

The Elimination of Whiskers from Electroplated Tin

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Southington CT

After the implementation of RoHS and the discontinued use of lead bearing products and the introduction of lead free (LF) solders, tin and its alloys have come to the forefront as the first choice of replacement to tin-lead.

On the solder side the transition has moved forward and solutions have been implemented, like the SAC family of LF solders for paste reflow and tin-copper for HASL (hot air solder leveling). The industry is constantly making progress adapting its materials and processes to the higher reflow temperature profile for these LF solders. Today there is a much better understanding of the types of solder joints that are formed; their reliability and the type of intermetallic compound (IMC) formed.

On the surface finish side, replacing tin-lead has posed greater challenges. Component leads and connector finishes were being converted to tin as an obvious alternative. This works well as a soldering surface, however any part of the lead or the connection surface that is not soldered to, has shown a potential to form tin whiskers over the life of the part. Internal stresses in the deposit due to IMC formation or external stresses on the deposit are known to initiate whisker formation.

In this paper two approaches are implemented to dissipate the stress that is formed, the first is to modify the substrate surface to control the growth in thickness and direction of propagation of the IMC and the second is to modify the large columnar tin deposit crystal structure to mimic the fine equiaxed structure of tin-lead solder. The former is achieved thru controlled micro roughening of the substrate and the latter by the use of additives to the plating bath.

Data will be presented to show the effect of each of the two approaches on the dissipation of the stress, resulting from IMC formation. As the stress is dissipated the primary cause of whisker formation is eliminated.

Introduction

Electroplated pure tin and tin based alloys, are being used as alternatives to tin-lead in the majority of electronic components. These alternatives are known to produce tin whiskers which may give rise to short circuits on these components.

In the case of tin finish on copper and copper based alloys, the major cause of tin whisker formation is compressive stress. The stress is mainly caused by irregular growth of copper-tin intermetallic compound (IMC) at ambient conditions [1].

It is known that tin whiskers are readily formed on electroplated tin deposits on copper and are not observed on electroplated tin-lead deposits. The tin deposit and tin-lead deposit are different in the crystal structure. Crystal Structure has a direct impact on tin whiskers formation [2] [3].

A tin deposit with modified crystal structure (similar to tin-lead deposits) is capable of preventing whisker formation by dissipating and delocalizing the stress that cause whiskers.

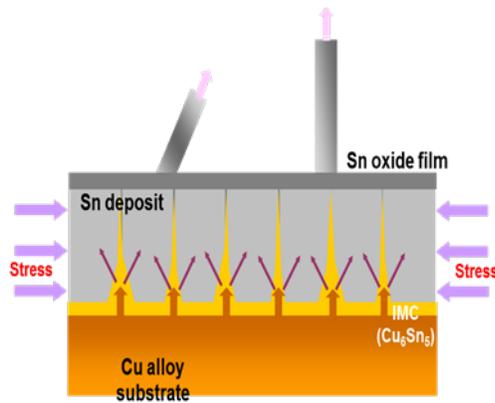
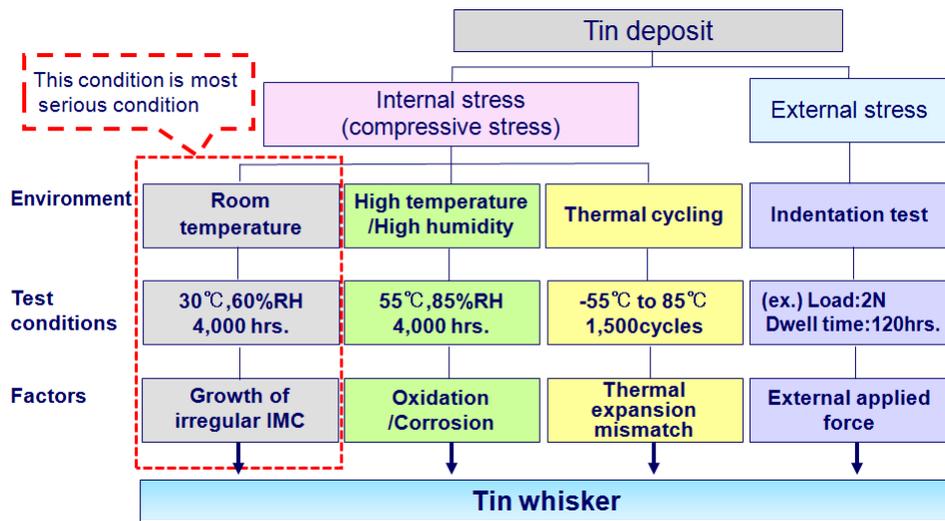


Figure 1. Shows a schematic of tin whisker formation



As shown in Figure 1, stress, channeled along the boundaries of the large grained columnar tin deposit, is responsible for the emergence of tin whiskers. Stress may be internal or external (refer to figure 2). The primary source of internal stress is attributed to the non uniform increase in the thickness of the IMC layer over time at ambient conditions (30°C, 60%RH for 4000 hours). Another condition that produces internal stress is exposure to high temperature and high humidity (55°C, 85%RH 4,000 hours) for extended periods of time which gives rise to oxidation and/or corrosion. Internal stress could also be induced by thermal cycling (-55°C to 85°C 1,500cycles) due to mismatched CTE (coefficient of thermal expansion). The latter two forms are commonly used to induce internal stress in controlled experiments. External stress is also known to initiate whisker growth. An example is the stress induced by press fit connectors.

The approach taken in this study is to control the thickness of the IMC, as well as modifying the crystal structure of the tin deposit from large grained columnar to a small grain equiaxed structure. The former is achieved by increasing the area of the copper substrate, through chemical micro-roughening means. The grain structure is altered by the use of specific chemical additives to the plating bath. All testing was done under ambient conditions as listed above.

Experiments and Results

A. Copper Surface Modification

A study was conducted on the morphology of the copper substrate prior to plating. A series of substrates varying in roughness were evaluated for whisker formation after electroplated tin deposition. The roughness was controlled by chemical etching procedures. Average roughness “Ra”, varied between 0.13 to 0.47 microns. As shown in figure 4, 0.47um Ra has a much larger surface area as compared to 0.13um Ra. The propensity to whisker was evaluated as follows:

Test Vehicle

The test vehicle - CDA19400 (Cu-2.3Fe-0.03P-0.12Zn) leadframe; refer to figure 3.

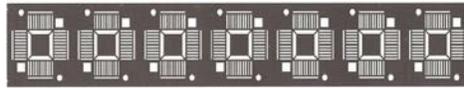


Figure 3. Test Vehicle

Tin plating

The plating bath was MSA based matte tin. The plating was run at a current density of 10A/dm². Plating time was varied to produce a 3 um and a 10 um thick deposit. The former was for short term whisker evaluation and the latter which is typical of lead frame plating was used for long term evaluations.

Methodology

The test vehicles were subjected to chemical micro-roughening to produce a set of specific Ra values (Figure 4) The figure shows the SEM micrographs of the different degrees of micro-roughening as measured in Ra um.

The samples were then run thru a standard plating process as outlined in Figure 5. The samples were then stored under controlled ambient conditions (30°C/60%RH) for extended periods of time (1000 hours). The samples were examined for whisker formation at various time intervals.

