



Electrodeposited copper using direct and pulse currents from electrolytes containing low concentration of additives

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ABSTRACT

This work examines the effect of pulse deposition using a “lean” electrolyte, i.e., an acid-free bath with low cupric ion and additive concentrations using direct and pulse current. To this end, 25 μm copper films have been plated on stainless steel substrates from electrolytes containing only cupric ions, chloride and commercial additives. Films have been deposited from electrolytes containing different concentrations of additives ranging from 17% to 200% of the levels recommended by the supplier. The morphology of deposits was characterised using scanning electron microscopy and grain size has been determined using electron backscattered diffraction (EBSD). The crystalline structure has been examined using x-ray diffraction (XRD). It was found that although pulse currents or increasing amounts of chemical additive can reduce the grain size, the mechanisms for size reduction may be different. Whilst current pulsing helps the generation of new nuclei, using additives suppresses grain growth. Mechanical and electrical measurements of these films showed that pulsing currents provide deposits with better mechanical and electrical properties. This has been attributed to lower number of defects when pulse currents are used. Our results also show that by using pulse currents, electrolytes containing low levels of additives and metal ions can be used to obtain copper deposits attaining industry specifications. Combining pulse currents with lean electrolytes may be therefore beneficial to the environment.

1. Introduction

Copper is the main material used to fabricate interconnects for electronic devices and in printed circuit boards (PCBs) [1,2]. These industries typically require copper deposits to have certain attributes; in particular, low electrical resistance must be coupled with good mechanical properties [3]. Such specific properties are imparted by using electroplating processes where acid concentration and metal ions are prescribed through experience, which are typically 2.0 M H₂SO₄, and 0.6 M CuSO₄, respectively [4]. In addition, particular amounts of commercially available additives are also recommended by suppliers [4].

A recent advance in electrochemical mask-less patterning [5] process showed that micro-scale copper features, such as those required in PCBs, can be formed by dissolution [6] or deposition [7] using an acid-free, low copper ion concentration (0.1 M CuSO₄) electrolyte [8]. Their research also showed that lower concentrations of commercial plating additives could be added to improve deposit morphology and properties, so that they are suitable for industrial applications [9].

Indeed, using such ‘lean’ electrolytes, i.e. acid-free, and containing low concentration of metal ions and additives can significantly reduce

environmental impact of deposition processes [9,10]. Although there have been investigations on metal recovery from rinse waters or spent electrolytes [11,12] which contain low concentrations of metal ions and additives, but the quality of deposit is not important in those operations. Much less research has been carried out to determine if ‘lean’ electrolytes can be used for plating high quality deposits which is the focus of the current paper.

One methodology that has been used to eliminate or lower additives in electrolytes is the use of pulsing currents [13] which has been applied successfully to plate chromium [14] and copper [15]. Whilst in direct current (DC) deposition a constant current is applied, in pulsed current (PC) deposition the applied current is switched on and off repeatedly [16]. Prior research has already shown that pulse currents can change grain size due to generation of new nuclei [17–19]. In addition, there is sufficient evidence that pulse currents can influence the action of levelling agents for higher levels of metal ion concentrations and additives [13,20–23]. These earlier studies indicate that current modulation could become a significant factor in modification of deposit properties when metal ion and additive levels are low. This work aims to elucidate: (i) how the content of commercial additives influences the properties of pulse plated deposits from lean electrolytes; (ii) how do

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these two parameters interact when they are used in unison, and (iii) can pulse deposition be used to match industry specifications when low levels of metal ions and additives are used.

For this purpose, copper was deposited using direct and pulse currents (DC and PC). The additives used were Gleam A and B (Dow Chemical) which are typically used in PCB manufacturing. The lean electrolyte consisted of 0.1 M CuSO₄ and 17%, 33%, 50%, 100% and 200% of the additive concentration recommended by the supplier. In order to compare deposit properties obtained using these parameters, a standard deposition process using a solution of 0.63 M CuSO₄ with 2.0 M H₂SO₄ with recommended levels of additives (by supplier) was also used.

Copper films of 25 μm thickness were plated on polished dog-bone shaped steel substrates as per standards of the Institute of Interconnecting and Packaging Electronic Circuits (IPC) without agitation [24]. Deposit morphology of the films was examined using scanning electron microscope (SEM), and grain size and texture were determined using electron backscatter diffraction (EBSD). Crystal structure was ascertained by x-ray diffraction (XRD). The yield strength and resistivity of the foils were measured to compare against those recommended by IPC. Deposit properties are interpreted in terms of additive concentration and the mode of current applied. The findings were used to determine if pulse currents could be used to obtain deposit properties of industry standard using electrolytes containing low concentration of metals and addition agents.

