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ORIGINAL PAPER

Influence of plating parameters and solution chemistry on the voiding propensity at electroplated copper–solder interface

Plating in acidic copper solution with and without polyethylene glycol

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Abstract Interfacial voiding in solder joints formed with Sn–Ag–Cu solder alloys and electroplated Cu was examined as a function of the plating solution chemistry and parameters. Galvanostatic Cu plating of ~10 μm thick Cu films was performed in a commercially available plating solution, and in model generic plating solutions. Analysis of the current voltage behavior along with Secondary Ion Mass Spectrometry studies of organic impurity content of two plated and a wrought copper samples, yielded a conclusion that for certain chemistry solutions (e.g., H_2SO_4 + $CuSO_4$ + Cl^- + PEG) and current density ranges above 2.5 mA cm^{-2}, organic impurities were incorporated into the growing Cu. Solder joints were produced with a variety of electroplated Cu samples. These joints were, then, annealed at a temperature of 175 °C for 1 week, cross sectioned and examined. In general, it was observed that interfacial voiding in laboratory electroplated Cu layers was qualitatively similar to the unexplained voiding observed in some industrially plated Cu products. More specifically, it was found that the propensity for voiding could be correlated with specific electroplating parameters that in turn were associated with significant incorporation of organic impurities in the Cu deposit.

Keywords Copper · Solder joints · Voiding · Electroplating · Impurity incorporation

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1 Introduction

Recent studies on solder joints formed using high-Sn solders has revealed that some solder joints with Cu pad structures are susceptible to premature failure under shock loading [1–4]. These failures have been associated with prolific void formation and growth at the interface between the interfacial, intermetallic, compound (IMC) and the Cu pad during thermal aging. Such behavior has been correlated with specific electroplated Cu samples [4], i.e. not all plated Cu demonstrates this severe voiding behavior. Although some indication exists that this voiding phenomenon may be associated with impurity levels in Cu samples, the mechanisms for void formation, and any microstructural features responsible for this voiding, have not been previously identified.

The degree of voiding observed in solder joints comprised of high-Sn solders and Cu pad structures, during thermal aging, has been found to vary significantly with different Cu samples [4]. Notably, such voiding is not limited to specific suppliers, particular plating chemistry or general plating approach (DC, pulsed, electroless) [4]. The voiding phenomenon was not correlated with properties of the Cu, such as ductility or tensile strength. Sometimes a single plating batch has been known to give serious

voiding, while both preceding and subsequent batches from the same plating tank would produce virtually no significant voiding, during annealing of solder joints [4]. A range of solder reflow and annealing conditions on certain electroplated Cu samples resulted in the formation of an almost continuous line of interfacial voids. In many other Cu samples, using similar annealing conditions, these voids remain very low in density, too small to be visible by optical microscopy [5]. For instance, soldering on high purity wrought Cu foil and subsequent thermal aging were seen to result in a very low level of voiding in association with the interfacial, Cu_3Sn, phase [6, 7].

Previous publications have suggested that the impurity content of Cu samples determines their propensity for voiding. In Ref. 6 the significant voiding at the electroplated Cu–solder interface—in comparison to the absence of voids when solder was used with a wrought Cu foil—is attributed to impurities in the plated Cu. Yang and Messler [7] suggested that hydrogen introduced during the electroplating process accelerates void formation in the Cu_3Sn, IMC, layer. In a study of the impact of varying Cu electroplating parameters on voiding in Cu–high-Sn solder joints, De Sousa et al. [8] reported that higher agitation rates increased the propensity for voiding. Kim et al. [9] found a dramatically higher voiding propensity in solder joints with Cu plated in the presence of an unspecified additive in comparison with “no additive” grown Cu.

In fact, standard electroplating procedures utilize organic additives in a fashion which may result in incorporation of some organic molecules into the Cu material. Producing Cu samples by typical electroplating processes involves the adsorption of organic molecules on Cu surfaces, continuously, during the plating process. In the optimal case, as this process continues, these complexes ideally migrate onto the top of the growing Cu layer, and are thus not likely to be incorporated in to the growing Cu layer.

Two key parameters determine the probability for incorporation of a surfactant molecule into a growing layer. These are the rate of molecular migration to the top of the growing film and the film deposition rate. The migration rate is determined by the bond strength between the metal surface and the adsorbed molecule, which is strongly dependent upon the applied electrode potential and electrode charge. For instance, ions adhere to metal surfaces, when an opposite charge is provided by the applied potential. Organic molecules preferentially attach to a neutralized metal surface. The stronger the molecule adsorption, the easier the unwanted incorporation would take place. Also, at a given electrode potential, higher deposition rates (which are dependent upon overpotentials) would nominally result in a higher rate of incorporation.

While no detailed picture is presented for additive incorporation during Cu electroplating, it has been shown that incorporation of saccharin molecules into the growing layer, during saccharin mediated CoFe alloy electrodeposition, could take place either via an adsorption-electroreduction mechanism [10, 11] or via physical incorporation of entire molecules during deposit growth [12]. In the first case [10, 11], the organic molecule would first adsorb on the top of the growing surface; then, it would undergo some kind of reduction to yield species that would eventually be incorporated into the deposit. In the second case, physically adsorbed organic molecules would be incorporated partially or completely into the growing layer. A quantitative model proposed for the second route of incorporation emphasizes a strong correlation between the saccharin adsorption properties and the extent of incorporation into the growing layer [12]. The similar role of additives in the Cu electroplating process would suggest a possibility for incorporation of organic impurities in to the growing Cu layer.

In the industrial context the organic molecules under consideration in the present study are generally delivered to the plating bath through the addition of complex, and often proprietary, combinations of organic species. Generally there are three basic types of organic additives in acid copper plating [13, 14].

