The effect of electroplating parameters and substrate material on tin whisker formation

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Abstract
Electroplated tin finishes are widely used in the electronics industry due to their excellent solderability, electrical conductivity and corrosion resistance. However, the spontaneous growth of tin whiskers during service can result in localised electrical shorting or other harmful effects. Until recently, the growth of tin whiskers was successfully mitigated by alloying the tin with lead. However, restriction in the use of lead in electronics as a result of EU legislation (RoHS) has led to renewed interest in finding a successful alternative mitigation strategy.

Whisker formation has been investigated for a bright tin electrodeposits to determine whether whisker growth can, at least partially, be mitigated by control of electroplating parameters such as deposition current density and deposit thickness. The influence of substrate material and storage at 55 °C/85% humidity on whisker growth have also been investigated.

Whisker growth studies indicate that deposition parameters have a significant effect on both whisker density and whisker morphology. As deposition current density is increased there is a reduction in whisker density and a transition towards the formation of large eruptions rather than potentially more harmful filament whiskers. Increasing the tin coating thickness also results in a reduction in whisker density. Results demonstrate that whisker growth is most prolific from tin deposits on brass, whilst from tin deposits on rolled silver is greater than that observed for tin deposits on copper.

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1. Introduction

The move towards lead-free electronics manufacture, in the wake of EU legislation, such as RoHS (Restriction of Hazardous Substances Directive) [1], restricting the use of lead in electronics, has resulted in considerable research effort being directed towards the development of alternative strategies to mitigate tin whisker growth from solder finishes used in the fabrication of electronic components. Until 2006, when the legislation came into effect, problems associated with tin whisker growth and their potential to instigate failures in electronic components were effectively controlled through the use of Sn–Pb alloy finishes.

A variety of approaches have been developed to minimise, prevent or inhibit the growth of tin whiskers; these include, (i) alloying the tin with either Bi [2–4] or Ag [3] to produce a deposit microstructure that is more resistant to whisker growth, (ii) annealing the tin electrodeposits at 150 °C within 24 h of electroplating [5,6] to reduce residual stress and develop a more uniform layer of intermetallic comprised of Cu6Sn5 and Cu5Sn compounds [7] and (iii) the use of a nickel underlayer to prevent the formation of Sn–Cu intermetallic [8,9]. The application of polymeric conformal coatings has also been shown to impede the growth of tin whiskers and reduce the risk of electrical short circuits; however, the effectiveness of the most widely used conformal coatings is very much dependent on the thickness of the applied coating [10], which can be considerably reduced at edges and corners [11,12].

The aim of the current investigation was to determine whether an additional level of whisker mitigation could be achieved for pure tin electrodeposits through control of the deposit microstructure. This would be achieved through the use of electroplating parameters that would engender the tin electrodeposits with a microstructure and grain orientation that were inherently resistant to whisker growth; for example it is commonly accepted that deposits with columnar grain structures are more susceptible to whisker growth than those with equiaxed grain structures [13].

Moon et al. [14] studied the effect of deposition current density on hillock formation from a bright tin finish. They observed that hillock formation reduced with increasing current density despite
the transition to an increasingly fine grained columnar structure, which is generally considered more prone to whisker formation [13,15], and an increase in measured as-deposited stress levels. They attributed the reduced hillock formation to a change in deposit orientation towards [001] and a decrease in columnar grain diameter, which they thought increased the likelihood of ‘pinched’ grains. A strong influence of deposition current density on whisker growth was also observed by Sauter et al. for thermally cycled tin deposits on copper [16]; reduced whisker growth at higher deposition current densities was ascribed to the formation of a ‘globular’ microstructure rather than the columnar structure formed at low current density. An earlier study by Lee and Lee [17] showed no systematic effect of current density on whisker growth whilst a recent investigation by Sharma et al. showed that whisker growth on pulse electrodeposited coatings increased with increasing deposition current density due to a change in the orientation of the deposit [18].

