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Assessment of activated polyacrylamide and guar as organic additives in copper electrodeposition

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Abstract

The effect of current density, temperature, diffusion layer thickness (δ), deposition time, Guarfloc66 (Guar) and activated polyacrylamide (APAM) on the topography (surface roughness) of electrodeposited copper was studied. The level of these variables approximates current commercial copper electrowinning (EW) and electrorefining (ER) operating conditions. The effect of Guar and APAM on surface roughness and number of Peaks-per-Centimeter was assessed both in combination and alone using a rotating cylinder electrode (RCE) for up to 6-hour EW time. Observed effects on surface roughness indicate that a more uniform surface and lower roughness/smoother copper deposits were obtained using the additive APAM rather than Guar. Regression models indicate APAM has a significant effect on reducing surface roughness at 65 °C.

Bench-scale *continuou*s electrowinning tests were carried out at 50 °C for 44.6 h using parallel plate electrodes into which APAM and Guar were dosed continuously and independently. These tests also indicated that APAM produces smoother deposits than Guar. The cross sections of the copper deposits from these tests showed that APAM exhibits a *slightly columnar* copper deposit and Guar produced a *porous* copper deposit. The copper deposit produced with additive APAM was brighter and produced greater amounts of both smaller and larger crystallite sizes than those obtained with Guar. This infers that APAM favours higher nucleation rates and greater 3D crystallite growth and coalescence than Guar.

Keywords: Copper; Electrodeposition; Electrowinning; Electrorefining; Polyacrylamide; Rotating cylinder electrode; Guar; Surface roughness; Statistical analysis

1. Introduction

In the copper deposition industry in general, organic additives and chloride ions need to be dosed to produce smooth deposits, free of voids or porosity. It is also known that organic additives significantly influence the current–potential relationship due to their competition for surface coverage with the components of the electrolyte system including chloride ions. Therefore these organic additives must be carefully selected according to their role at the metal/electrolyte interface to control the nucleation and growth during the deposition process. Table 1 summarizes the industry-standard additives used in copper EW, ER and in the damascene process for micro-electronics industry. Table 1 shows the typical concentration of these organic additives in

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the electrolyte bath and their respective roles. An electrode is polarized when, under constant experimental conditions, the potential in the presence of an additive, e.g., animal glue, PEG, is more negative than the potential without the additive. An electrode is depolarized when the potential in the presence of an additive, e.g., chloride ions, is less negative. The polarizer/inhibitor/leveller controls the vertical growth to produce smooth deposits by conferring preferential adsorption on the peaks or active sites. The grain refiner/accelerator may predominantly control the nucleation process or promote the formation of new nuclei to possibly form new crystallites at the recesses (Vereecken et al., 2005). This synergistic process between the inhibitor and grain refiner is aimed at improving the overall quality of the copper deposit: purity, smoothness and plant productivity i.e., elimination/reduction of short-circuits caused by dendrites.

The first step of metal deposition is the formation of nuclei of the depositing metal on a foreign substrate and on a substrate of the same metal. The structure of the first monolayer(s), has an impact on the deposition of further layers and therefore on the morphology of the deposited metal. The competition between nucleation and growth determines the smoothness of the deposit: the higher the nucleation rate; the finer the crystal size (Budevski et al., 1996). Moreover, the forms of the growing crystals determine their physical appearance and structure. A higher crystal size growth rate, normal to the substrate, leads to a more fibrous/columnar structure. A brightening effect can be achieved when large developed crystal faces grow parallel to the substrate (Budevski et al., 1996).

It has been shown elsewhere (Fabian, 2005; Fabian et al., 2006b) that a rotating cylinder electrode (RCE) may be applied as a novel method of determining the effect of the preparation media of polyacrylamide (PAM) on the surface roughness of electrodeposited copper. It has been shown that when a high molecular weight PAM (MW 15 million Dalton) is prepared in 16-fold diluted copper electrolyte at 50 °C for 2 h and dosed into an EW cell, the electrodeposited copper had a significantly lower mean surface roughness than was the case when polyacrylamide was prepared in water or full-strength electrolyte or alkaline solution. The hydrolysis of PAM in pH 2 solutions is reported to produce a block copolymer (Halverson et al., 1985; Panzer and Halverson, 1988; Panzer et al., 1984). The PAM hydrolysed in 16-fold diluted copper electrolyte (pH 1.5) was named 'activated polyacrylamide' (APAM). It has been also shown that APAM also produced deposits exhibiting a lower surface roughness than polyacrylic acid (Fabian, 2005).

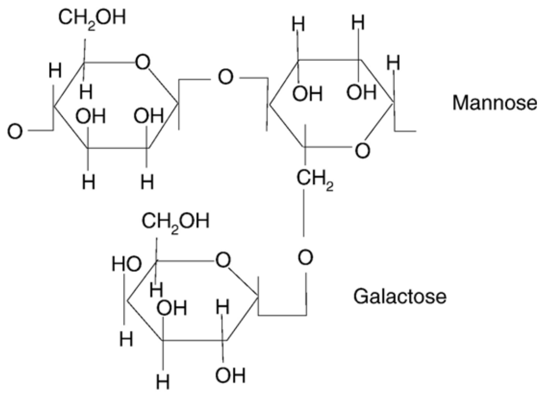

Fig. 1. The chemical structure of Guar based on Mark et al. (1969).

Guar is a naturally occurring galacto-mannan polymer, a polysaccharide, used as flocculant and coagulant with typical molecular weights ranging from 200,000 to 500,000 Da. Guar is a linear D-mannose sugar with a D-galactose sugar chain on every other mannose as shown below, Fig. 1 (Mark et al., 1969). Guar is the industry-standard organic additive used in copper EW as a weak levelling agent for about 40 years to produce bright copper deposits (Langner et al., 1989; Stantke, 1999).

Pye and Schurz (1957) patented the electrowinning of zinc and copper in the presence of polyacrylamide. They reported that acrylamide polymer can be dissolved in water or electrolyte. Vereecken and Winand (1976) compared the influence of non-ionic and cationic

Table 1
Industry-standard additives used in copper electrometallurgy

Role of the additive	Electrorefining		Electrowinning		Micro-electronics, PCB and IC	
	Additive	mg/L	Additive	mg/L	Additive	mg/L
Leveller	Glue	1	Nil	Nil	PEG* and JGB	100–300 and 1
Brightener**			Guar	0.25–5		
Grain refiner***	Thiourea	2	Nil	Nil	SPS/MPSA	1/1
Depolarizer	Cl^-	50–60	Cl^-	20–25	Cl^-	40–60

*PEG, polyethylene glycol; SPS, bis(3-sulfo-propyl) disulfide; JGB, Janus Green B (safranine dye); MPSA, 3-mercapto-1-propanesulfinate. **Guar is also known as weak polarizer in the industry. ***Grain refiner or accelerator.