(1) Suppressors, are also referred to as carriers. Suppressors are adsorbed at the cathode surface and act, in concert with chloride ions, to suppress the plating rate. The suppressor essentially increases the thickness of the diffusion layer, and improves the plating distribution without “burning” the deposit. Suppressors are typically large molecular weight (2,000–8,000) polyethylene glycol (PEG) or other polyoxyalkyl type compounds.
(2) Brighteners, also referred to as accelerators or catalysts, are typically small molecular weight, sulfur-containing, compounds that increase the plating reaction by displacing adsorbed suppressors. Their random adsorption tends to produce a film that will suppress the formation of large, course-grained Cu microstructures. Examples are thiourea and bis(3-sulfopropyl) disulfide (SPS).
(3) Levelers, are typically nitrogen-bearing heterocyclic or non-heterocyclic aromatic compounds that act by displacing brightener species at high current density sites (protrusions). The plating rate is, thus, suppressed at these protrusions. An example is Janus Green B (JGB).

The observed severe voiding in annealed solder joints with Cu pads may be consistent with the influence of incorporated organic impurities on the propensity for solid-state, ‘Kirkendall’, void formation in the reactive, Cu–Sn, interdiffusion couples [4], represented by the solder joints. The ‘Kirkendall voiding’ is supposed to result from the production of excess atomic vacancies within the Cu_3Sn

and Cu_6Sn_5 interfacial layers, growing at the Cu–solder interface, as Cu and Sn reactively interdiffuse [5, 15]. If dislocation climb or other vacancy annihilation means do not allow these vacancies to escape the sample, a supersaturation of vacancies occurs as a result. These supersaturated vacancies may overcome a nucleation barrier and form voids. It is concluded in previous papers [4, 16] that impurities in the Cu may block dislocation climb, resulting in vacancy supersaturation, and allowing the possibility of void nucleation. Alternatively, these same impurities may facilitate the nucleation event by simply providing nucleation sites for voids. In either picture, the formation of vacancies in a particular sample may depend upon the purity of the sample.

The present work examines the influence of plating bath parameters on the propensity for void formation in electroplated Cu–solder joints during annealing (thermal aging). Focus is on the effect of variations in plating bath chemistry on subsequent formation of voids in intermetallic compounds growing at Cu–solder interfaces, during annealing. Cu samples are produced with either commercially available plating solutions (CAPS), or from model, i.e. generic, plating solutions (GPS). The GPS's are formulated with various mixtures of chemicals of the type that are known to be indispensable in super conformal Cu plating: Cu sulfate, sulfuric acid, Cl^- ions and organic additives, such as polyethylene glycol (PEG) [17–20]. The morphology and organic impurity levels of selected plated Cu samples are examined. Near eutectic SnAgCu solder and electroplated Cu were used to form solder joints with a standard reflow process, and then annealed. Microstructural examinations of cross sections of solder joints, after annealing, were performed. This work seeks correlations between plating bath parameters, the incorporation of organic impurities in electroplated Cu, and the formation of voids during annealing of solder joints with high-Sn solders and electroplated Cu pad structures, in an effort to better understand and control this phenomenon.

2 Experimental

2.1 Cu electroplating

Cu disks (99.99%, Advent Research Materials, Ltd), 6 mm in diameter and 1 mm thick were used as working cathodic electrodes (plating substrates). Prior to the plating process the electrodes were mechanically polished on clothes soaked with progressively smaller in size alumina slurries (Buehler), down to 0.05 μm. Immediately before the plating of Cu, the mechanically polished disks were electropolished, following a procedure described elsewhere [21]. Next the Cu surface was thoroughly rinsed with Barnstead Nanopure® water ($R > 18.2\ \Omega$ cm) and dried with high purity nitrogen gas. Immediately, the samples were mounted into a holder of a rotating disk plating apparatus (PINE Instruments Rotator with MSPX Speed Control) as a working electrode. Constant potential or constant current density was applied, using a three-electrode Potentiostat/Galvanostat Model 273 (Princeton Applied Research). Pure Cu wire (99.99%, Surepure Chemetals) and a 0.04–0.06% P, phosphorized, Cu, anode (Kocour) serving as a reference and counter electrode, respectively, were pretreated by etching in 8 M nitric acid and rinsing thoroughly with Barnstead Nanopure® water. The phosphorized Cu anode was prepared (filmed) prior to each plating experiment. The filming procedure was developed according to the recommendations in the CAPS data sheet and involved anodization of the electrode in 0.26 M $CuSO_4$ + 2 M H_2SO_4 + 1.13 mM Cl^- solution for 30 min at current density of 12–15 mA cm^{-2}. All potentials in the present work are measured with respect to a Cu, pseudo-reference, electrode (PRE) and reported as overpotentials $\eta = |E - E_{Cu^{2+}/Cu}|$. Two different types of plating solutions were used.

(A) "Acid copper", based CAPS for semiconductor applications from undisclosed commercial vendor that consists of three unit components: (i) $CuSO_4$ + H_2SO_4 + Cl^-, (ii) additive A, and (iii) additive B. These proprietary commercial additives are selected to facilitate uniform deposition of copper films with desired microstructures and related properties, e.g. ductility and tensile strength. Cu samples were produced in CAPS with concentrations of the additives, (A + B), varied by a factor of up to 20.

(B) A GPS was formulated in our lab to consist of 0.26 M $CuSO_4 \cdot 5H_2O$ (Sigma-Aldrich), 2 M H_2SO_4 (doubly distilled, GFS), 1.13 mM HCl (doubly distilled, Sigma-Aldrich), 0.02 mM polyethylene glycol 4000 (PEG) (Fluka). All chemicals were highest purity brands and were used as-provided by the respective vendors. Unless stated otherwise, different solution compositions were achieved by mixing the above chemicals at the specified concentration values. Cu samples were produced in the GPS plating bath with different component mixtures, some with PEG, and some without.

Electroplated Cu layers, approximately 10 μm in thickness, were produced for each plating bath chemistry at a constant current density. Except when specifically stated otherwise the current density was 10 mA cm^{-2}. When necessary, the specific plating conditions for each experiment are described in the results and discussion section. After the plating, the sample was rinsed with Barnstead Nanopure® water and dried with high-purity nitrogen (less than 1 ppb oxygen, CO, CO_2, and moisture content). Finally, the sample was subjected to soldering, heat

treatment and characterization (as detailed in the next paragraph).