The tendency of an electrodeposits to grow whiskers may also be influenced by the texture of the deposited coating. Certain grain orientations are considered more whisker resistant than others [19–21]. For example deposits with a (220) texture are reported to offer greater whisker growth resistance [20,22]. Alloying with lead also generally results in the formation of a (220) orientation [13,23,24]. Zhang et al. [21] reported that bright pure tin deposits with a mixed (112):(101):103 multi-peak texture (measured using X-ray diffraction) displayed a low tendency to form whiskers. A transition towards an [001] deposit texture with increasing deposition current density was also thought by Moon et al. [14] to contribute to reduced hillock growth. In addition, it has been predicted, on the basis of creep mechanisms, that deposits having substantially [001] orientated grains, with a grain size less than a critical value, are resistant to whisker growth [25].

The tin grain structure and deposit orientation is also likely to affect the development of the Sn–Cu intermetallic at the coating-substrate interface, which is considered to be one of the main driving forces for whisker growth from tin deposits on copper [9]. However, there is often a lack of a direct correlation between whisker/hillock formation and intermetallic distribution at the whisker root [26–28].

Despite the considerable number of tin whisker related studies, there are few that systematically investigate the effect of electrodeposition variables on the structure of the deposit and the ensuing whisker growth [14,16–18,29]. In this paper, the effect of electroplating variables, in particular deposition current density, on whisker growth is investigated for a bright acid-tin finish. Whisker growth has been evaluated for both tin deposits on copper and tin deposits on brass, the latter used to promote accelerated whisker growth. An increased whisker growth rate from tin deposits on brass occurs as a result of zinc diffusion through the tin and the subsequent formation of zinc oxide both on the surface of the deposit and at tin grain boundaries [30–34]. The effect of storage at elevated temperature and humidity on whisker growth has also been investigated for both tin deposits on copper and tin deposits on brass. Preliminary investigations of whisker growth from tin deposits on rolled silver have also been carried out since silver has been considered as a potential underlayer material [6,8]. Profuse whisker growth from tin deposits on silver was previously reported by Crandall [35], however, no explanation was proffered to explain this behaviour.

2. Experimental

2.1. Tin electrodeposition

Pure tin was electrodeposited onto copper (99.9%, 0.1 mm thickness), brass (63% Cu/37% Zn, 0.38 mm thickness) and silver substrates (as cold-rolled 99.97% purity, 0.175 mm thickness), using a bright acid tin electroplating solution, which was comprised of 60 g L\(^{-1}\) tin sulphate, 70 ml L\(^{-1}\) sulphuric acid and Tinmac Stannolyte, a proprietary additive (MacDermid).

Test coupons with dimensions 2 × 4 cm were used with an electroplated area of 2 × 2 cm. The coupons were used in the as-supplied condition with no additional polishing or grinding operations. Electrodeposition of pure tin was carried out using a 99.95% Sn foil anode (0.25 mm). Immediately prior to electrodeposition, the substrates were degreased using acetone, pickled for 60 s in a 20% v/v solution of sulphuric acid (SG 1.83), rinsed in deionised water and dried using hot air. Galvanostatic deposition using direct current was carried out at room temperature (~20 °C) using current densities of 5, 10, 20, 30, 40 and 50 mA cm\(^{-2}\). The thickness of the Sn deposit was 2, 5 or 10 μm. Typically, three identical test samples were prepared for each set of deposition conditions.