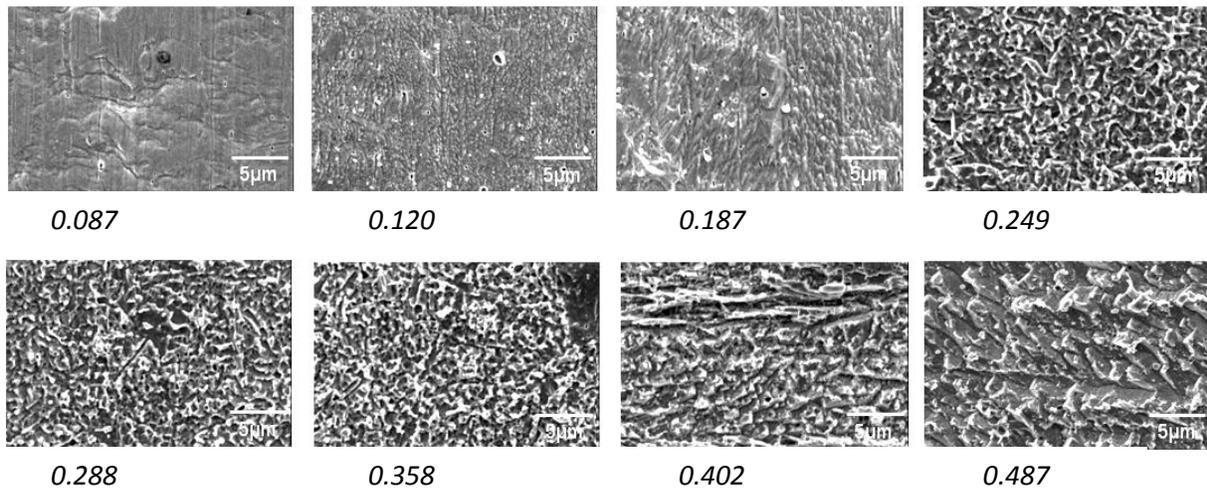


Figure 4. SEM micrographs of different Ra values

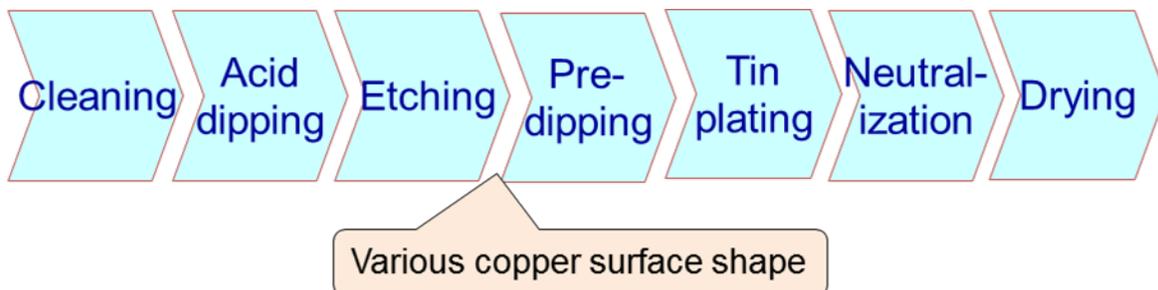


Figure 5. Showing the process used for this study (typical plating sequence)

Definition of a “Whisker”

A whisker is a protrusion >10um in length and that has an aspect ratio (length/diameter) >2.

Measurement of whisker length

The measurement according to JEITA ET-7410 is the straight line distance from the point of emergence of the whisker to the most distant point on the whisker.

Results and Discussion

Whiskers were examined, measured and tabulated after 1000 hours of storage under controlled ambient conditions (30°C/60%RH). The data gathered from whisker examination on the various morphologies of roughening are graphed in Figure 6 and 7. Figure 6 looks at maximum whisker length as a function of roughness. Figure 7 looks at the whisker density per mm² as a function of roughness.

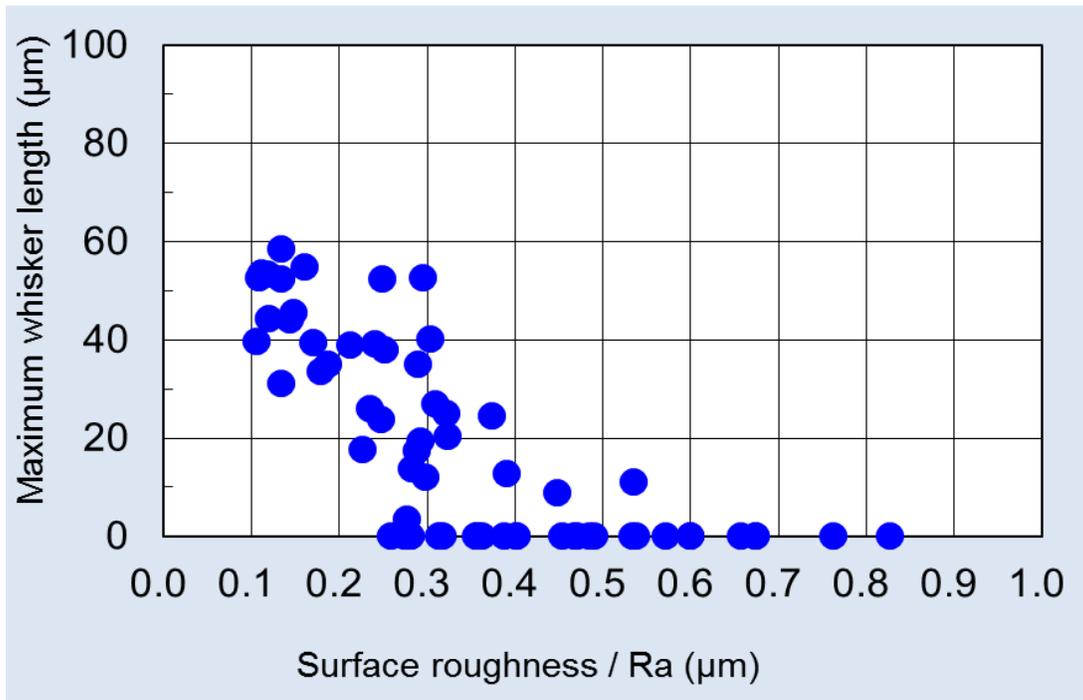


Figure 6. Maximum Whisker Length vs Surface Roughness (1000 Hrs at 30°C/60%RH)