2.2 Electroplated Cu and solder joints—reflow, heat treatment, and characterization

Before soldering, selected electroplated Cu samples were examined for surface morphology, using scanning electron microscopy. Additionally SIMS results were obtained for selected GPS elelctroplated Cu samples, using a Cameca ims-6f SIMS instrument using Cs primaries at 9.5 keV, fast etching (ca. 5 nm/s,) and negative ion detection of a 30 μm diameter circle within a larger rastered area. Enough mass resolution was used to separate S from O_2. Ion implants of ^{13}C, ^{18}O, F, S, and Cl into copper were used to quantify the SIMS. With some samples being too rough to properly measure craters, copper etch rates from the standards were used to estimate nominal depths. One special feature for these rough copper samples is finding sharp spikes in O, C in the plated film, and S in the wrought copper substrate. It is shown, by repeating profiles with single mass monitoring, that these correspond to very small (sub μm) impurities where the small lateral size gives rise to SIMS spikes in spite of the craters being very rough. Thus the SIMS gives highly localized information in this special situation.

Solder joints were prepared by introducing commercial hypereutectic NEMI (SAC) (Sn–3.9Ag–0.6Cu wt.%) solder spheres (760 μm in diameter) on electrodeposited Cu films which had been pretreated with flux (to react with the surface oxides and sulfides). Solder reflow on these Cu substrates was conducted in the Perkin Elmer DSC-7 differential scanning calorimeter. The reflow profile included a peak temperature of 240 °C, and a nominal time above liquidus (217 °C) of 90 s. After reflow, solder joints were annealed at 175 °C for a week in air. After thermal aging, the samples were cross-sectioned and polished by standard metallurgical sample preparation procedures, where the final polishing step was performed with a 0.02 μm colloidal silica suspension.

The concentration of voids in the cross sectioned, annealed solder joints was assessed using LEICA 440 SEM using the back-scattered scanning electron imaging mode (BSEM).

3 Results and discussion

The effects of variation of Cu electroplating bath parameters on the incorporation of organic impurities in the Cu, and on the tendency of voids to form in electroplated Cu–high-Sn solder joints during annealing, were investigated. In the following—after presentation of a simple, more common, example of a solder joint with high-Sn solder and a Cu pad structure with little or no voiding, despite prolonged annealing—solder joints with Cu, electroplated in our laboratory in a CAPS solution with additives (with vendor recommended A and B concentrations), were examined and are reported, as a function of annealing time. After solder joints produced with this plated Cu showed prolific voiding, under certain conditions, the amounts of additives (A and B) were systematically decreased in the electroplating solution, and the effect on void formation investigated. Finally, electroplating solutions (GPS) were formulated in the laboratory. The organic impurity content of Cu electroplated in selected GPS solutions was examined by SIMS and correlated with the propensity for void formation in the electroplated Cu–high-Sn solder joints, during annealing. The effect of variations in the chemical content of the electroplating solutions and the current density on final propensity for voiding was also carefully examined.

3.1 Growth of intermetallic compounds in high-Sn solder-electroplated Cu solder joints

The formation of interfacial, intermetallic, compounds (IMCs) at solder—electroplated Cu interfaces was examined in metallurgical cross sections by means of optical and electron microscopy, immediately after reflow, and also after prolonged annealing (usually, for several days). After reflow, a Cu_6Sn_5 intermetallic compound layer was observed, having a scalloped geometry, similar to previous results for interdiffusion at temperatures above the liquidus [4]. After prolonged (minimum of 1 week) annealing at a temperature of 175 °C, a Cu_3Sn layer was observed between the Cu and the Cu_6Sn_5 layer. The latter was observed to have increased in thickness, and assumed a flat, uniform thickness, morphology. The appearance of a few, small, isolated voids is fairly common [4, 5, 15] for such a lengthy heat treatment (Fig. 1).

Prolonged annealing of solder joints produced with some samples of electroplated Cu results in prolific void formation in association with the Cu_3Sn phase, at or near the IMC–Cu interface. An example of such voiding is shown in the SEM micrographs of Fig. 2, where the copper was electroplated in our laboratory, using the CAPS at a

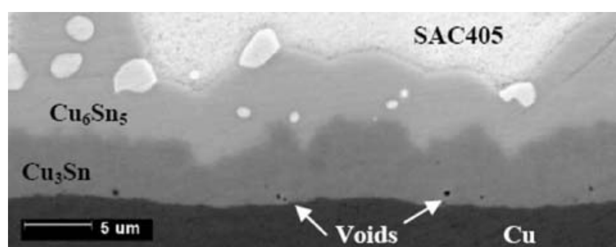

Fig. 1 Cross section of SAC on Cu pad after reflow and 1,000 h at 175 °C

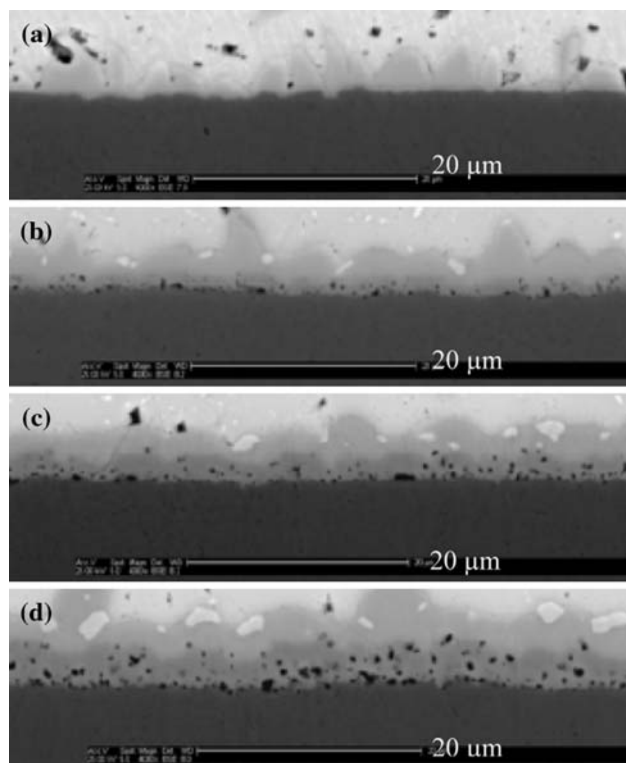

Fig. 2 SEM micrographs of Cu-SAC cross sections showing void evolution in copper solder joint upon heat treatment at 175 °C: (**a**) immediately after reflow, (**b**) after 24 h, (**c**) after 72 h and (**d**) after 168 h

