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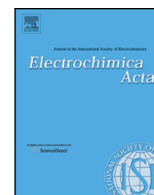

The impact of cations on nucleus density during copper electrodeposition

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ABSTRACT

High nucleus density is among the most important factors in determining the success of the direct-copper-electrodeposition technique. A group of inorganic species including potassium sulfate (K_2SO_4), sodium sulfate (Na_2SO_4), magnesium sulfate ($MgSO_4$), and copper sulfate ($CuSO_4$) were investigated in terms of their impact on copper nucleus density during galvanostatic electrodeposition of copper onto foreign substrates. Newly formed copper nuclei on the substrate were observed using scanning electron microscopy (SEM) and then manually counted to obtain nucleus density data. Results show that in the presence of K_2SO_4, copper nucleus density can be increased by a factor of up to 7, while Na_2SO_4 may lead to at least double increase of nucleus density. Electroanalysis indicates that the overpotential increase as a result of adding relevant sulfate salts may account for the increased nucleus density.

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1. Introduction

Since its first application as interconnects in the semiconductor industry in 1997, copper (Cu), with its lower resistivity that leads to decreased resistance-capacity (RC) delay, has been replacing the historically dominant interconnect material aluminum (Al). The formation of a continuous and void-free Cu thin film is key to the fabrication of Cu interconnects in microelectronics. Among the various techniques of Cu thin film deposition such as chemical vapor deposition (CVD), physical vapor deposition (PVD) and sputtering, the electrodeposition method stands out as least expensive, easily compatible and highly productive [1–4]. In a typical dual damascene process, prior to the bulk electrodeposition of Cu, a thin Cu seed layer (~20 nm thick) is deposited usually by sputtering or atomic layer deposition (ALD) onto the foreign barrier layer that covers the underlining features [4–6]. However, as the feature sizes of the integrated circuits are driven by Moore's Law to decrease year by year, it has become more challenging to form a continuous Cu seed layer onto the miniaturized features especially when they are below 30 nm in size. Therefore, in the recent years, much attention has been focused on directly electrodepositing Cu onto barrier layers [7–10].

Since foreign substrates possess significantly different platforms for copper nucleation and growth, the initial stages of Cu electrodeposition may serve as an important role in determining the quality of the final Cu film [11,12]. As shown in Fig. 1, the formation of a Cu film on a foreign substrate consists of four stages (nucleation; nucleus growth; start of coalescence; and film formation) assuming that Cu nuclei follow a three-dimensional (3D) hemispherical growth mode. The nucleus density in Stage I directly influences the thickness of the newly formed film in Stage IV, with higher nucleus density leading to thinner film thickness. Furthermore, the coalescence thickness b_{coal}, defined as the thickness of the film when Cu nuclei begin to coalesce to a continuous film, is inversely proportional to the square root of the nucleus density $N: b_{coal} \propto N^{-0.5}$ [13,14]. Therefore, a high nucleus density is the prerequisite to obtaining a thin and void-free Cu film. Many experimental conditions have been investigated in order to increase the nucleus density such as cupric ion (Cu^{2+}) concentration, acid concentration, organic additives, diffusion barrier material, and the rate and waveform of the plating [2,11,13,15–19]. Others have also studied the impact of inorganic species which is primarily used as background electrolyte for improving electrolyte conductivity: Grujicic et al. reported that the sodium sulfate (Na_2SO_4) as a background electrolyte influenced the copper nucleation mechanism as well as the morphology of copper nuclei [2]; Majidi et al. reported that the background electrolyte (potassium sulfate, K_2SO_4) may cause electrodeposition of Cu to occur at more negative potential [3]; and Nagar et al. have shown that some compositions of cupric sulfate ($CuSO_4$), chloride ion (Cl^-) and sulfuric acid (H_2SO_4) may result in high nucleus density [13]. However, a systematic investigation of the relation between the inorganic species and Cu nucleus density under galvanostatic condition is lacking.

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Nomenclature

List of symbols

N	Cu nucleus density in unit cm^{-2}
b_{coal}	coalescence thickness in unit nm
η	cathodic overpotential in unit V
t	time in unit s
F	Faraday constant, 96,485 C/mol
R	gas constant, 8.314 J/(mol K)
T	temperature in unit K
a,b, a' and b'	constants used in nucleation equations

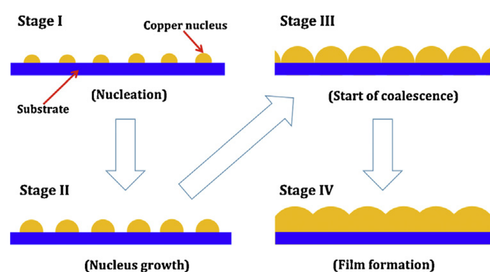

Fig. 1. Four stages of Cu film formation on a foreign substrate.

In this work, we show the impact of several inorganic species on the nucleus density during the initial stage of direct copper electrodeposition onto two substrates (glassy carbon and ruthenium coated silicon wafer) under galvanostatic operation. Results are interpreted with electrochemical analysis and show that nucleus density can be correlated with overpotential, which varies with the cation of the supporting electrolyte.

