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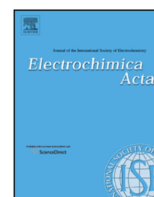

Plating Uniformity of Bottom-up Copper Pillars and Patterns for IC Substrates with Additive-assisted Electrodeposition

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ABSTRACT

Electrochemical behaviors of the base electrolyte containing different additives were investigated by galvanostatic potential transient measurements (GM), cyclic voltammetry tests (CV) and potentiostatic measurements. Copper deposits on sputtering copper seed from physical vapor deposition (PVD) were examined by a scanning electron microscope and X-ray diffraction spectra. Cross sections of copper pillars and fine line patterns were observed by metallographic microscope. GM result revealed ethylene oxide-propylene oxide co-polymer (EO/PO) performed a further inhibition on copper deposition in the presence of 60 ppm chloride ions as the increment of EO/PO concentration. GM, CV and potentiostatic results indicated that copper deposition was accelerated by synergetic effects of additives in the base electrolyte containing 60 ppm chloride ions, 20 mg/L EO/PO and 0.7 mg/L bis-(sodium sulfopropyl)-disulfide. Sputtering PVD copper seed with even deposit surface was recommended to form the uniformity of copper deposition through increasing the growing density of copper particles. Oscillatory was employed to form uniform distribution of copper deposits in thickness. Copper grain growth was preferentially [111] textured. Bottom-up copper pillars and fine line patterns with plating uniformity were fabricated to meet the requirement of an accurate impedance and the high density interconnection for IC substrates.

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1. Introduction

Defect-free copper electrodeposition for interconnection has become increasingly important for its good reliability and electrical performance [1–5], compared to conductive paste filling interconnection [6,7]. Metallization by copper electroplating is involved in through holes and microvias of printed circuit boards. However, barrel electroplating through holes with large-diameter hinder the development of high density interconnection of electronic products with the demand of the miniaturization and multi-functionalization. Stacked microvias with copper superfilling promote the copper metallization technologies to cope with the shrinking interconnect dimensions of printed circuit boards [8], especially integrated circuit (IC) substrates directly used for chip integration.

The filling property of an electrolyte for vias depends on organic additives. Organic additives can enable void-free filling in features, minimal topography of the final copper surface, and controllable impurity incorporated in the copper deposits [1,9–12]. These additives synergistically contribute to bottom-up filling behavior of copper deposits in the vias, making the plating rate at the bottom of features much faster than that at the top. The accelerator and chloride ions synergistically activate the electrodeposition process at the via bottom while the suppressor forms a complex Cu^{+} and Cl^{-} inhibition layers adsorbing on copper surface to limit the deposition of copper at the via opening and promote the acceleration reaction at the via bottom. [5,13–15]

Plating uniformity is emphasized due to the stricter requirement of z-interconnects between chip and IC substrates while uneven copper deposits could increase soldering stress from thickness distribution difference. Plating copper with rough deposits could cause significant skin effect during electric signal transferring at high frequency. Many studies were carried out to improve copper metallization uniformity in high-density z-interconnects. Early work by Yung et al. [16] proposed pulse plating to pursue the uniform distribution of copper plating in microvias by investigating the effect of reverse plating time, reverse current density, the shape of waveforms and agitation. Yang et al. [17] pointed out that the plating uniformity could be significantly enhanced with segmented anode by controlling the current allocation. Various levelers (ie. Janus Green B and Diazine Black) were used for the

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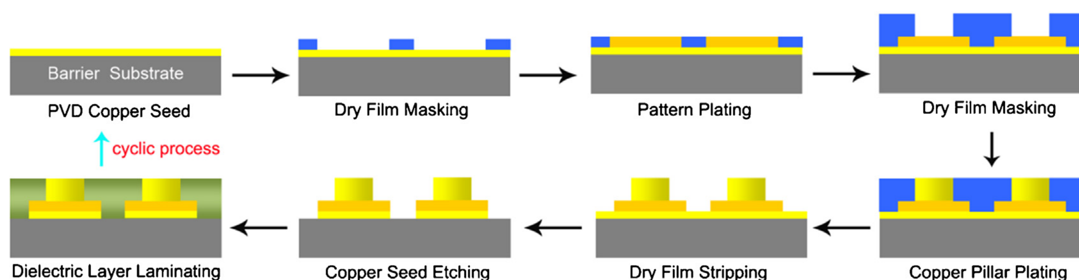

Fig. 1. Processes of bottom-up fill for z-interconnection with copper electrodeposition.

copper plating process in order to adsorb preferentially on the protrusion of copper deposits, attributing to the selective adsorption of the quaternary ammonium cation [18–20], but these dye-type levelers were not preferred to bottom-up fill process because they would cause grain boundary defects of the copper deposits. Dow et al. [10,19] found small nodules and pinholes concentrated in the surface of copper deposits when diazine black was used as leveler in copper electrodeposition. Plating uniformity of copper deposits could also be increased through optimizing additive concentration and plating parameters [21].