constant current density of 10 mA cm^{-2} and with the supplier recommended additive concentrations. These micrographs are of cross sectioned, Cu-SAC solder joints, which had been annealed at a temperature of 175 °C for periods of time ranging from zero (Fig. 2a) to 24, 72, or 168 h (Fig. 2b–d, respectively). As is typical, few voids could be detected at this magnification (4,000×, 0.048 µm/pixel) immediately after the reflow (Fig. 2a). However, heat treatment for 24 h at a temperature of 175 °C resulted in growth of a Cu_3Sn layer, approximately one micron in thickness, and growth of a significant number of voids that were relatively uniform in size (Fig. 2b). The number and size of voids was increased after 72 h of heat treatment at the same temperature, and the thickness of the Cu_3Sn layer increased to 3–4 microns (Fig. 2c). The voids continue to grow in size and number after annealing for 168 h (Fig. 2d). Similar void evolution behaviors have been previously reported for solder joints with specific electroplated, Cu, samples [8, 22].

3.2 Effect of variation of the additives concentration in the CAPS on void formation

The concentration of additives (A and B) in CAPS, during electroplating, was varied in order to investigate the effect upon void formation in electroplated Cu–high-Sn solder joints. Electroplated samples were produced with CAPS with additives (A and B) at the recommended level (labeled 1), and then at progressively decreasing levels (half, one-tenth, or one-twentieth of recommended levels). The current/voltage behavior for different additive concentrations is monitored (Fig. 3a), as a function of time during electroplating at a current density of 10 mA cm^{-2} in 100 mL solution, and different additive levels. In general, the potential was observed to decrease upon decrease of the additive concentration. Such a result is consistent with reducing amounts of organic molecules adsorbed on the Cu surface with reducing bath concentrations [12]. Indeed, fewer organic molecules would mean less surface resistance, and would eventually result in a lower overpotential at the same current density. Thus, the overpotential measurements of Fig. 3a are consistent with a previous study which concluded that variation of the concentration of commercial additives in Cu electroplating baths varied the concentration of organic molecules in the electroplated Cu produced by these baths [8].

Solder joints were formed with electroplated Cu samples, produced at each of the additive concentrations of Fig. 3a, annealed, cross sectioned and examined. Figure 3b–d represent four SEM micrographs, showing the Cu–IMC interface of samples grown in solutions with decreasing content of additives (A and B). Inspection of these images indicates a steady decrease in the degree of interfacial voiding with the decrease in the concentration of additives in the Cu electroplating bath. The sample, resulting from a plating bath with 20 times less concentration of additives, displayed interfacial voiding that is close to virtually negligible values. This result is consistent with the reported difference in voiding by Kim et al. [9], when a comparison was made for Cu layers grown in presence and absence of additives. While the trend in voiding is clearly seen in Fig. 3 with minimizing the additive content, no feasible set of growth control parameters was identified for void-free Cu deposits grown in CAPS solution with the manufacturer recommended additive concentrations.

3.3 Effects of variation of the GPS composition on void formation in electroplated Cu-SAC solder joints

A systematic study was conducted of the impact of the organic content of electroplated Cu on the voiding propensity of electroplated Cu-SAC solder joints. Cu samples were first produced with basic plating solution ($CuSO_4$ + H_2SO_4) and, then, the addition of other chemicals (HCl and PEG) was included on an individual basis and in combination in the evaluations. Furthermore, the current density was varied during the production of Cu in these plating

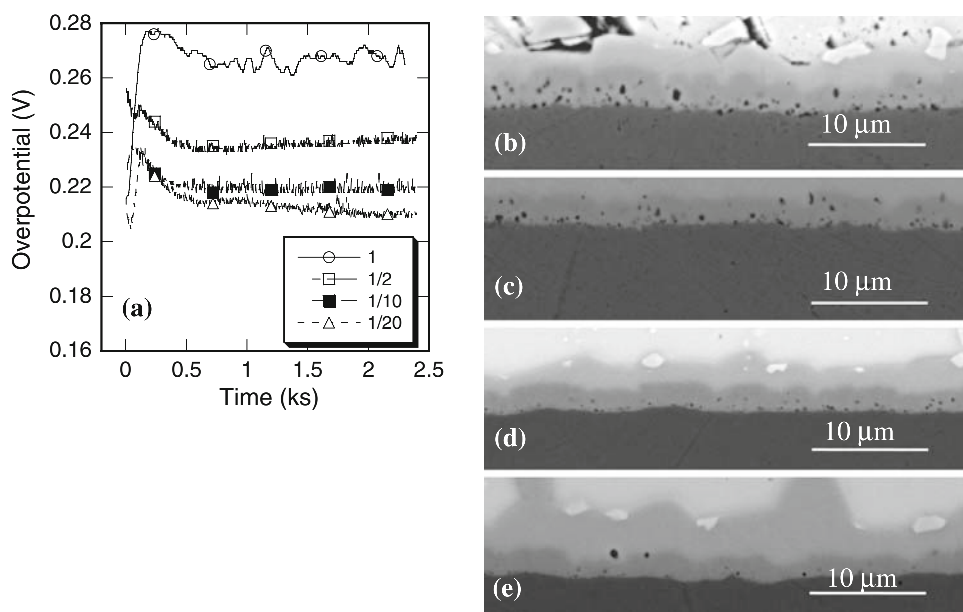

Fig. 3 (**a**) Current voltage behavior during Cu growth at a current density of 10 mA cm^{-2} in 100 mL solution with black phosphorized Cu anode. SEM micrographs (cross section of SAC on Cu) showing the influence of the additive content (**b**, default; **c**, 2 times less; **d**, 10 times less; and **e**, 20 times)

solutions. These experiments sought correlations between the voiding propensity of electroplated Cu–solder joints and the chemicals used in the Cu electroplating bath. Results of microstructural analysis of selected electroplated Cu samples are first presented, followed by the examination of voiding propensity as a function of electroplated Cu organic content.