2. Experimental

Polarization curves of the plating baths were measured on both a lab-fabricated Cu rotating disk electrode (RDE) and a glassy carbon RDE (Pine Instrument) with a rotation speed of 900 rpm. The Cu RDE was made by pre-depositing Cu onto a platinum (Pt) RDE (Pine Instrument) at a current density of -40 mA/cm^2 in a plating bath containing 0.5 M $CuSO_4$, 0.3 M H_2SO_4 and 1.4 mM HCl for 4 min with a rotation speed of 900 rpm. In each experiment, a linear sweep voltammetry (LSV) was carried out from 0.2 V to -0.4 V (vs Ag/AgCl reference electrode (RE)) with a scan rate of 10 mV/s using an EcoChemie type III μ Autolab potentiostat.

Several glassy carbon plates (Alfa Aesar) and a ruthenium (Ru) coated silicon (Si) wafer (Lam Research) were used as working electrodes (WE) in the electrodeposition experiments to provide the foreign substrate surface for direct Cu plating. The Ru coated Si wafer was covered by 10 nm thick Ru using PVD method, and its sheet resistance was measured to be 38.9 $\Omega/\square$ using a four-point probe. Glassy carbon plates were cut into coupons with a dimension of 1.5 cm x 1 cm using an IsoMet® low speed saw (Buehler) while the Ru coated wafer was cleaved into coupons of the same dimension with a diamond scriber. Then each coupon was attached to one end of a copper strip (2 cm x 3 cm in dimension) using silver paste (Ted Pella). The copper strip with the coupon was covered by Kapton tape leaving a circular region on the coupon surface with a diameter of 3 mm by a hole-punch tool. The preparation process proved to help minimize the resistance between the electrical contact and the exposed area, resulting in reproducible potential transients during galvanostatic electrodeposition experiments.

An acidic electrolyte with 0.25 M $CuSO_4$ (Fisher Scientific), 0.3 M H_2SO_4 (EMD Chemicals) and 50 ppm Cl^- (added as 1.4 mM HCl (Fisher Scientific)) was used as the main plating bath which is termed as VMS. In industrial production, a small amount of one or several organic additives categorized as suppressor, accelerator and so forth are usually utilized in the plating bath to help achieve specific goals such as bottom-up filling or so-called "super filling" of Cu within high-aspect-ratio features. Polyethlylene glycol (PEG) is among the commonly used additives as a suppressor and has been extensively characterized [20]. In order to approximate industrial application, 300 ppm PEG was added to all the plating baths. The inorganic species investigated in this study are Na_2SO_4, K_2SO_4, $MgSO_4$, and $CuSO_4$. A series of candidate plating baths were made by separately adding 0.3 M of one of the above sulfate salts to the VMS. The PH of all the plating baths was measured to be around 0.25 since the concentration of H_2SO_4 and HCl was fixed in all experiments.

Electrodeposition experiments were controlled using an EcoChemie type III μ Autolab potentiostat. The galvanostatic electrodeposition method was chosen in order to be consistent with industrial application. In addition, the applied current density is a key parameter to control nucleation rates. Current density was fixed at -20 mA/cm^2 for galvanostatic electrodeposition. Plating time was set to 0.96 s, the value calculated from Faraday's law in order to form a 7 nm thick Cu film (0.019 C/cm^2 charge passed) by assuming 100% current efficiency. The electrodeposition experiments were conducted in a beaker set-up with three electrodes: working electrode (WE), counter electrode (CE), and reference electrode (RE). A Ag/AgCl RE was used to measure the potential of the WE, and a Pt wire was used as the CE. As the plating time of 0.96 s was rather short, the possible leakage of the Cl^- ion from the Ag/AgCl RE to the plating bath could be safely neglected. Either a glassy carbon coupon or a Ru coated wafer coupon was used as the WE in each electrodeposition experiment. The distance between the WE and CE was ~2 cm while that between the WE and RE was ~0.5 cm. The electrodeposition experiment started within 2 seconds after immersion of the WE into the plating bath, after making sure there was no bubble on the WE surface. Then, within 1 s after the completion of electrodeposition, the WE was removed from the plating bath, flushed with deionized (DI) water, and dried with pure nitrogen (N_2). Under such treatment, the dissolution of the deposited Cu back to the plating bath was assumed to be negligible.

A Hitachi 4700 scanning electron microscope (SEM) was used to observe copper nuclei on the samples. For each sample, six SEM images were captured from six different locations on the sample to estimate its average nucleus density. In order to ensure data reproducibility of nucleus density, at least three samples were made under the same experimental condition.

3. Results and Discussion

Fig. 2 shows the polarization curves for plating baths with different inorganic species on a lab-fabricated Cu RDE. For all the curves, a reduction current commences at around 0 V vs RE. At the current density of -20 mA/cm^2 which was used in electrodeposition experiments, the addition of Na_2SO_4, K_2SO_4, and $MgSO_4$ to the PEG–containing VMS all increase the cathodic overpotential by more than 10 mV, with K_2SO_4 resulting in the highest overpotential increase of ~70 mV, Na_2SO_4 resulting in ~50 mV increase, and $MgSO_4$ resulting in ~15 mV increase. In contrast, an additional amount of $CuSO_4$ has no obvious impact on the overpotential. Cu nucleation might occur via instantaneous nucleation mode or progressive nucleation mode [2,21]. It has been known that the overpotential serves as an important driving force for increasing nucleus density [22,23]. Specifically, the copper nucleus density is usually assumed to increase exponentially with overpotential.

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