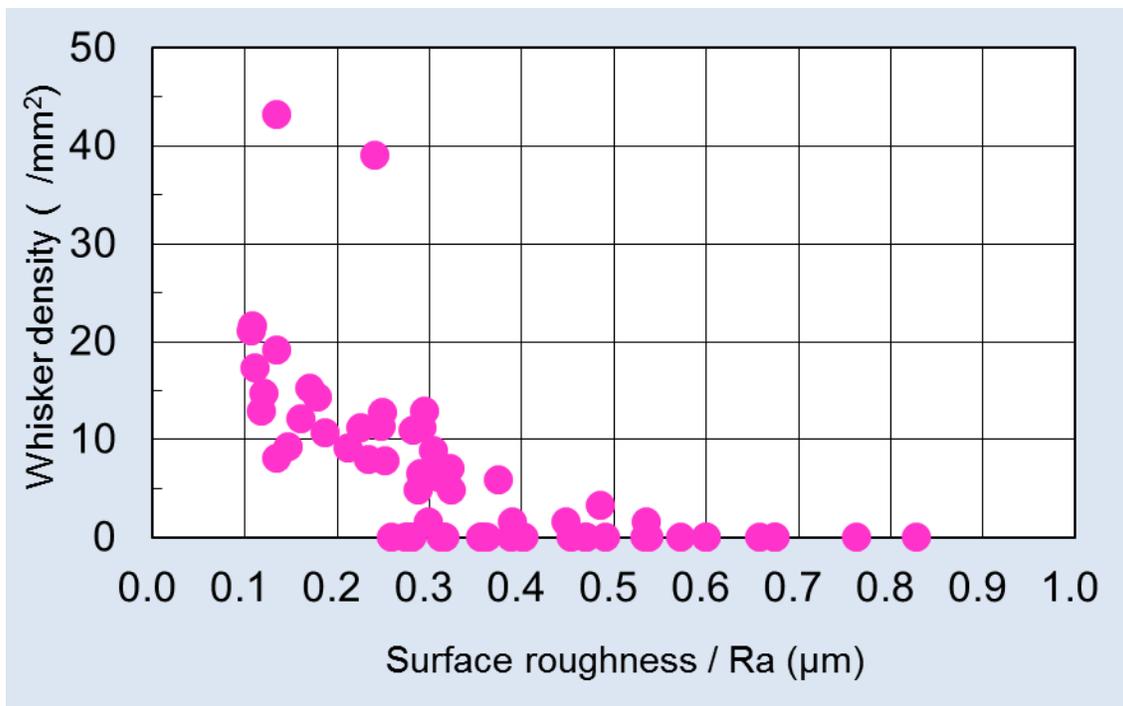


Figure 7. Whisker Density vs Surface Roughness (1000 Hrs at 30°C/60%RH)

The data clearly indicates that there is clear correlation between surface roughness and whisker propensity. The rougher surface produces lower whisker length and also lower density per mm². Figure 8 shows whisker growth on 3 um of tin plated on smoother copper (Ra0.13) as compared to no whiskers on the rougher surface (Ra 0.47)

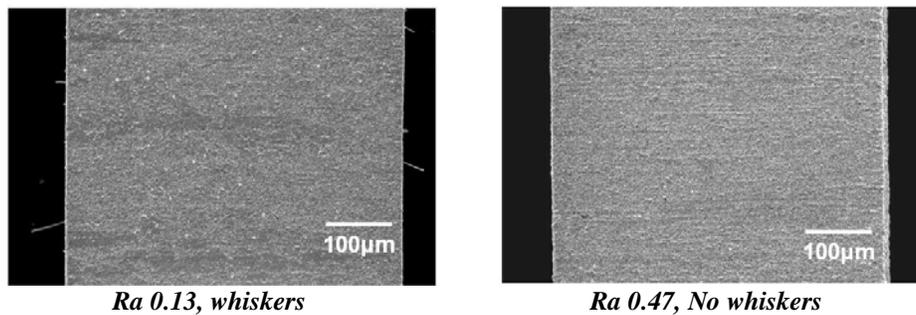


Figure 8. 3 um Tin after 1000 hours at 30°C/60%RH

In an effort to explain this more work was done. Samples with a tin deposit thickness of 10 um were stored for 7000 hours at 30°C/60% RH. The tin was then stripped by chemical means and the IMC morphology was examined. In addition cross sections were prepared and examined to verify the top down observation.

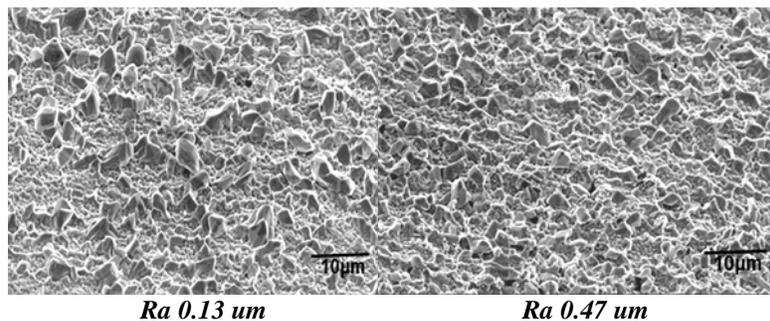


Figure 9. Morphology of IMC surface after tin stripping

Figure 9 shows the top view of the IMC after tin stripping on two extremes of Ra namely Ra:0.13 um and Ra:0.47 um. Figure 10 shows cross-sections of the same Ra values. It is clear that the rougher Ra of 0.47um produced a thinner more uniform IMC, compared to the smoother Ra of 0.13um which showed increased IMC thickness in localized areas. A plausible explanation is that the IMC is spread over a much larger area on the rougher morphology (Ra 0.47um) as compared to the smaller area of the smoother surface (Ra 0.13um). It follows then that the stress resulting from IMC formation would be highly reduced and dissipated with increased surface roughness of the underlying copper substrate.

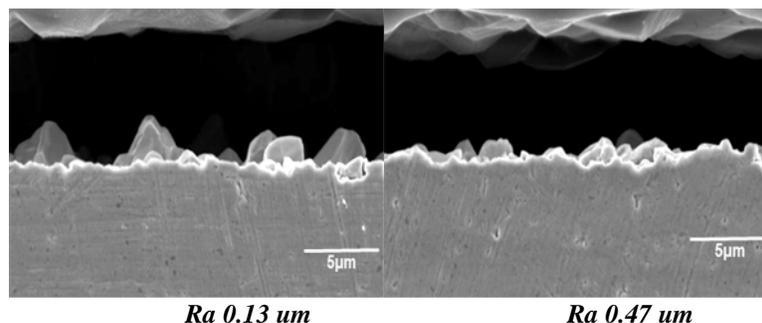


Figure 10. Cross section showing the IMC after tin strip

The solderability and the ductility of a 10 um tin deposit on the 2 extremes of surface morphology were examined using “Wetting Balance Testing” as well as the “Bend test”. There was virtually no difference in performance Refer to Figure 11.

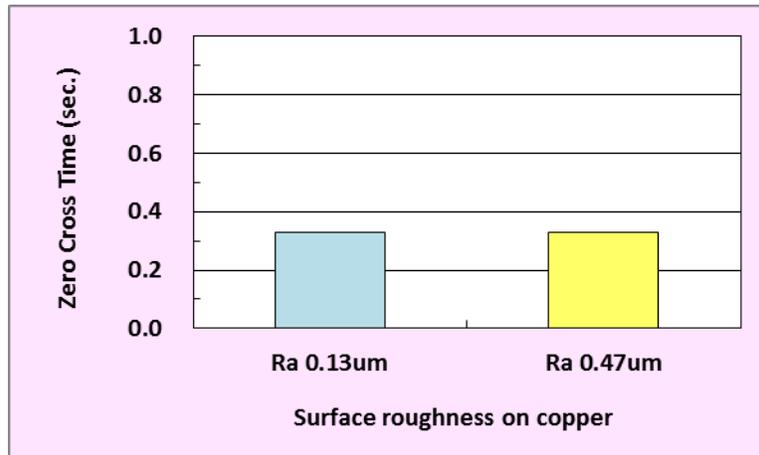


Figure 11. Comparison of Zero Cross Time of 10 um tin deposit for 2 levels of roughness

B. Modifying the Crystal Structure of the Tin Deposit

A close examination of the crystal structure of both tin and tin-lead alloy shows a clear difference between the 2 deposits. The tin-lead which does not whisker has an equiaxed relatively fine grained deposit. The tin on the other hand shows larger columnar crystals. Figure 12 shows the difference in crystal structure between tin and tin-lead alloy (10 wt%Pb).