3.3.1 Overpotential versus time during the electroplating of Cu from GPS with different composition

As discussed earlier in this paper the plating overpotential measured, during the Cu deposition process, could be correlated with the kinetics of the growth process. Within this context, the plating overpotential at 10 mA cm^{-2} in H_2SO_4 + $CuSO_4$ (150 mV, Fig. 4a) serves as a reference point in comparing the suppressing and/or catalytic effect of other additives. At the same current density adding Cl^- to this solution lowers the overpotential to about 110 mV (Fig. 4a). The result confirms the role of Cl^- ions as catalyst in the copper plating process. According to the chronopotentiometry results, presented in Fig. 4a, the curve for H_2SO_4 + $CuSO_4$ + PEG solution is similar to the one for H_2SO_4 + $CuSO_4$ solution (overpotential of 150 mV, Fig. 4a). This indicates that PEG barely affects the Cu plating kinetics. Yet, in the damascene process, PEG is known as an inhibitor. But, it is known this inhibition effect becomes stronger in the presence of Cl^- ion in the solution [23–25]. In fact, substantially different results are obtained upon the combination of PEG and Cl^- into the H_2SO_4 + $CuSO_4$ solution. The overpotential in that case increases noticeably [to 300 mV (Fig. 4a)] at the same current density, indicating that PEG is most likely forming a complex with Cl^- ions and that in this solution, PEG acts as an inhibitor in the plating process. That is to say, the increase in the overpotential is consistent with increased adsorption of PEG on the Cu surface.

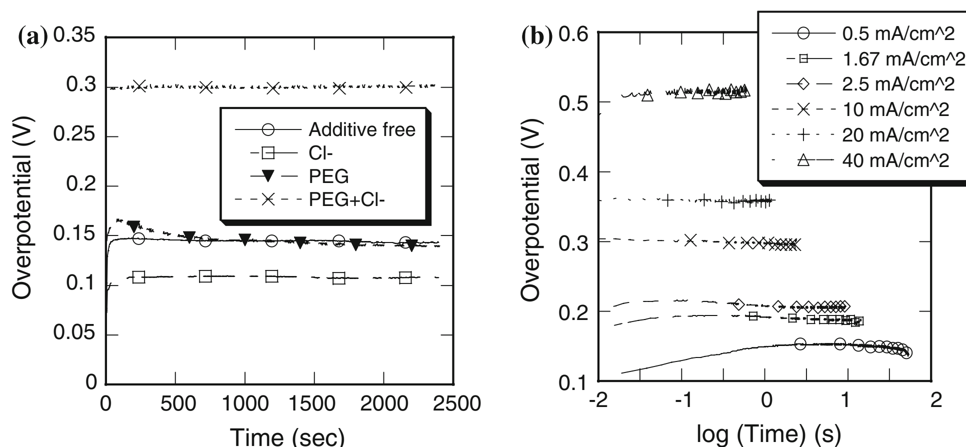

Fig. 4 Potential vs. time curve for plating in (**a**) GPS with different composition and (**b**) GPS containing $CuSO_4$, H_2SO_4, Cl^- and PEG at different current density

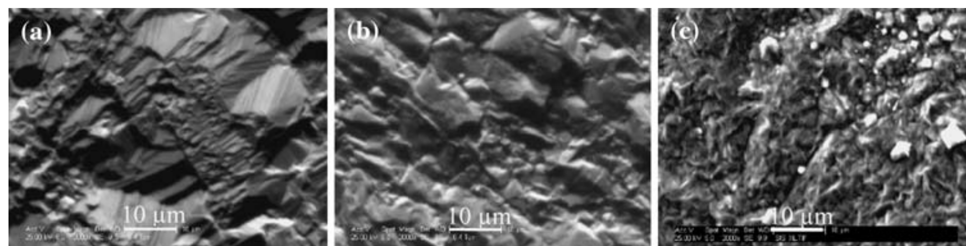

Fig. 5 SEM micrographs (top view) of Cu deposits grown in (**a**) additive free, (**b**) Cl^-, and (**c**) PEG + Cl^- at current density of 10 mA cm^{-2}

All of the overpotential versus time curves in Fig. 3a are registered at a constant current density of 10 mA cm^{-2}. For Cu electroplating with H_2SO_4, $CuSO_4$, PEG, and Cl added to the solution, variation of the current density results in variations in the overpotential (Fig. 4b) in accordance with basic electrochemical kinetics. Inspection of Fig. 4b reveals a monotonic dependence of overpotential on current density, consistent with charge transfer limited kinetics that is described by Butler–Volmer formalism (diffusion limitations are not yet manifested).

3.3.2 *Effect of variation of the GPS composition on microstructure*

Examination of the surface morphology of electroplated Cu samples revealed significant variations with changes in plating solution at constant current density. Figure 5 shows significant increases in surface roughness with the addition of Cl^- and PEG to the electroplating bath. At the same time no significant impact of Cl^- ions could be observed in comparison with the additive free solution. In general, this result suggests that the PEG + Cl^- complex influences substantially, not only the kinetics, but also the morphology of the Cu deposit.

