Tin whisker mitigation: research into mechanisms and strategies. Part 2, Post-plating mitigation methods

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PART 1: EFFECT OF PLATING METHODOLOGIES

PART 2: POST-PLATING MITIGATION METHODS
Part 2: Outline of presentation

- Introduction
- Novel conformal coatings
- Electrochemical oxidation
- Atomic layer deposition
- Summary
Introduction

- Although whisker growth may be reduced by choice of electroplating bath composition and optimisation of deposition parameters, such methods cannot be relied upon to fully mitigate whisker growth.
- Given the unpredictable nature of whisker growth, even the ‘best’ electroplated tin coatings should be considered ‘whisker-resistant’ rather than ‘whisker-proof’.
- Additional control measures, in the form of surface coatings or treatments, are required to further suppress the growth of whiskers.
1. NOVEL CONFORMAL COATINGS

Post-plating mitigation methods
Tin whiskers and conformal coatings

• Conformal coatings are applied to protect printed circuit boards and associated electronic components

• Currently, tin whisker mitigation is attempted with conformal coatings that have not been designed to prevent whisker growth

• WHISKERMIT 2 research programme aimed to develop novel conformal coatings specifically designed to mitigate whisker growth
Research Aims and Objectives

• Engender polymers with physical barriers to whisker growth through the inclusion of nano-fillers in the conformal coating polymer formulation.

• Apply concept to commercial conformal coatings that are currently used for environmental protection in electronic components

• Evaluate the microstructure, mechanical properties and whisker resistance of the modified coating formulations
Evaluation of whisker mitigation

- Whisker growth has been investigated using brass coupons electroplated with 2 µm of bright tin at 10 mA cm$^{-2}$
- Modified coatings based on a HumiSeal acrylic formulation
- All conformal coatings applied by spraying
- Three sets of trials currently under evaluation (batches 1, 2 and 3)
- Samples stored in an environmental chamber at 55°C/85% humidity
- Whisker growth evaluated at periodic intervals using a stereo microscope
Evaluation of whisker growth: Batch 1

3% nanofiller modified acrylic coatings vs. unmodified

2x coating (29-7-15), Samples stored throughout at 55 °C/85% humidity

Whisker penetration reduced by ~ 2/3 for 3% nanofiller modified samples

Days after coating

Whisker density (cm⁻²)

N.b. 418 days analysis conducted using x64 magnification; all others used 50x
Evaluation of whisker growth: Batch 2

3% nanofiller modified acrylic coatings vs. unmodified

*2x coating (9-10-15), Samples stored at 55 °C/85% humidity and RT*

Whisker penetration reduced by ~ 2/3 for 3% nanofiller modified samples
Evaluation of whisker growth: Batch 3

Modified acrylic coatings vs. unmodified

2x coating (11-5-16), Samples stored at 55 °C/85% humidity

- Unmodified
- 3% nanofiller
- 5% nanofiller
- 7% nanofiller

Average coating thickness (µm)

- Top of sample
- Middle of sample
- Base of sample

3% modified samples are typically thinner than unmodified
5% modified samples are comparable or thicker than the unmodified
7% modified samples are thicker than unmodified

Very significant reduction in whisker penetration
Batch 2: mechanical property data

Samples tested approximately 1 month after fabrication

Modulus and yield strength are significantly improved for the modified formulations whilst elongation to failure is only slightly reduced.
Post-plating mitigation methods

2. ELECTROCHEMICAL OXIDATION
The role of the surface oxide in whisker growth

In 1994, Tu proposed his “cracked oxide theory” ¹

- Whisker growth occurs at certain weak spots on the surface where the oxide has been broken
- In the absence of an oxide no whisker growth would occur

Later adding ² …

- “If the surface oxide is very thick, it will physically block the growth of any hillocks and whiskers”

¹ Physical Review B 49, 2030, 1994
² Proceedings of the IEEE Electronic Components and Technology Conference, 2002 p1194–1200
Can we mitigate whisker growth by increasing the thickness of the surface oxide?

- Electrochemical oxidation in borate buffer and potassium carbonate/bicarbonate solutions used to develop thicker oxides
- Although the oxide film thickness is increased, other characteristics of the Sn coating (e.g. grain size, grain orientation and residual plating stresses) should be unaffected
- XPS analysis to evaluate the thickness and composition of the oxide layers formed
- Whisker growth evaluated using SEM and optical microscopy
Electrochemical oxidation

- Electrochemical oxidation can be used to develop oxide films that are much greater in thickness than a native Sn oxide.

XPS sputter depth profiles comparing the thickness of the oxide films 1 day after Sn deposition and electrochemical oxidation (at 1.2 V vs. SCE).

Comparable thicknesses of oxide are developed for borate buffer and potassium bicarbonate-carbonate baths.