It is believed that if the crystal structure of the tin deposit can be modified to the tin-lead crystal structure, the stresses will be dissipated and whiskers will not form.

Tests were conducted using the same test vehicle and the same plating conditions as outlined earlier in the copper surface roughness study above.

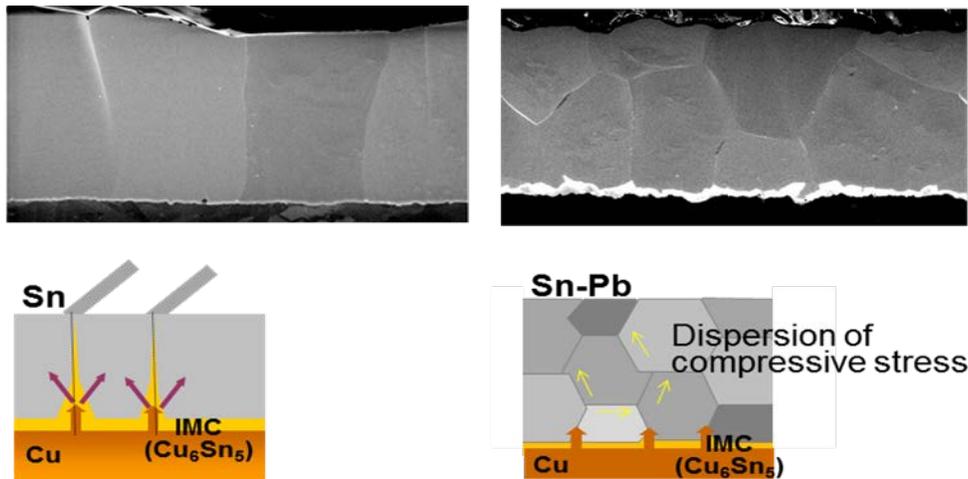


Figure 12. SEM and schematics of the tin vs the tin-lead deposit structures

Three types of tin deposits were produced by the use of specific plating additives to the bath; type “A” is a standard tin deposit characterized by large columnar crystals, type “B” is modified to produce smaller columnar grain structure. Type “C” was further modified to produce a still smaller grain that is both columnar as well as equiaxed, almost mimicking the tin-lead structure. Refer to Figure 13 below. The level of additive in the bath is maintained by continuous dosing. Dosing is based on AmpHrs of plating and results on consistent crystal structure throughout the life of the bath.

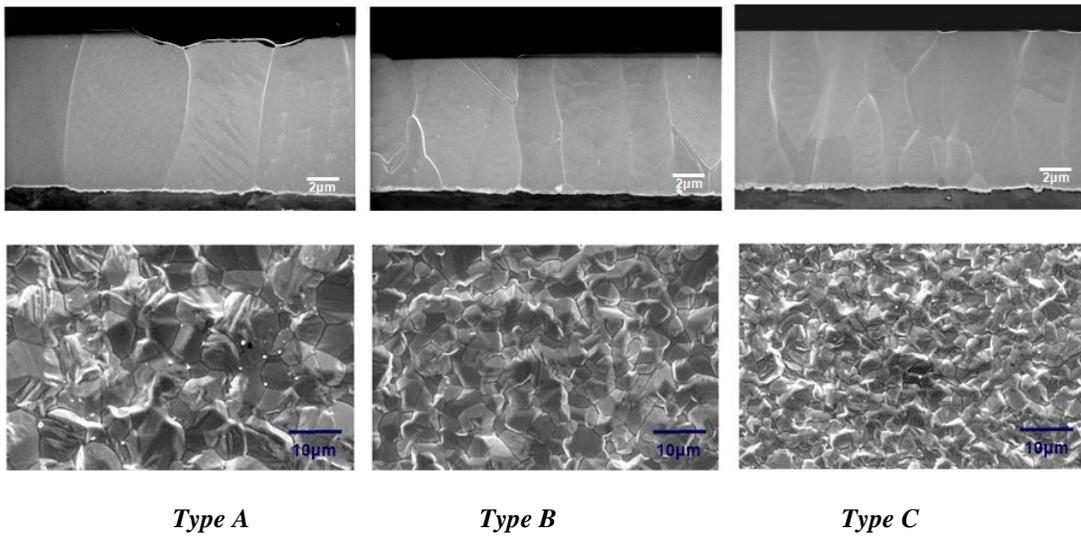


Figure 13. shows the SEM of a cross-section and surface morphology in the 3 types of tin deposits.

Results and Discussion

All three types were plated to the typical thickness of 10 µm (thickness typical of lead frames) and were placed in an ambient environment (30°C/60%RH) for 4000 hours. Figure 14 shows Type A tin deposit with relatively long whiskers developed. Figure 15 shows type B, with whiskers that are shorter than the type A whiskers. Figure 16 shows no whisker formation with a Type C crystal structure stored under the same conditions.

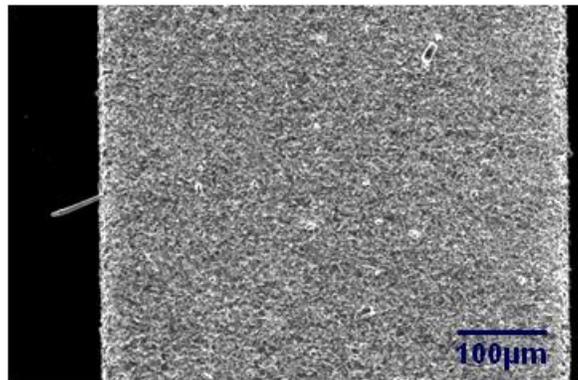


Figure 14. Type A, Whiskers (long)

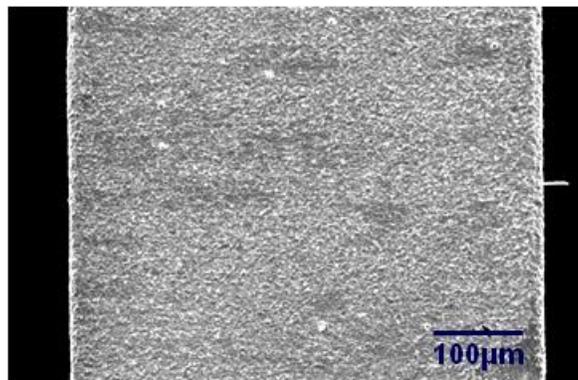


Figure 15. Type B, Whiskers (short)

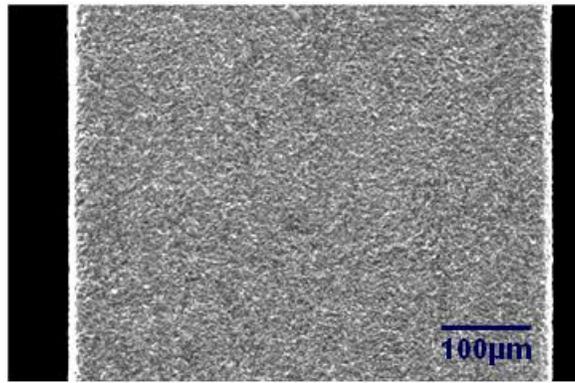


Figure 16. Type C, No Whiskers

Figure 17 shows a graph depicting the length of whisker vs storage time of the 3 crystal types of tin deposits.