3.3.3 *Results of SIMS analysis*

A SIMS study was conducted for selected GPS electroplated Cu samples. Copper electrodeposited in the PEG + Cl^- solution at two very different current densities, 10 and 0.5 mA cm^{-2}, was examined as a function of depth. The results are presented in Fig. 6. We note that the plated thicknesses were different in the two cases, approximately 9 µm for the higher current density and 5 µm for the lower one (the SIMS etch rates are very nominal for these rough samples). In either case the onset of a spiky S signal, and in

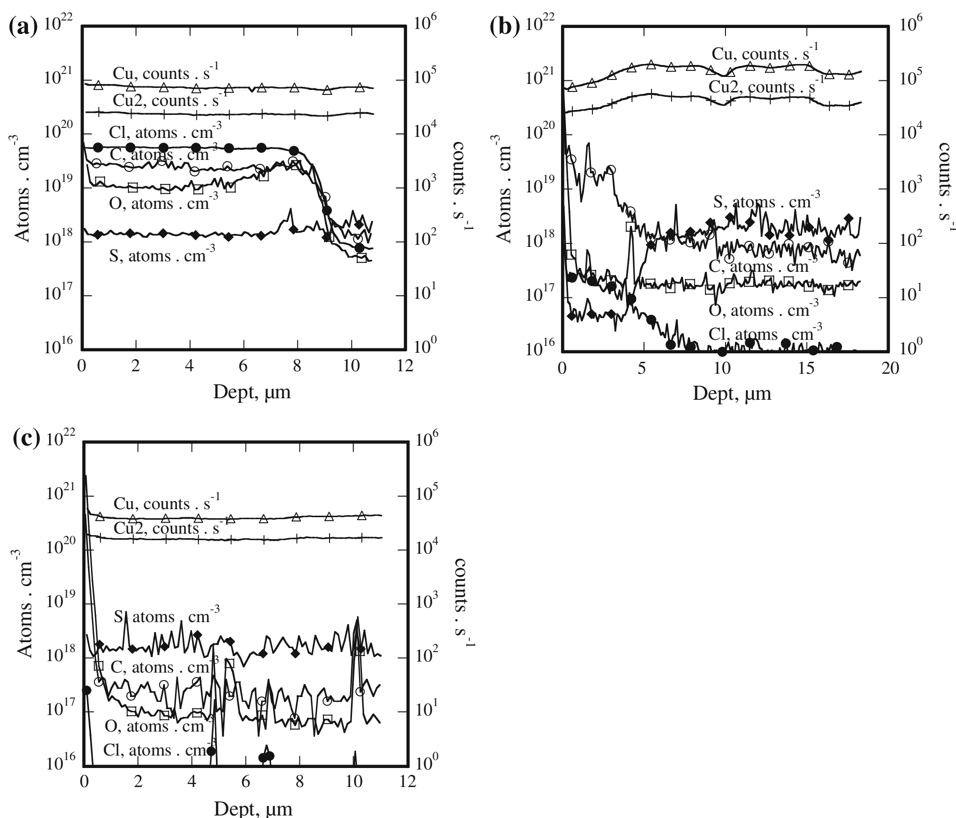

Fig. 6 SIMS Results on GPS (PEG + Cl^-) plated (**a**) 10 mA cm^{-2}, (**b**) 0.5 mA cm^{-2}, and on high purity wrought Cu (**c**)

one case an O spike, marks the beginning of the wrought copper substrate. A comparison shows 200× higher Cl and 45× higher O in the Cu layer that was deposited at 10 mA cm^{-2} than in the one deposited at 0.5 mA cm^{-2}. The 0.5 mA cm^{-2} sample contains some localized carbon: repeat profiles show the C signal to fluctuate from spot to spot. As a note, the 0.5 mA cm^{-2} sample had anomalous changes in matrix Cu and Cu_2 signals, perhaps indicating a different roughness than the other samples. While impurity levels for the 10 mA cm^{-2} material is comparatively high we note that values are still trace at only 670 ppma for chlorine, for instance, given the excellent sensitivity of SIMS.

The SIMS data of Fig. 6a, and the observation of an above-background H signal (not shown) is consistent with an dramatically increased incorporation of PEG into the copper layer at higher current densities in this plating solution. This statement could be further supported by the comparison of Fig. 6a, b with results presented in Fig. 6c where SIMS analysis is conducted on an as-polished high purity wrought Cu sample. It is clearly seen that with minor exceptions owing to reasons outlined in the previous paragraph the C, O, and Cl levels impurity levels in the 0.5 mA cm^{-2} plated Cu are at or below the high purity wrought Cu values (Fig. 6c). The higher content of impurities registered at high current densities (Fig. 6a) in the SIMS experiments is consistent also with the variation of the overpotential with plating conditions, outlined in the detailed discussion of the results presented in Fig. 4.

It is noted that Kang and Gewirth, reported no incorporation of PEG and/or its breakdown products in a study of electrodeposited Cu [26]. This result, however, does not necessarily contradict the present work as the sample analyzed in Ref. 25 was plated at 5 mA cm^{-2} in a solution with a lower concentration of $CuSO_4$. As it is shown in this study, the plating condition could influence the incorporation of PEG + Cl^- complex, even in the same solution. Also, the PEG used in our experiment is 600 a.u. heavier than the one mediating the growth in Kang and Gewirth's experiment. Dow et al. [27] have pointed out that the strength of adsorption is molecular weight dependent and thus a higher molecular weight molecule would adsorb more strongly. In general the SIMS results clearly show that organic impurities are incorporated in the Cu under certain plating conditions.

3.3.4 *Effect of organic molecules incorporated in Cu on voiding in Cu–solder joints*

Experiments were conducted to determine the effect of organic impurities in Cu on the propensity for voiding in Cu–high-Sn solder joints. The most obvious comparison is between different solder joints fabricated with Cu samples—shown by SIMS study—to have very different organic impurity content, i.e. Cu samples produced by electroplating in H_2SO_4 + $CuSO_4$ + PEG +Cl solution at 10 and 0.5 mA cm^{-2} (cf. Fig. 6). Electron micrographs of cross sections of corresponding solder joints, which had been annealed for 1 week at a temperature of 175 °C, are presented in Fig. 7, where the current density for Cu electroplating was 10 mA cm^{-2} for Fig. 7a and 0.5 mA cm^{-2} for the sample in Fig. 7b. A clear correlation is observed for these two different Cu samples. The Cu with the high organic impurity content revealed extreme interfacial voiding behavior during annealing. The effect of systematic variations of plating parameters on the voiding behavior of Cu-SAC solder joints are reported below.

3.3.5 *Effect of variation of the GPS composition on voiding behavior in solder joints*

The dependence of the propensity for voiding in solder joints on the Cu electroplating bath chemistry, when plating at a current density of 10 mA cm^{-2}, was examined. Solder joints were fabricated for Cu samples corresponding to each of the bath chemistries represented in Fig. 4a. These were annealed, cross sectioned and examined. The results are presented in Fig. 8.