2.2. Characterisation of deposits

Scanning electron microscopy (SEM) was carried out using a Carl Zeiss Leo 1530 VP FEG SEM to determine the characteristic structure of the tin electrodeposits and subsequent whisker growth. The system is equipped with an Oxford Instruments X-Max 80 mm\(^{2}\) Detector for energy dispersive X-ray spectroscopy (EDS). Electron backscatter diffraction (EBSD), using a HKL Nordlys F high speed camera, was performed to determine the crystallographic orientation of the deposits. The grain structure of the electrodeposited tin was investigated by means of cross-sections prepared by focussed ion beam (FIB) milling using a FEI Nova 600 Nanolab Dual Beam FIB–SEM. Ion beam milling was performed at a 52° tilt angle with a 30 kV gallium (Ga) ion beam. Initial trench milling was carried out at 20 mA, and the final face milling was done at 3 mA with a tilt angle of 53.5°. Ion beam images were acquired using the Ga-ion beam at a current of 30 pA. The crystallographic structure of the deposits was determined using a Bruker D2 Phaser diffractometer system scanned from 25° to 120° in 2θ, with a step size of 0.02° and a dwell of 0.1 s.

2.3. Evaluation of whisker growth

After deposition the samples were either stored at room temperature or exposed to elevated temperature and humidity to accelerate whisker growth. Test conditions of 55 °C and 85% humidity were chosen to accelerate whisker growth based on the JEDEC standard [36,37] and previous investigations [38,39,15].

The effect of deposition parameters on whisker growth was evaluated using SEM. Whisker densities were measured using secondary electron images (at 300× magnification) acquired at random locations. Average whisker densities for each sample were calculated from 10 frames. Measured whiskers were divided into 3 categories; filament whiskers, large eruptions and eruptions/nodules <10 μm in diameter.

3. Results

3.1. Characterisation of tin electrodeposit microstructure

From Fig. 1, it is evident that the grain structure of the electrodeposited tin coating is strongly influenced by deposition current density. As the deposition current density is increased from 5 to 30 mA cm\(^{-2}\) the grain size of the electrodeposited tin decreases. For deposits electroplated at 40 and 50 mA cm\(^{-2}\) the apparent grain size is increased slightly compared with that at 30 mA cm\(^{-2}\). The increased grain size might be as a result of hydrogen evolution,
which was observed at the deposit surface during electroplating for deposition current densities in excess of 30 mA cm\(^{-2}\); increasing levels of hydrogen evolution may hinder the adsorption of the plating additives onto the sample surface of the tin during deposition and result in an increased tin grain size. Hydrogen evolution may also increase mass transport and encourage grain growth rather than fresh nucleation.

At a deposition current density of 5 mA cm\(^{-2}\) the tin grains frequently have a cubic morphology and their size approaches 5 \(\mu\)m. As the deposition current density increases the tin grain boundaries become progressively less facetted. Focussed ion beam (FIB) cross sections illustrating the tin grain structure are shown in Fig. 2 for deposition current densities of 5, 20 and 40 mA cm\(^{-2}\). Deposition at 5 mA cm\(^{-2}\) results in a deposit having a hybrid equiaxed/columnar grain structure. As the deposition current density is increased the deposit becomes increasingly columnar and the width of the columnar grains reduces, reflecting the reduction in grain size observed on the surface of the deposit. It should be noted that the light contrast features decorating the tin grain boundaries in Fig. 2 are milling artefacts that result from preparation of the FIB cross-section.

The effect of deposition current density on the orientation of the electrodeposited tin grains is shown in Fig. 3 for 10 \(\mu\)m deposits electroplated at 5, 20 and 40 mA cm\(^{-2}\). The orientation image maps and folded inverse pole figures show that all the deposits possess a strong [001] orientation, which was not greatly influenced by deposition current density.

3.2. Tin deposits on copper: characterisation of room temperature whisker growth

After storage at room temperature for 2 years, whisker growth has been assessed for tin deposits on copper as a function of deposition current density (10, 20, 30 and 40 mA cm\(^{-2}\)) for different deposit thicknesses (2, 5 and 10 \(\mu\)m). The effect of 5000 h storage at 55 °C and 85% humidity, during the 2 year period, on whisker growth has also been evaluated. Whisker growth observed on these samples is summarised in Fig. 4; the inset table shows the samples on which whisker growth was observed whilst the accompanying images illustrate the typical size and morphology of the whiskers present on the deposits.