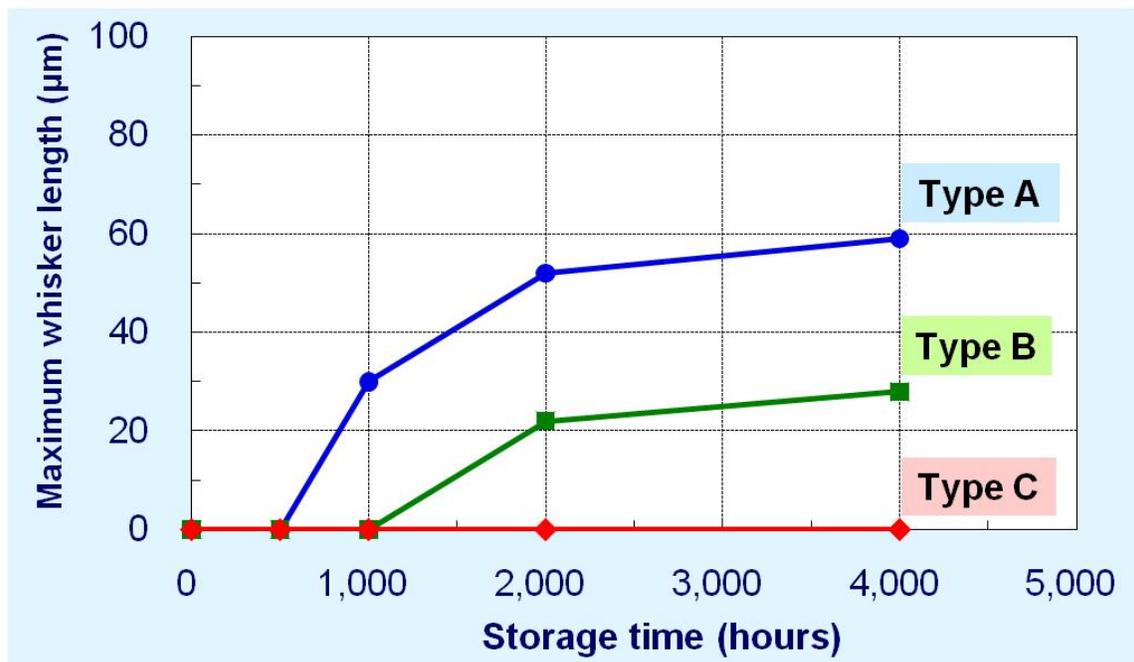


Figure 17. Storage time vs Maximum whisker length of 3 types of tin structures

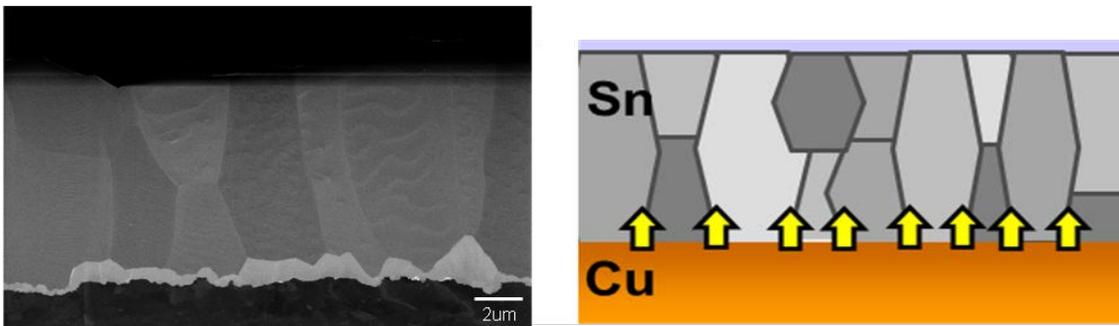


Figure 18. shows the actual SEM of a cross-section and a graphic presentation of the same.

Figure 18 is the result of the fine grained equiaxed crystal structure (type C deposit) achieved by modifying the plating bath with specific types of additives.

The result is a very controlled evenly distributed relatively thin IMC, producing minimum stress. The equiaxed crystal structure dissipates the stress resulting in no whisker formation. In this study no whiskers were observed with fine grained equiaxed tin deposits stored under ambient conditions for up to 22000 (twenty-two thousand) hours.

Conclusion

In this study two distinct approaches were attempted to restrain whisker growth in tin deposits over copper. The first approach was to create a uniform IMC, by micro-roughening the copper substrate before tin deposition. A uniform IMC would eliminate high stress in localized areas. The second approach was to modify the grain, from a large columnar structure to a fine grained equiaxed structure, resembling the structure of tin-lead deposit. Tin deposit which had crystal structure similar to tin-lead deposit restrained tin whisker formation effectively. Crystal structure modification of the tin deposit was demonstrated to be a very effective way to restrain tin whisker formation.

Reference

- [1] P. Oberndorff, M. Dittes, P. Crema, and S.Chopin ; “Whisker Formation on Matte Sn Influence of High Humidity”, 55thECTC, 2005.
- [2] W.J. Boettinger, C.E. Johnson, L.A. Bendersky, K.-W. Moon, M.E. Williams, and G.R. Stafford: “Whisker and hillock formation on Sn, Sn-Cu and Sn-Pb electrodeposits”, Acta Mater., Vol.53, pp.5033-5050, 2005.
- [3] W. Zhan and F. Schwager: “Effects of Lead on Tin Whisker Elimination - efforts toward lead-free and whisker-free electrodeposition of tin”, Journal of The Electrochemical Society, Vol. 153 (5), pp. C337-C343, 2006.



IPC Symposium on Tin Whiskers

Study of Tin Whisker Inhibiting Systems
Controlling the copper substrate roughness
Controlling the tin deposit crystal structure

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- Background
- Factors affecting tin whisker formation
- Mechanism of tin whisker formation at ambient conditions
- Checking the effect of copper surface roughness in tin whisker formation
- Checking the effect of tin deposit crystal structure in tin whisker formation
- Conclusion

Background

- Pure tin and tin based alloys plating for alternative of tin-lead finish is being used on the majority of electronic components.
- Tin whisker of tin and tin based alloy deposits are commonly known to cause the short circuits in electronic components.
- In the case of tin finish on copper and copper based alloys, the major cause of tin whisker formation is compressive stress which is increased by irregular growth of copper-tin intermetallic compound (IMC) at ambient conditions.

Background

- It is known that tin whiskers are formed easily on the plated tin deposit, and are prevented on the tin-lead deposit.
- The tin deposit and tin-lead deposit are different in the crystal structure.
- Crystal Structure has a direct impact on tin whiskers formation.
- A Tin Deposit with modified crystal structure (similar to tin-lead deposits) is capable of preventing whisker formation by dissipating and delocalizing the stress that cause whiskers.