It can be seen (Fig. 8) that significant voiding is, *only*, observed for Cu samples produced in the H_2SO_4 + $CuSO_4$ + Cl + PEG solution. A solder joint with a Cu sample plated at a constant current of 10 mA cm^{-2} in H_2SO_4 + $CuSO_4$ solution did not reveal significant voiding, as seen in the SEM image (Fig. 8b). It was previously shown by high-resolution, in-situ, STM study that in a similar solution, SO_4^{2-} and Cl^- adsorbed onto the Cu metal surface, forming organized anion layers [28]. Thus, some incorporation of SO_4^{2-} and Cl^- into the copper deposit would be expected. We find that, at least under the present conditions, these impurities are not as effective in facilitating void formation.

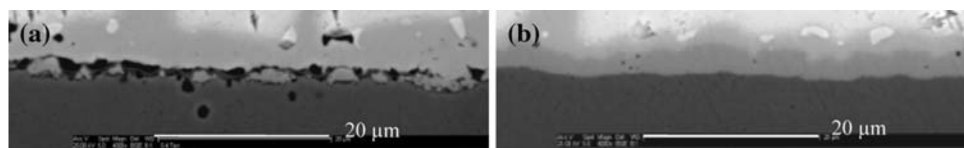

Fig. 7 SEM micrographs of Cu-SAC cross sections showing samples plated in GPS with (PEG + Cl^-) at a current density of (**a**) 10 mA cm^{-2} and (**b**) 0.5 mA cm^{-2}

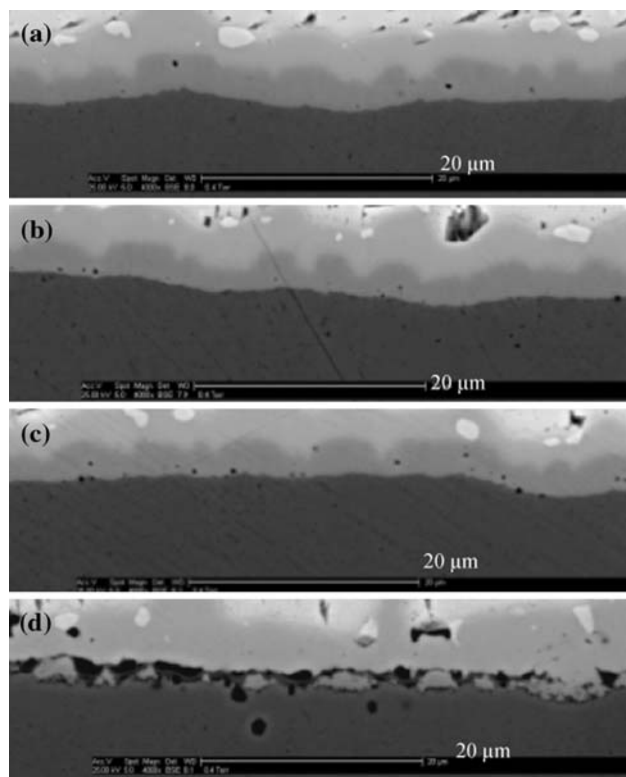

Fig. 8 SEM images of Cu-SAC cross sections showing samples plated in the solutions of (**a**) $H_2SO_4 + CuSO_4$, (**b**) $H_2SO_4 + CuSO_4 + Cl^-$, (**c**) $H_2SO_4 + CuSO_4$ + PEG, and (**d**) $H_2SO_4 + CuSO_4 + Cl^-$ + PEG at the deposition rate of 10 mA cm^{-2}

The lack of voiding behavior in solder joints (Fig. 8d) fabricated with Cu made in a $H_2SO_4 + CuSO_4$ + PEG solution is consistent with the observed behavior of the overpotential with different plating solution additives. As noted above, little change in the overpotential was found with the addition of only PEG to the $H_2SO_4 + CuSO_4$ solution, implying that few molecules were adsorbed on the growing Cu surface in these solutions. Furthermore, few voids were formed in solder joints (Fig. 8c) constructed with Cu electroplated in a $H_2SO_4 + CuSO_4$ + Cl solution. Overpotential measurements showed a significant decrease in the overpotential during this plating process. Apparently any Cl^- ions incorporated in to the Cu at the concentration found in these experiments were not effective in causing void formation.

3.3.6 Propensity for void formation in electroplated Cu–high-Sn solder joints versus Cu deposition rate in PEG + Cl^- solution

Previous work has indicated that film deposition rate is a key determiner of the probability for incorporation of a surfactant molecule into a growing layer. The rationale here could be sought based on the strong potential dependence of PEG and Cl^- complex adsorption on copper surface [29]. Therefore, given the present contention that incorporated PEG molecules facilitate void formation in electroplated Cu–high Sn solder joints, the dependence of voiding propensity on deposition rate in the electroplating of Cu was investigated. This portion of the study focused on electroplating $H_2SO_4 + CuSO_4$ solutions with PEG and Cl^- added. Solder joints were fabricated for Cu samples with plating currents ranging from 0.5 to 40 mA cm^{-2} as presented in Fig. 4b. These were annealed, cross sectioned and examined. The results are presented in Fig. 9.

