Sensitization/Activation	O	O	O	O	O	O	O

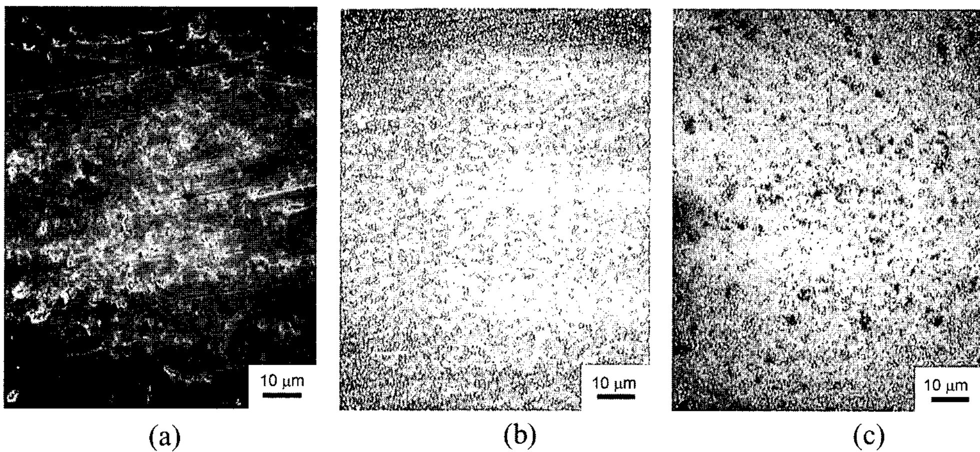


Fig. 5. SEM images of surface with pH (a) pH 11 (b) pH 12 (c) pH 13.

and hydrogen was evolved at the same time. As pH increased, the reaction proceeded to right by Le Chatelier's principles. Since then, deposition rate was sensitively changed with pH. Fig. 5 shows surface morphology at different pH. Copper was not deposited under pH 11. It is due to the electrode potential of formaldehyde is not low enough to reduce copper at low pH solution. Copper was deposited over pH 11 and formed uniform coating. At pH 13, grain size was getting bigger due to high deposition rate.

3.3 Effects of stabilizer

To reduce surface tension and residual stress, sta-

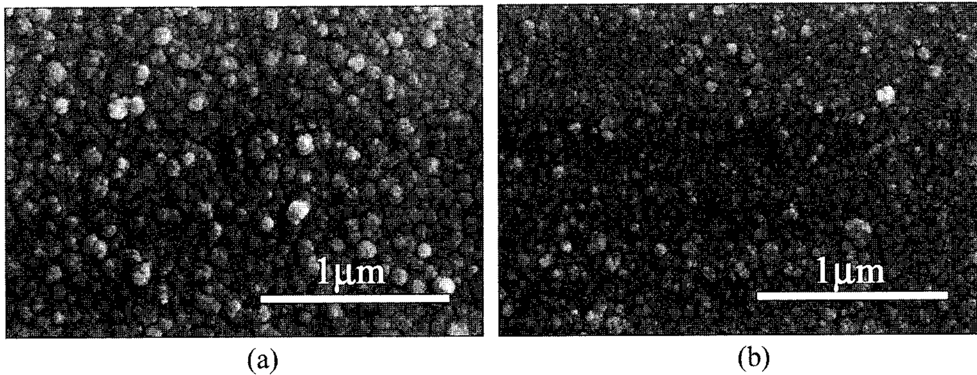


Fig. 6. SEM images of copper deposited copper on Ta substrate with stabilizer addition. (a) 2 ppm (b) 3 ppm.