Significant whisker growth was only observed on a 2 \(\mu\)m deposit electroplated at 10 mA cm\(^{-2}\) and stored at room temperature. In this case, long filament whiskers greater than 100 \(\mu\)m in length were observed. No whiskers were present on a second sample electroplated using the same conditions and stored at room temperature. Notably, comparatively high densities of short whiskers and small hillocks/eruptions were evident on 5 \(\mu\)m and 10 \(\mu\)m deposits electroplated at 10 mA cm\(^{-2}\); see for example Fig. 5, which illustrates the distribution and morphology of whiskers present on a 10 \(\mu\)m thick deposit electroplated at 10 mA cm\(^{-2}\) after 29 months storage at room temperature.

For deposits electroplated at 20 and 30 mA cm\(^{-2}\) only short whiskers or small eruptions were observed (as shown in Fig. 4), irrespective of deposit thickness. To date, no whiskers have been observed on samples electroplated at 40 mA cm\(^{-2}\). It is noteworthy that, to date, no whiskers have been observed on the samples designated batch #2 that were electrodeposited, from the same batch of electrolyte onto identical copper substrates, 1 week after the batch #1 samples. With the exception of the 2 \(\mu\)m thick deposit electroplated at 10 mA cm\(^{-2}\) whisker growth for the tin deposits on copper is relatively low (as shown in Fig. 4); as such the absence of whisker growth on the batch 2 samples may simply reflect a statistical variation in the propensity of nominally identical samples to develop whiskers [40].

3.3. Tin deposits on copper: influence of elevated temperature/humidity storage

From Fig. 4 it is apparent that exposure to elevated temperature and humidity has had no observable effect on whisker growth compared with samples stored solely at room temperature, i.e. in
the current study whisker growth is not accelerated by exposure to elevated temperature and humidity.

To investigate the effect of storage at elevated temperature and humidity on intermetallic formation at the tin/copper interface, and the possible implications this might have for whisker growth, focussed ion beam (FIB) cross-sections were prepared. Intermetallic compound formation, for samples stored solely at room temperature for ~2 years and those subjected to 5000 h at 55%/85% humidity during that period, is compared in Fig. 6. It is evident from Fig. 6(b) that partial storage at elevated temperature has resulted in the formation of two types of intermetallic compound whilst storage at room temperature results in the formation of a single type of intermetallic (Fig. 6d). For the sample subjected to 5000 h at elevated temperature and humidity, a thin (~0.5 μm) uniform layer of intermetallic is present adjacent to the copper substrate together with a thicker (~1–1.5 μm) intermetallic compound closest to the tin; these phases are thought to be Cu₆Sn₅ and Cu₆Sn₈, respectively. For the sample stored entirely at room temperature the intermetallic layer, assumed to be Cu₆Sn₅, is both thinner and less uniform.

3.4. Tin deposits on brass: characterisation of room temperature whisker growth

The effect of electrodeposition parameters on whisker growth has also been investigated for tin deposits on brass. The secondary electron images in Fig. 7 demonstrate the effect of deposition current density (10–40 mA cm⁻²) on whisker growth from 2 and 10 μm deposits after 2 years storage at room temperature.

Whisker densities measured for these samples, using secondary electron images, are shown in Fig. 8. From Figs. 7 and 8 (and examination of 5 μm deposits that are not presented here) the following trends may be established; firstly, the density of filament whiskers and eruptions is significantly reduced as the deposition current density is increased. Secondly, the density of both filament whiskers and eruptions is reduced for the 10 μm thick deposits. From Fig. 7 it is also apparent that eruptions are also greatly increased in size on the 10 μm deposits compared with the 2 μm deposits. For 10 μm deposits, only the sample electroplated at 10 mA cm⁻² shows significant filament whisker formation; a high density of sites for potential whisker growth are also observed, as shown in Fig. 5, however, even after 2 years storage the majority of these whisker growths are only ~1 μm in height. The size and shape of these features corresponds closely to the tin grain size after deposition at 10 μm (Fig. 1(b)), i.e. each of these incipient whisker growths corresponds to a single raised tin grain.