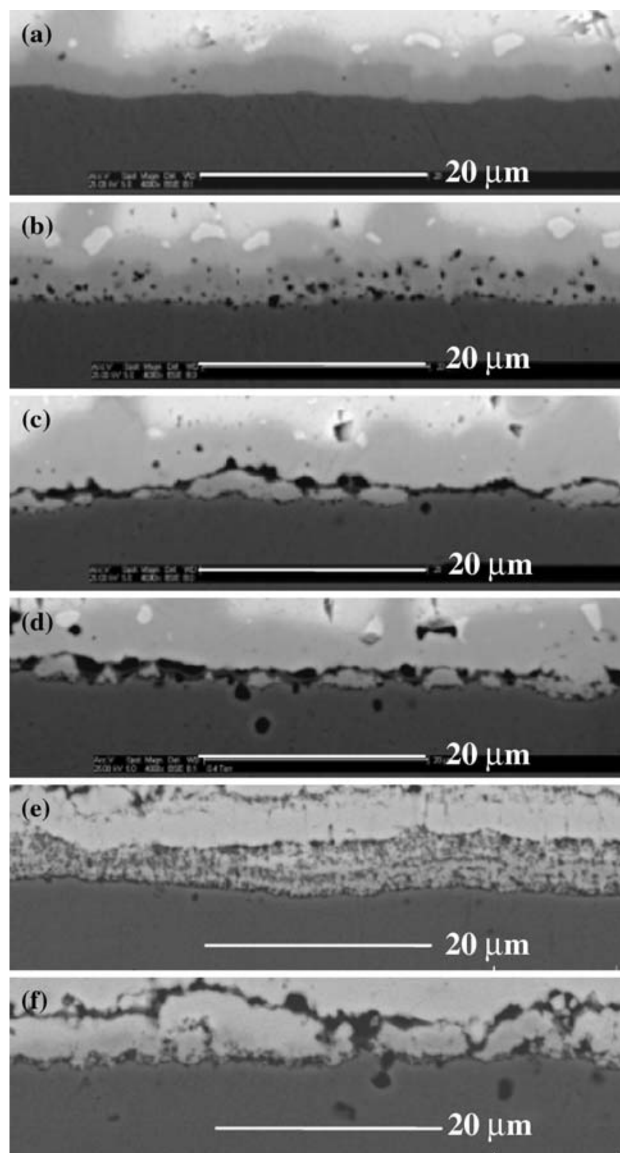

Fig. 9 SEM images of Cu-SAC cross sections showing samples plated in the solution of $H_2SO_4 + CuSO_4 + Cl^-$ + PEG with various deposition rate: (**a**) 0.5 mA cm^{-2}, (**b**) 1.67 mA cm^{-2}, (**c**) 2.5 mA cm^{-2}, (**d**) 10 mA cm^{-2}, (**e**) 20 mA cm^{-2} and (**f**) 40 mA cm^{-2}

It is clearly seen from the SEM micrographs in Fig. 9 that, while electroplated Cu samples plated at a current

density of 0.5 mA cm^{-2} resulted in solder joints which were relatively void free (Fig. 9b) after thermal aging, an increase of the current density to a value of 1.7 mA cm^{-2} resulted in significant voiding in corresponding solder joints. A further increase in the current density to 2.5 mA cm^{-2} revealed solder joints with a continuous line of voids. All samples examined, which were produced with current densities of greater than 2.5 mA cm^{-2} also displayed continuous lines of voids. Such a level of voiding is essentially the upper limit; no significant delineations between levels of voiding could be discerned for current densities of 2.5 mA cm^{-2} and above. One spike away from this trend is the voiding registered at 20 mA cm^{-2}. This represents an expansion of the voiding from one line to a layered region of fine voids that mark the maximum of voiding propensity seen in the current set of experiments. It is interesting that this region collapses again back to a line (or two) of voids at 40 mA cm^{-2}. While it is generally unclear, if the voiding at 20 mA cm^{-2} is qualitatively different to that observed at higher and lower current densities, a speculation could attribute such difference to differences in the additives' adsorption behavior as a function of the electrode potential.

3.3.7 *Proposed voiding mechanism*

Impurities associated with PEG and/or its breakdown products were found in this work to incorporate in the electroplated Cu. These impurities may facilitate void formation trends by creating vacancy super-saturation during thermal aging. Vacancies in the Cu–Sn reactive inter-diffusion system are produced at the Cu/Cu_3Sn and Cu_3Sn/Cu_6Sn_5 interfaces by "vacancy injection" mechanisms, deriving from the phase consumption at both interfaces [4]. Normally, most of these vacancies would annihilate through "vacancy sinks", such as dislocations, other defects or interfaces. In the presence of incorporated impurities these vacancy sinks are blocked by impurity atoms/molecules and are thereby less effective to annihilate vacancies. Consequently, local vacancy concentrations could rise significantly above the thermodynamic equilibrium values. This super-saturation is believed to be a necessary condition for vacancy condensation into voids. In addition to that, the impurities might also promote directly the nucleation of vacancies into larger two-dimensional vacancy clusters or three-dimensional voids by providing heterogeneous void nucleation sites. In either picture, the void nucleation would be facilitated by the presence of impurities in the electroplated copper layer. Thus, in recent work "vacancy sink deactivation" owing to interfacial Bi segregation was held responsible for the void formation at the Cu–Cu_3Sn interface in copper solder joints [30].

4 Conclusions

Cu was electroplated with both a commercially available plating solution with unknown (proprietary) additives, and with plating solutions formulated in the laboratory. Overpotentials were measured during electroplating. Variations in electroplating bath chemistries resulted in specific variations in values of overpotentials which were connected with adsorption and functionality of molecules on growing Cu surfaces. Current densities were found to vary monotonically with overpotentials, as expected for the kinetic regime. Based upon such expected behavior, and upon SIMS studies of organic impurity content of two samples, it was concluded that for certain chemistry solutions ($H_2SO_4 + CuSO_4 + Cl^- +$ PEG) and current density levels (2.5 mA cm^{-2} and more), organic impurities were incorporated in to the growing Cu.

Solder joints were produced with different electroplated samples; these joints were annealed at a temperature of 175 °C for 1 week, cross sectioned and examined. In general, it was observed that voiding in laboratory electroplated copper layers was qualitatively similar to the voiding observed in industrially plated copper batches. More specifically, it was found that the propensity for voiding could be correlated with specific electroplating parameters, the same parameter values that resulted in significant incorporation of organic impurities in to the growing Cu (2.5 mA cm^{-2} and more in $H_2SO_4 + CuSO_4 + Cl^- +$ PEG solutions). Thus the formation of significant voiding in electroplated Cu–high-Sn solder joints was correlated with the incorporation of organic impurities to the growing Cu. A mechanism of void nucleation facilitated by the presence of impurities into the electroplated copper layer was also proposed.

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