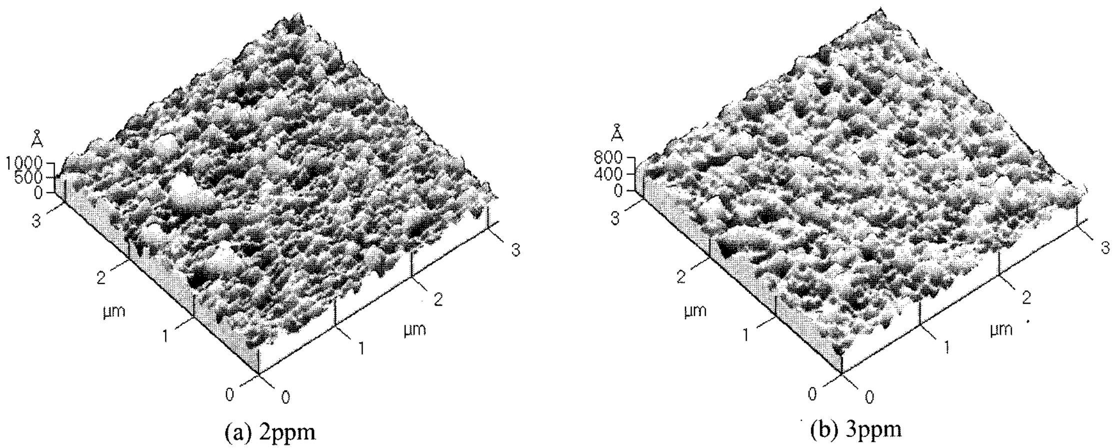


Fig. 7. AFM micrograph of copper layer (1500) on Ta substrate with stabilizer addition. Average Ra(a)=125Å (b)=69Å.

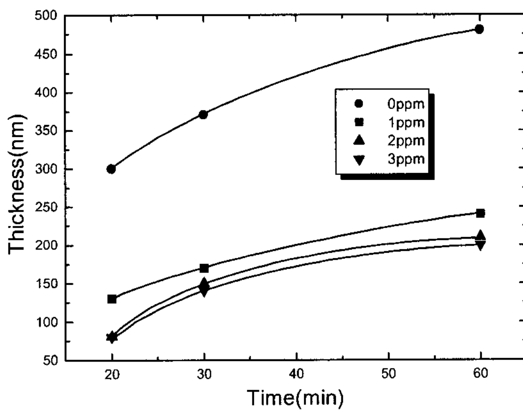


Fig. 8. Deposit ion rate of electroless copper on titanium nitride with time.

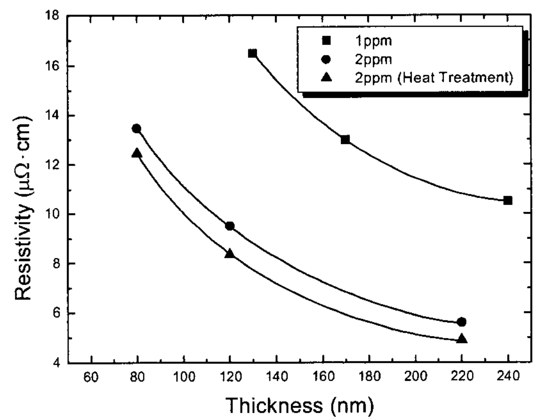


Fig. 9. Resistivity of electroless copper layer with thickness.

bilizer was added to plating bath. In this research, 2,2-bipylidyl was used as stabilizer[12]. Fig. 6 shows typical surface morphology of copper coating with stabilizer addition. The copper coating is uniform and dense. The adhesion is very good and the interface was broken at 15N from scratch test. The grain

is finer when stabilizer concentration was increased. Surface roughness was improved with 3 ppm addition. Fig. 7 shows the AFM images of copper surface.

The deposition rate was decreased with addition of stabilizer. Fig. 8 shows deposition rate with time at different stabilizer concentration. Even sacrificing deposition rate, the resistivity of copper was improved with addition of stabilizer. After heat treatment resistivity was lower about 25%. Fig. 9 shows resistivity of copper coatings. As coating is thinner, the resistivity increased. It is due to interface effects on resistivity of copper.

4. Conclusion

The important conclusions derived from the research conducted are enumerated below.

1. From the results of selectivity test, copper was deposited only on catalyzed surface. The selectivity of electroless copper plating was sensitively changed with pretreatments. To improve uniformity and adhesion of copper on silicon and glass, mechanical or chemical eching is required.

2. The deposition rate was affected by pH. Under pH 11, copper cannot be deposited due to the electrode potential of formaldehyde is not low enough to reduce copper.

3. The uniform copper layer on TiN or Ta substrate was obtained at 30°C, 5 gpl cupric sulfate, 10 gpl formaldehyde, 40 gpl EDTA and pH 12. The deposition rate was 5 nm/min with 2 ppm stabilizer addition.

4. The resistivity of copper was decreased with addition of stabilizer and after heat treatment.

Acknowledgement

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