To further investigate the effect of deposition current density on whisker growth, additional 5 μm deposits were electroplated at 5 and 50 mA cm⁻². As shown in Fig. 10, whisker growth follows the same general trend as that previously demonstrated in Fig. 7 for 2 and 10 μm deposits, namely the formation of a high density of long filament whiskers at 5 mA cm⁻² and the formation of a reduced density of larger eruptions at 50 mA cm⁻². Measured whisker densities for these samples are shown in Fig. 11. Whisker growth results for 5 μm deposits electroplated at 10 and 40 mA cm⁻² are included in Figs. 10 and 11 for comparison. It is evident that the deposit electroplated at 5 mA cm⁻² shows a much higher density of whiskers than that electroplated at 10 mA cm⁻² (603 ± 121 mm⁻² compared with 21 ± 8 mm⁻²), despite the reduced storage time. Moreover, the deposit prepared at 50 mA cm⁻² shows a slightly reduced whisker density compared with the sample electroplated at 40 mA cm⁻².

The FIB image in Fig. 12 shows the cause of the increased whisker growth from the tin deposits on brass. The light contrast phase at both the deposit surface and along the surface of the short whiskers corresponds to zinc oxide, which forms as a result of zinc diffusion from the brass substrate into the tin deposit [33]. Considerable intermetallic formation has also occurred, although compared with equivalent tin deposits on copper the distribution is less uniform and the coverage along the Sn–Cu interface is less complete. It is also observed that intermetallic formation may also have occurred within the brass substrate, however, such an interpretation must be treated with caution due to the potential for Cu redeposition during preparation of the FIB cross-section.

3.5. Tin on brass: effect of elevated temperature/humidity on whisker growth

Unlike tin deposits on copper where exposure to elevated temperature and humidity had no observable effect on whisker growth rates, for tin deposits on brass there is a significant increase in whisker growth rates. The secondary electron images in Fig. 13 compare 2 μm tin deposits electroplated at 10 mA cm⁻² after 2 months storage at room temperature and 2 months storage at...
55 °C/85% humidity, respectively. It is clear that exposure to elevated temperature and humidity has resulted in a dramatic increase in whisker growth compared with storage at room temperature.

Storage at 55 °C/85% humidity also results in the formation very different whisker growth morphologies. Fig. 14 shows the surface of a 5 μm tin deposit electroplated at 40 mA cm\(^{-2}\) and exposed to 55 °C/85% for 11 days. Eruptions on the thermally exposed sample appear to break through a ‘crust’, approximately 2 μm in thickness (Fig. 14 b), which has developed on the deposit surface.

Examination of the deposit surfaces shows that zinc oxide formation (corresponding to the dark contrast phase decorating the grain boundary [33]) at the tin grain boundaries is very pronounced for the heat treated sample.

Fig. 15 shows a FIB cross-section obtained from an eruption similar to that shown in Fig. 14(b). It is observed that zinc oxide has formed along the columnar grain boundaries of the tin deposit to a depth of at least 2 μm, which is comparable to the thickness of the ‘crust’ observed in Fig. 14(b). Substantial zinc oxide formation has also occurred within the coarse grained region that corre-
sponds to the growth of the whisker/eruption. As previously shown for samples stored at room temperature (Fig. 12), coverage of the Sn–Cu interface by the intermetallic phase is not complete. There is no indication that more than a single type of intermetallic phase has formed at the tin coating/brass substrate interface during elevated temperature/humidity storage. From SEM/FIB analyses it is

Fig. 5. SEM images showing incipient whisker formation on a 10 μm tin deposit on copper electroplated at 10 mA cm$^{-2}$ after storage for ~29 months: (a) low magnification image showing typical distribution of features and (b)–(d) high magnification images showing a short whisker, a small conical eruption and a nodule, respectively.