Factors affecting “Tin Whisker” formation

Tin oxide film ; SnO, SnO₂

Tin deposit or Tin alloy deposit ;
Surface morphology (grain size, crystal structure),
Thickness,
Alloy element, Carbon content, Crystal orientation,
Internal stress

Intermetallic compound ; Cu₆Sn₅, Cu₃Sn, Ni₃Sn₄

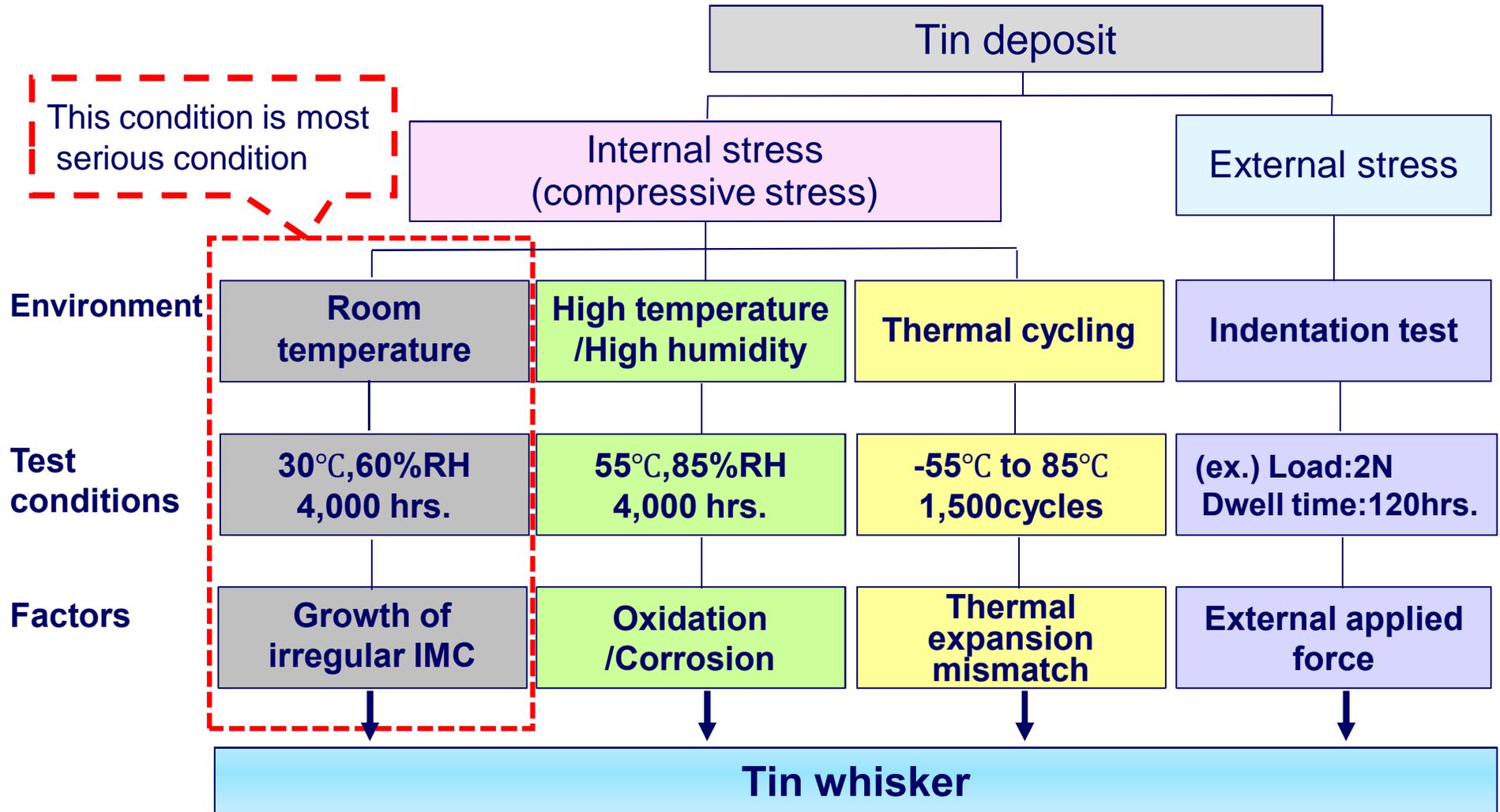
Underlayer ; Nickel, Copper, etc.

Substrate ;
Material ; Copper, Alloy42, Brass, etc.
Stress ; Etching, Stamping, Baking

After treatment ; Baking, Reflow

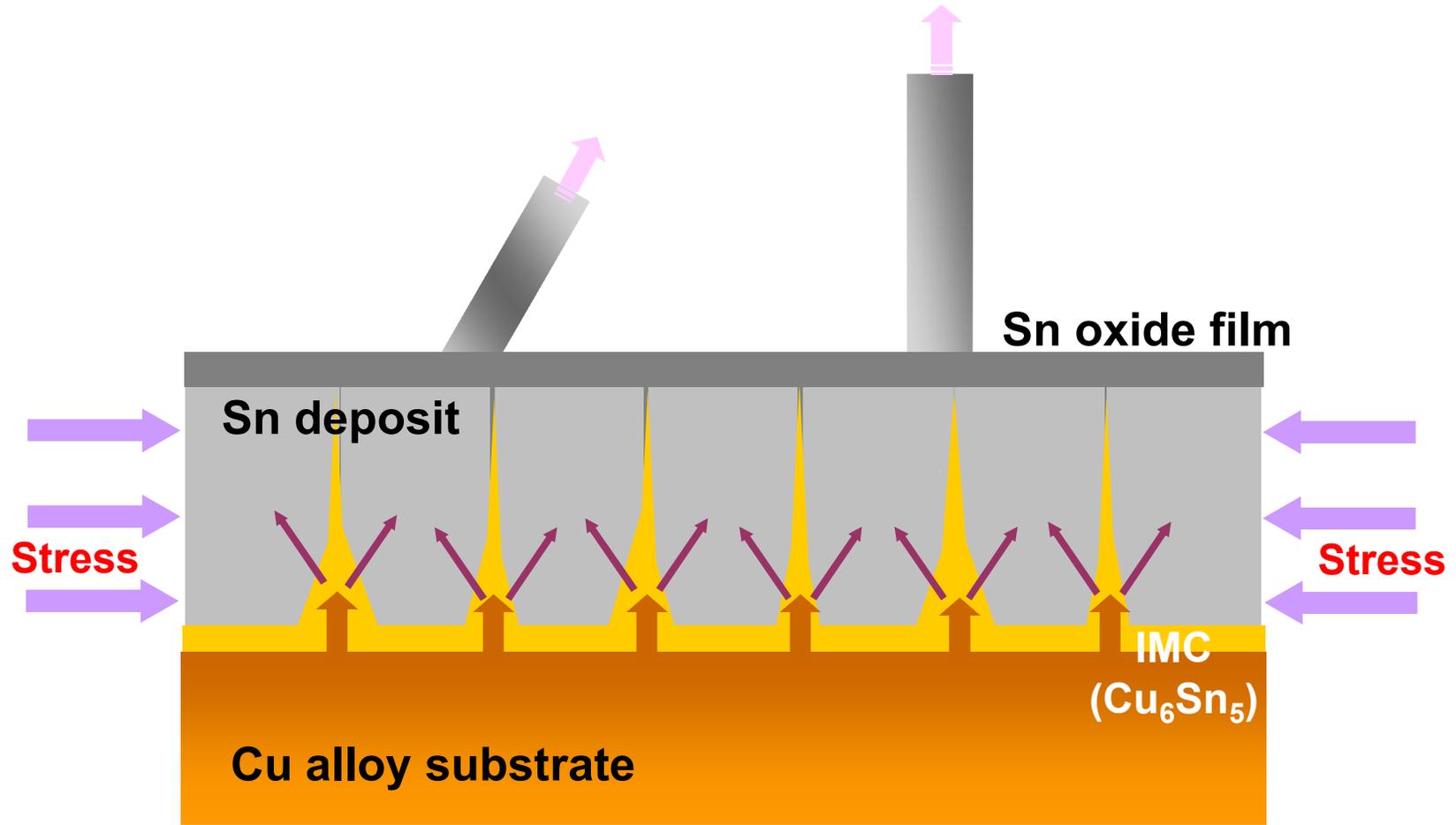
Environment ; Temperature, Humidity, Thermal cycle, Mechanical stress