Increased oxide thickness
Effect of electrochemical oxide on whisker growth

Whisker growth evaluated over ~ 3 years
Electrochemical oxidation at 1.2 V vs SCE

Whisker growth is considerably reduced for samples given a post electroplating oxidation treatment at 1.2 V vs SCE. Comparable reduction in whisker growth achieved for borate buffer and potassium bicarbonate-carbonate solutions. Still effective at mitigating whisker growth after ~ 3 years.
Whisker development with time

- Study underway to compare the growth of whiskers, and the development of the oxide film, on native and electrochemically oxidised deposits as a function of time
- 2 µm SnCu deposits on Cu
- Electrochemical oxidation at 2 V vs. SCE in potassium bicarbonate/carbonate solution
Electrochemical oxidation at higher potentials

Electrochemical oxidation of SnCu deposits on Cu in potassium bicarbonate-carbonate electrolyte

Oxide film thickness is increased at higher potentials

However, there is no clear improvement in whisker mitigation at higher oxidation potentials compared with 1.2 V
Whisker mitigation: Sn deposits on brass

- Electrochemical oxidation of 2 µm pure Sn deposits on brass in borate buffer solution
- Whisker growth is greatly reduced for electrochemically oxidised Sn deposits on brass
- Whisker mitigation is more effective at the higher oxidation potential
- Still an effective barrier to whisker growth after almost 4 years
Whisker mitigation mechanisms

For Sn deposits on Cu, IMC formation appears unaffected by electrochemical oxidation. Whisker mitigation must simply be derived from the increased thickness of the oxide layer. No reduction in the driving force for tin whisker growth (intermetallic formation)

For Sn deposits on brass, electrochemical oxidation reduces whisker growth by preventing the formation of Zn oxide at the deposit surface. Reduced IMC formation may also influence whisker formation. Reduced driving force for whisker growth.
3. ATOMIC LAYER DEPOSITION

Post-plating mitigation methods
ALD as a whisker mitigation strategy

• Atomic layer deposition (ALD) has been investigated as a potential whisker mitigation strategy

• ESA funded collaborative research programme between Loughborough University, Picosun and Oy Poltronic Ab

• Initial studies to investigate the effect of coating process variables on whisker mitigation
Experimental approach

- Copper coupons electroplated with 2 µm Sn-Cu to promote whisker growth
- Electroplated coupons shipped to Picosun for ALD coating
- A range of pre-treatments and process conditions investigated
- Uncoated control samples included in each batch of ALD processed samples
- Whisker growth evaluated over ~12 month period using optical and scanning electron microscopy
## ALD Coating Trials

<table>
<thead>
<tr>
<th>Batch</th>
<th>Pre-treatment</th>
<th>Coating Material</th>
<th>Coating Thickness</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Pre-treatment trials</td>
<td>‘ALD 1’</td>
<td>‘Standard’</td>
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<tr>
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<td>-</td>
<td>‘ALD 2’</td>
<td>‘Standard’</td>
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<td>3</td>
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<td>‘ALD 3’</td>
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<td>8</td>
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<td>5x ‘standard’</td>
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Whisker growth test coupons
Analysis of whisker growth

For the majority of the process batches investigated, Filament whisker growth is considerably reduced on the ALD coated samples compared with control samples.

Batch 4
(‘ALD 1’, 5x standard thickness)

Batch 6
(‘ALD 2’, 5x standard thickness)
Effect of ALD coating on filament whisker growth

For batches 3, 4, 5 and 6 the growth of filament whiskers is almost fully prevented by ALD coating (‘ALD 1 and 2’).

Batches 1 and 2 showed increased whisker growth but had a longer delay between electroplating and ALD coating.

Suffix ‘C’ refers to control samples.

Reduced whisker mitigation for batches 7 and 8 (‘ALD 3’).
Whisker growth prior to coating?

- SEM analysis indicates that the whiskers on the ALD processed samples are typically encased within a shell of oxide, i.e. they were already present at the time of coating.
- No examples where whisker growth has definitely initiated post ALD coating.

Examples of whisker growth on Batch 4 ('ALD 1', 5x thickness):

- Exposed Sn whisker
- Cracked ALD coating
- Exposed tin whisker

Examples of whisker growth on Batch 7 ('ALD 3'):

- Exposed Sn whisker

Examples of whisker growth on Batch 2 ('ALD 1'):

- Exposed Sn whisker
SEM analysis of batch 8 (‘ALD 3’)

Filament whisker density for batch 8 was comparable to that of the uncoated samples.

However, SEM analysis suggests whiskers were present prior to deposition of the ALD coating.

Coating failure may be attributed to the combined effect of coating material, lack of pre-treatment and the application of too thick a layer.

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Summary

• **Conformal coating studies**
  Novel conformal coatings are under development. Whisker growth studies show a significant improvement in whisker mitigation compared with unmodified coatings.

• **Electrochemical oxidation treatment**
  Electrochemical oxidation has been shown to provide long term whisker mitigation for both SnCu deposits on Cu and Sn deposits on brass.

• **Atomic layer deposition**
  Significant reductions in whisker growth have been achieved as a result of ALD processing.
Any questions or comments?