Fig. 6. Focussed ion beam images showing the effect of storage at elevated temperature and humidity on the formation of Sn–Cu intermetallic compounds at the interface between the Sn deposit (electroplated at 20 mA cm$^{-2}$) and the Cu substrate (a) and (b) 2 years after tin deposition, including 5000 h at 55 °C/85% humidity with the remainder at room temperature (RT) and (c) and (d) 2 years storage at room temperature (RT).
evident that, for tin deposits on brass stored at elevated temperature and humidity, increased whisker growth results from the increased formation of zinc oxide at the tin grain boundaries at the deposit surface, which is brought about by accelerated zinc diffusion from the underlying brass substrate into the tin deposit at the elevated storage temperature.

Although the examples shown in Figs. 13 and 14 were prepared using different deposit thicknesses and exposed to temperature and humidity for different times, it is clear that deposition current density has a similar influence on whisker formation for deposits exposed to elevated temperature and humidity as it does for samples stored entirely at room temperature, i.e. a high density of long filament whiskers is formed on deposits electroplated at 10 mA cm$^{-2}$ (2 months storage at 55°C/85% humidity) whilst large eruptions are formed on deposits electroplated at 40 mA cm$^{-2}$ (11 days storage at 55°C/85% humidity).

3.6. Tin deposits on silver: characterisation of whisker growth

Whisker growth from 2 μm tin deposits on silver has also been investigated using samples electroplated at 20 mA cm$^{-2}$. Compared with equivalent tin electrodeposits on copper, whisker growth is more pronounced. After storage at room temperature for 22 months (shown in Fig. 16) a considerable number of long filament whiskers (>100 μm) were present. To investigate the reason for the increased whisker formation for tin deposits on silver, FIB cross-sections were prepared. The secondary electron image in Fig. 16(b) shows that Sn–Ag intermetallic formation has occurred within the Sn deposit. Compared with the Cu$_6$Sn$_5$ observed for tin deposits on copper, the Sn–Ag intermetallic is less uniform and has a 'wedge' shaped morphology. At the whisker root (Fig. 16(c)) the tin grain size is considerably increased due to recrystallisation, compared with the as-deposited columnar
4. Discussion

4.1. Effect of deposition current density on whisker formation

It is evident that deposition current density has a significant influence on whisker formation for tin deposition onto both copper and brass substrates, as shown by Figs. 4, 7 and 8, respectively. Although only limited whisker growth has been observed for the tin deposits on copper it is clear that the most profuse whisker growth has occurred on deposits electroplated at 10 mA cm\(^{-2}\), whilst to date, no whisker growth has been observed on any of the deposits electroplated at 40 mA cm\(^{-2}\).

The effect of current density on whisker growth is more readily established for tin deposits on brass due to the increased whisker growth. The observed reduction in whisker density as deposition current density in increased is consistent with earlier studies by Moon et al. [14] and Sauter et al. [16]; however, in contrast with these previous studies there is neither a significant change in deposit orientation nor a transition towards a less columnar structure at higher current densities. At the latter, increasing amounts of hydrogen evolution were observed during deposition, which potentially results in increasing levels of dissolved hydrogen within the tin. However, this would be expected to result in increased whisker growth [41,42] rather than the observed reduction in whisker density.

4.2. Effect of deposit thickness on whisker formation

The effect of deposit thickness on whisker growth is readily established from the tin deposits on brass and in agreement with numerous previous studies [8,17,43–45], i.e. the whisker density decreases as the thickness of the deposit increases from 2 to 10 μm. Although it is harder to establish the influence of deposit thickness on whisker growth for tin deposits on copper due to the limited whisker growth, it is clear that the 2 μm deposits exhibit the most significant whisker growth. A reduction in whisker formation as the thickness of the deposit increases may be attributed to a reduction in compressive stress levels within the tin deposit due to active stress relaxation [27].