Factors affecting “Tin Whisker” formation and whisker evaluation methods

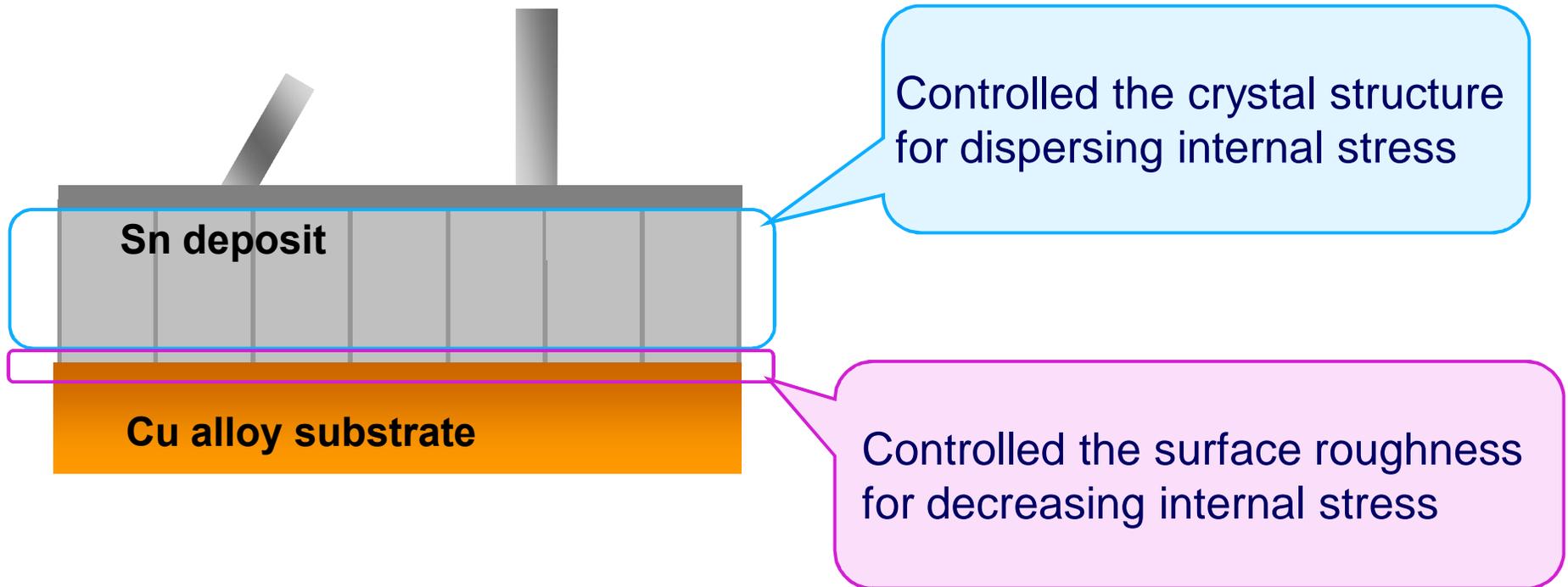


※ JESD201(JEDEC), RC-5241(JEITA)

The mechanism of “Tin Whisker” formation at ambient that is the most serious condition



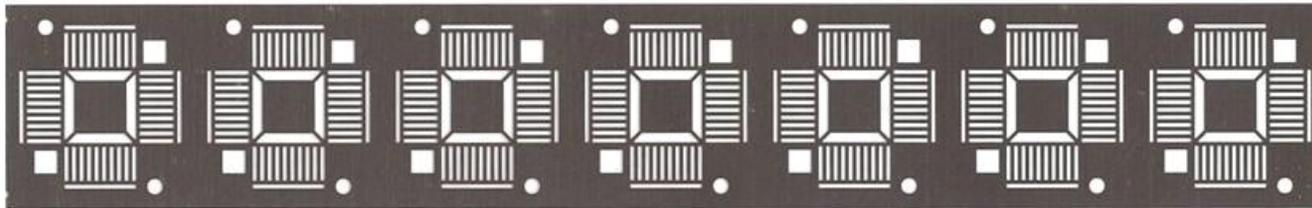
Approach to reduce “Tin Whisker” formation



**Study of
Copper Surface Morphology
vs.
Tin Whisker formation**

Test vehicle

- CDA19400 (Cu-2.3Fe-0.03P-0.12Zn) leadframe
(Original leadframe)



Tin plating

- Plating bath : MSA matte tin plating bath
- Cathode current density : $10\text{A}/\text{dm}^2$
- Thickness ; 3 μm (for evaluating whisker in the short term)
10 μm (typical thickness for leadframe)

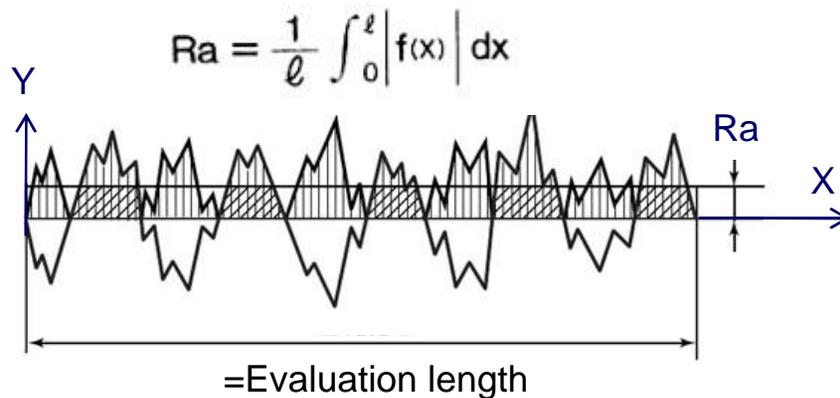
The copper surface control method

Etching

- Etchant : Various etchants were used for forming surface roughness on copper substrate.
- Measurement

Surface roughness was analyzed by laser microscope

Parameter : Ra(μ m) arithmetic average of absolute values



Ra ; From the direction of the average line of the roughness curve of a sampled standard length, plot the direction of the average line of the sampled section on the X axis and the direction of the vertical magnification on the Y axis, and express the roughness curve using the equation $y=f(x)$. The roughness value is then expressed in micrometers (μ m) as the value determined from the left expression.