2. Experimental

2.1. Plating apparatus

Both direct current (DC) and pulsed current (PC) plating were performed using a classic two-electrode plating cell. The details of the plating system are described in a previous work [9]. Steel cathodes (308 grade) were manufactured to the specifications of IPC-TM-650 (IPC-TM stands for The Institute for Interconnecting and Packaging Electronic Circuits Testing Methods) standard [24]. A Cu rod (99.999% purity) was used as the anode. The anode-to-cathode area ratio was set at 2:1 to minimise polarisation at the anode. A Thurlby Thandar (PL-303) power supply was the DC source, whilst the Plating Electronics (PE86CB 3HE) pulse rectifier was the PC supply.

2.2. Chemicals and electrolytes

Electrolytes were prepared using technical grade CuSO₄, and when needed, H₂SO₄, (Sigma-Aldrich), and deionised water. The additives used were from a commercially available acid copper plating process (Copper Gleam™ HS-200, Dow Chemicals). The roles of the different additive components have been investigated and reported [25] in an earlier paper. Reiterating those findings, the component Copper Gleam HS-200 A is an accelerator, containing bis (sodiumsulfopropyl) disulphide (SPS) or its derivative mercaptopropene sulfonic acid (MPS). The component Copper Gleam HS-200 B is a suppressor, based on a high-molecular weight polyalkyl glycol compound such as polyethylene glycol (PEG).

These additives require the addition of a promoter, Cl⁻, which was supplied using laboratory grade 37% HCl. It should be noted that the inclusion of HCl is in very low quantities, and is solely to enable additive action – it does not act as supporting electrolyte. Chemicals used for cleaning stainless steel (SS) substrates were concentrated HNO₃ and ethanol (Sigma-Aldrich). PRP200 photoresist (Electrolube) was used to insulate the back of the substrates. Table 1 lists the composition of the different plating electrolytes used in both DC and PC plating operation.

2.3. Plating procedure

Prior to plating, the stainless steel substrates were dipped in

concentrated nitric acid for 1 min, and rinsed in deionised water for another minute. One side of the substrate was mechanically polished using silicon carbide sheets starting at grit #220 up to #4000 to obtain a mirror finish. The other side was insulated with photoresist to ensure that metal deposition occurred only on the one side. The exposed part of the substrate was swabbed with acetone for 30 s and air-dried at room temperature before it was immersed in the electrolyte for deposition.

Electrodeposition was carried out first using DC and then by PC mode to decouple the effect of additives from current modulation. Table 2 shows the plating parameters used in the DC plating experiments. Table 3 presents the plating parameters used in the PC plating runs. The choice of pulse parameters is more complex than DC ones, and a detailed description governing their choice is presented in Section 3. As shown in the tables, for both DC and PC plating, the current was set at 40% of the corresponding limiting current. This current was chosen because it is well known that at this current density dendritic growth of deposit is unlikely. Plating efficiency for both current waveforms were determined from a separate set of experiments [25,26], which are also included in the tables. In both cases the plating time was adjusted to ensure that the nominal thickness was the same.

In the deposition experiments, no mechanical stirring was employed and the total plating time was set to obtain a nominal film thickness of 25 μm. After the allotted plating time was reached, the substrate was removed from the solution, washed with deionised water for 1 min, wiped with lint free cloth, and left to dry in air. The plated Cu films were then carefully peeled off from the SS substrate, and were prepared for subsequent characterisation.

2.4. Characterisation

The plated specimens were subjected to different characterisation techniques: (i) SEM and EBSD (Hitachi SU-6600 EBSD system) to determine morphology, grain size and texture; (ii) XRD (PANalytical X'pert Pro) to assess crystal orientation, (iii) tensile test (Tinius Olsen H50KS) to determine mechanical properties; and (iv) four-point probe (Sigmatone Pro4) to analyse electrical properties. In order to carry out these analyses, a total of five films from each electrolyte were used. One film was used for the SEM, EBSD and XRD analysis. A second film was used to carry out the four-point probe test, and the remaining three were used for tensile tests.

For SEM, XRD and EBSD analysis, a 2 × 2 cm² area was cut out from the central portion of the Cu film. Grain size was determined using the software TANGO (HKL Technology A/S, 2001), which can be used to study EBSD orientation maps and extract crystallographic information. The grain structure map was obtained by adjusting band contrast (i.e. noise reduction and wild spikes extrapolation) to clearly reveal grains. The grain size parameter used is the major and minor axis of a fitted ellipse, and the software automatically measured the grain size based on the delineation of all of the grain boundaries.

For mechanical and electrical resistivity tests, a full film was used. Necessary care was taken to prevent damage on the Cu films, particularly during handling and specimen mounting which could compromise the quality of the mechanical tests. The tensile measurements followed ASTM-E345 [27], which is the standard for metallic films.

3. Determination of pulse parameters

Compared to DC plating, a simple pulse current wave-form has several variables that can influence deposit properties [13–15,28–30]. Fig. 1 shows a unipolar waveform together with important pulse parameters. The pulse on time, T_{on} , is the length of time the peak-current is applied, whilst the pulse off time, T_{off} , is the duration when the current is switched off. The sum of T_{on} and T_{off} is the total pulse period, T_p . Often, for convenience, the parameters are expressed using duty cycle, γ , and T_p which are related by:

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