4.3. Effect of substrate material on whisker formation

The choice of substrate material has been shown to have a significant influence on whisker growth. For the bright tin finish utilised in this study only limited whisker growth has been observed for tin deposits on copper even after 29 months storage. Two possible explanations for the low whisker tendency of the tin deposits on copper are suggested by the microstructural characterisation. Firstly, the intermetallic compound formed in this system does not display the wedge shaped morphology that is generally thought to promote whisker growth, which demonstrates that the propensity of the intermetallic compound to generate whisker growth is likely a complex relationship between factors such as tin grain structure/deposit orientation and intermetallic morphology (e.g. wedge-shaped, blocky or planar). Secondly the [001] orientation of the tin grains may result in a deposit that has a low tendency to form whiskers [14,25]. Furthermore, deposits produced...
in the current study show a similar combination of reflections on XRD patterns (Fig. 17) to deposits reported by Zhang et al. [21] to be whisker resistant.

In comparison, profuse and rapid whisker growth has been observed from tin electrodeposits on brass. Results from the cur-

Fig. 10. Secondary electron images showing the effect of deposition current density on whisker formation for 5 μm tin electrodeposits on brass: (a) and (b) electroplated at 5 mA cm$^{-2}$ and 50 mA cm$^{-2}$, respectively, ~18 months after deposition and (c) and (d) electroplated at 10 mA cm$^{-2}$ and 40 mA cm$^{-2}$, respectively ~29 months after deposition.

Fig. 11. The effect of deposition current density on whisker density for 5 μm tin deposits on brass.

Fig. 12. FIB cross-section through two short whiskers similar to those illustrated in Fig. 9(b). 5 μm tin deposit on brass electroplated at 10 mA cm$^{-2}$. Sample stored for 29 months at room temperature.

Fig. 13. Secondary electron images showing the effect of elevated temperature and humidity on whisker growth from 2 μm tin deposits on brass electroplated at 10 mA cm$^{-2}$: (a) 2 months storage at room temperature and (b) 2 months storage at 55 °C/85% humidity.

in the current study show a similar combination of reflections on XRD patterns (Fig. 17) to deposits reported by Zhang et al. [21] to be whisker resistant.

In comparison, profuse and rapid whisker growth has been observed from tin electrodeposits on brass. Results from the cur-
rent study confirm that for tin deposits on brass the driving force for whisker formation is zinc diffusion to the surface of the deposit since only limited whisker growth has been observed for equivalent tin deposits on copper, despite the extensive formation of intermetallic at the coating substrate interface (see for example Fig. 6).

The increased whisker growth observed for tin deposited on silver compared with that from tin deposits on copper is particularly noteworthy. The FIB cross-sections shown in Fig. 16 indicate that although intermetallic growth has occurred within the tin there is no pronounced intermetallic formation at the whisker root. It is evident, however, that the silver foil used as the substrate in these investigations has a distinct as-rolled structure; thus, whisker growth might have been promoted by deformation induced residual stresses in the as-rolled silver substrate. Ag sheet was also used in the earlier study by Crandall [35] that observed rapid whis-

Fig. 14. Secondary electron images showing the whisker morphology for a 5 μm tin deposit on brass electroplated at 40 mA cm⁻² after 11 days storage at 55 °C/85% humidity: (a) low magnification image showing whisker density and distribution and (b) detail of whisker morphology and deposit surface.

Fig. 15. FIB cross-section showing the sub-surface microstructure of a 5 μm tin deposit on brass electroplated at 40 mA cm⁻². Sample stored for 11 days at elevated temperature and humidity followed by 20 months at room temperature: (a) cross-section of eruption and (b) image showing detail of deposit structure.