The purpose of this paper was to use effective additives to improve the plating uniformity of bottom-up copper pillars and fine line patterns with additive-assited copper deposition. Electrochemical behaviors of the base electrolyte containing different additives were investigated by a potentiostat. The copper deposits were characterized by SEM and XRD. Cross sections of copper pillars and fine line patterns were observed by metallographic microscope.

2. Experimental

Electrochemical behaviors of the base electrolyte with different additives in a glass vessel were characterized by an AUTOLAB potentiostat (AUT85266) with a three-electrode cell at 25 °C. A platinum rotating disk electrode (RDE) with a diameter of 3 mm was used as the working electrode. A small copper bar was employed as the counter electrode (CE) in a small glass tube separated from the main electrochemical cell. The end of the small glass tube was sealed with a porous ceramic material to prevent direct contact of the additives with the CE during analysis. Saturated mercurous sulfate electrode (SSE) was used as the reference electrode (RE). The base electrolyte for the electrochemical experiments contained 0.40 mol/L $CuSO_4{\cdot}5H_2O$ and 1.80 mol/L H_2SO_4 in distilled water. Bis-(sodium sulfopropyl)-disulfide (SPS) was diluted to 1 g/L by the distilled water to act as the accelerator. Ethylene oxide-propylene oxide co-polymer (EO/PO) with average molecular weight of 4000 was diluted to 2 g/L and used to suppress copper deposition. Effects of the additives on copper electrodeposition were analyzed to investigate their impacts on the bottom-up filling. Electrochemical tests of the electrolyte were involved in galvanostatic potential transient measurements (GM), cyclic voltammetry (CV) tests and potentiostatic measurements.

All copper seeds with 1 μm in thickness were sputtered on barrier substrate for 5 min using physical vapor deposition (PVD) in the condition of sputtering power of 20 kW and argon gas flow rate of 200 sccm. PVD copper seed on barrier substrate (40cm × 50 cm in area) was pretreated by degreasing, microetching and predipping processes before copper electrodeposition. Thereafter, the barrier substrate with a PVD copper seed was placed in the plating fixture to carry out copper electrodeposition in the base electrolyte containing 0.7 mg/L SPS, 20 mg/L EO/PO and 60 ppm chloride ions. The process of copper electrodeposition was performed in a vertical continuous plating (VCP) line with air agitation at the current density of -18~20 mA/cm^2. A 10 μm thick copper layer was deposited to evaluate the plating uniformity of copper deposits on barrier substrates with a copper seed or a rolled copper sheet. The surface morphologies of copper deposits were examined by a scanning electron microscope (SEM). The grain growth of copper deposits was monitored by X-ray diffraction spectra (XRD).

PVD copper seed on barrier substrate was pretreated by the same processes as above. Thereafter, dry film was through masking on PVD copper seed and was exposed and developed to form vias and parterns. Bottom-up copper pillars and fine line patterns were fabricated on through-masking PVD copper seed by copper electrodeposition at -18~20 mA/cm^2 current density in the condition of air agitation and oscillatory. Base electrolyte containing 0.7 mg/L SPS, 20 mL/L EO/PO and 60 ppm chloride ions was employed to accomplish copper electrodeposition. Fig. 1 displayed the processes of bottom-up filling copper pillars and patterns for z-interconnects of IC substrates. Cross sections of copper pillars and fine line patterns were observed by metallographic microscope, compared to that of fine line patterns formed by semi-additive process [22].

3. Results and Discussion

3.1. Effects of additives on electrochemical deposition of copper

The potential transients during galvanostatic plating with the injection of the suppressor (EO/PO) in different concentration were used to characterize the effects of EO/PO, as shown in Fig. 2. The potential of the electrolyte significantly decreased from −0.448 V to −0.484 V vs. SSE during the first 30 s, and shifted slightly towards higher overpotential of −0.495 V vs. SSE

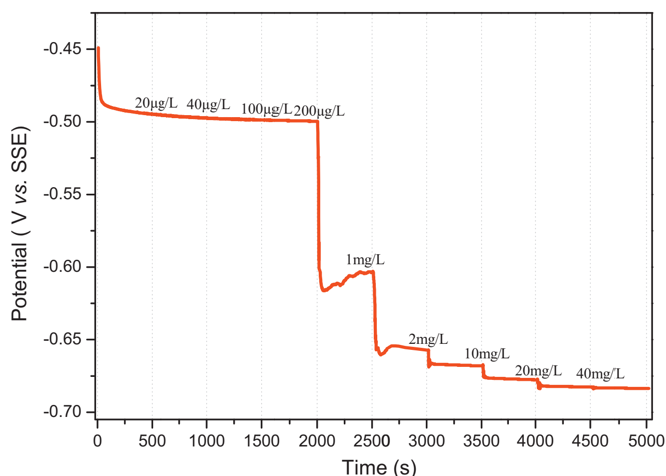

Fig. 2. Potential transients of GM during galvanostatic plating with different injecting concentration of EO/PO: Rotation speed of RDE at 3 mm diameter is 1000 rpm and the applied cathodic current was −1.4 mA; The electrolyte is composed of 0.40 mol/L $CuSO_4{\cdot}5H_2O$, 1.80 mol/L H_2SO_4 and 60 ppm chloride ions.

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