Fig. 16. SEM/FIB analysis of whisker growth from a 2 μm tin deposit electroplated onto rolled silver at 20 mA cm⁻² after 22 months storage at room temperature: (a) secondary electron image showing typical whisker formation, (b) secondary electron image showing intermetallic formation at the Sn–Ag interface and (c) ion beam image showing cross-sectioned whisker root.
Fracture the surface ‘crust’ along the zinc oxide decorated tin grain order for whiskers and eruptions to grow, it is first necessary to deposits electroplated at high current density. Furthermore, in density whilst a high density of large eruptions are formed on substrate material on whisker growth have been investigated for long filament type whiskers are formed from deposits electroplated at low current density. A combination of high deposition current density and increased deposit thickness would provide the most efficacious whisker mitigation strategy. Exposure of tin deposits on copper to 55 °C/85% humidity for 5000 h has not resulted in increased whisker growth rates; this is attributed to the formation of a relatively planar intermetallic layer comprised of both Cu₅Sn₃ and Cu₂Sn. For tin deposits on brass, exposure to elevated temperature and humidity results in greatly increased whisker growth rates as a result of increased zinc diffusion and subsequent zinc oxide formation at the deposit surface. The increased whisker growth rates for tin deposits on a silver substrate compared with those on copper suggest that further studies should be undertaken to confirm the suitability of silver as an underlay material to provide whisker mitigation for tin deposits on copper.

4.4. Effect of storage at 55 °C/85% humidity on whisker formation

For tin deposits on copper it is evident that the subjecting the samples to 5000 h at elevated temperature and humidity has had little or no effect on whisker growth rates, which raises questions about the use of such treatments as a means of accelerating whisker growth. The absence of accelerated whisker growth under non-condensing conditions (i.e. those that do not induce corrosion of the tin deposit) has been noted previously [8,40]. It is also noteworthy that storage at 55 °C/85% humidity for 5000 h has resulted in the formation of not only a continuous and relatively uniform layer of intermetallic at the interface (Fig. 6a and b) but also one in which more than a single intermetallic phase is present (Fig. 6b). It is thought that the thick uppermost layer is Cu₅Sn₃ whilst the thin layer adjacent to the copper substrate is Cu₂Sn, which is reported to form at temperatures greater than 60 °C [27,46]. The formation of Cu₂Sn under identical storage conditions was recently reported by Chang et al. [47] whilst an earlier study by Yu et al [38] did not report the presence of Cu₂Sn for samples stored under the same conditions for 1800 h.

The formation of the continuous and uniform Cu₅Sn₃ and Cu₂Sn layers may explain the lack of accelerated whisker growth during storage at 55 °C/85% humidity in a manner analogous to that which occurs for samples annealed at 150 °C to mitigate whisker growth [48], i.e. the wedge shaped intermetallic morphology, thought to significantly contribute to whisker growth [17,26,49], is not present.

In the case of tin deposits on brass, the influence of elevated temperature and humidity on whisker growth is more significant. Exposure to 55 °C/85% humidity generates a high density of long filament type whiskers (Fig. 13b) for deposits electroplated at low current density whilst a high density of large eruptions are formed on deposits electroplated at high current density. Furthermore, in order for whiskers and eruptions to grow, it is first necessary to fracture the surface ‘crust’ along the zinc oxide decorated tin grain boundaries, i.e. the whisker grain cannot simply ‘extrude’ from the surface.

5. Conclusions

The effect of deposition current density, deposit thickness and substrate material on whisker growth have been investigated for bright tin electrodeposits stored at room temperature and at elevated temperature/humidity. Low whisker growth rates have been observed for tin deposits on copper with no whiskers observed from deposits electroplated at 40 mA cm⁻² after 29 months storage. The low whisker tendency of the electrodeposits may be attributed to their pronounced [001] orientation. For tin deposition onto both copper and brass substrates whisker density is lowest for samples electroplated at higher current densities. This is shown most clearly by the tin deposits on brass; deposition at high current density results in the formation of low densities of large eruptions, whilst high densities of long filament type whiskers are formed from deposits electroplated at low current density. A combination of high deposition current density and increased deposit thickness would provide the most efficacious whisker mitigation strategy.

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