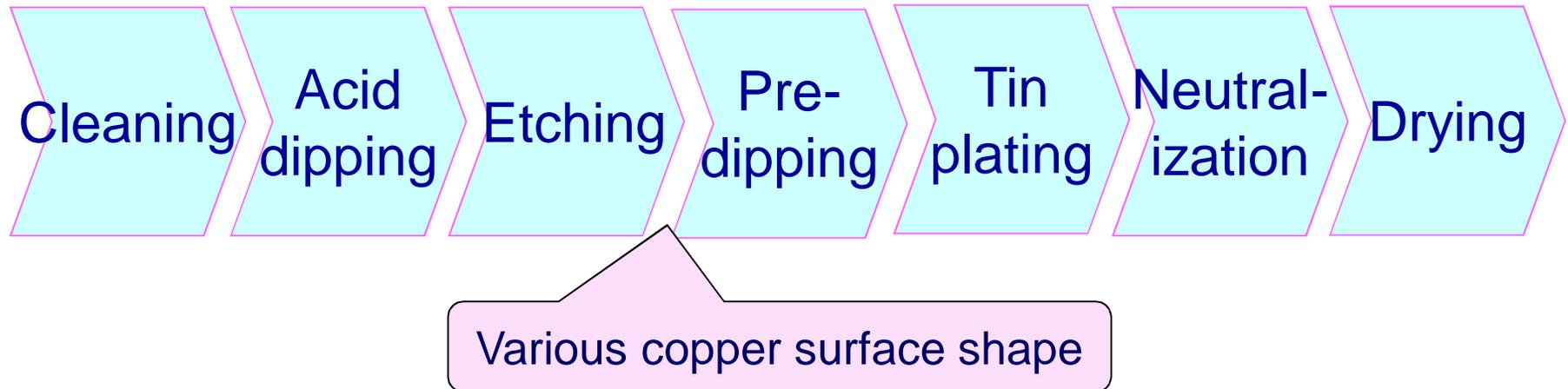
The evaluation method of tin whisker formation

Whisker test

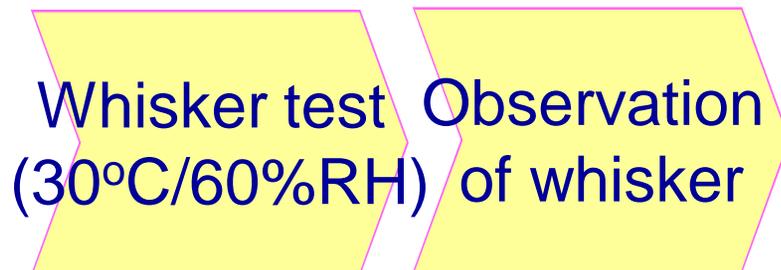
- Storage condition : 30°C / 60%RH
- Storage time : 1,000hours (for 3 μ m thickness tin deposit)
4,000hours (for 10 μ m thickness tin deposit)
- Parameter : Maximum whisker length
Whisker density
- Definition of whisker
Aspect ratio (length/diameter); more than 2
Whisker length; more than 10 μ m
- Measurement method of whisker length; JEITA ET-7410
The straight line distance from the point of emergence of the whisker to the most distant point on the whisker.

Outline of the evaluation

Plating process (Common process of tin plating)

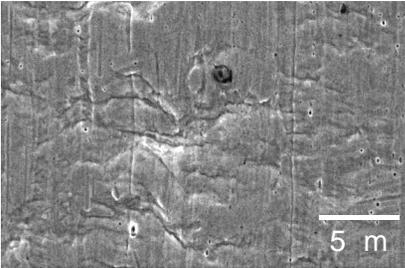
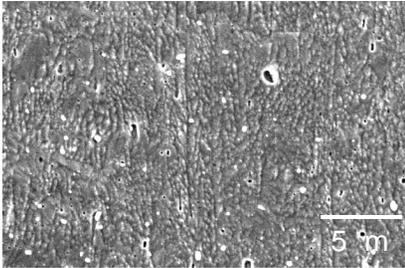
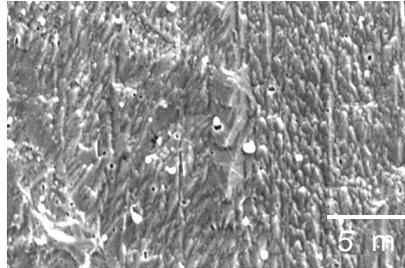
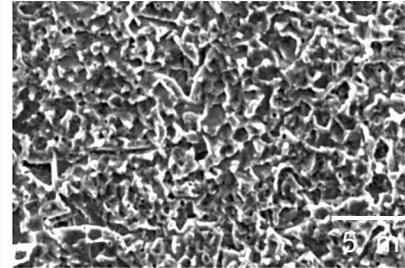
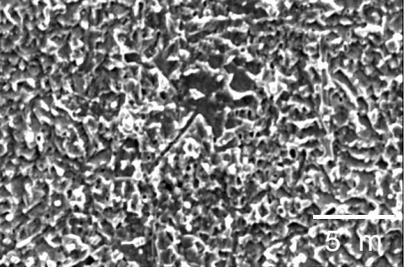
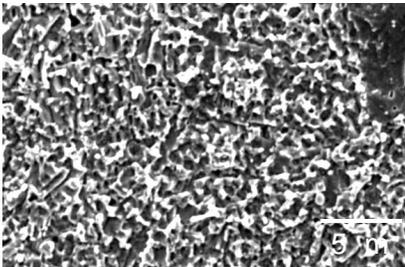
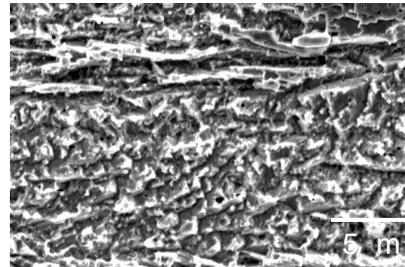
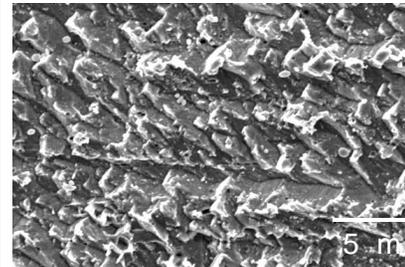


Whisker evaluation process



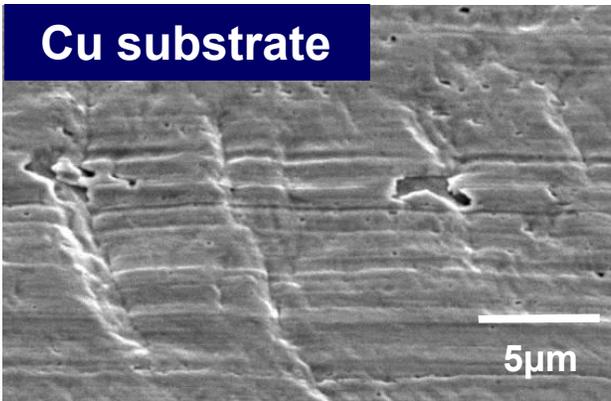
Shape vs. Ra the copper substrate surface

Ra (μ m)

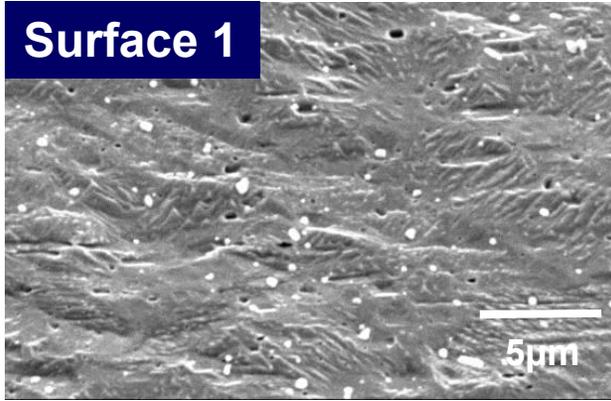
| 0.087(substrate) | 0.120 | 0.187 | 0.249 |
|---|--|---|---|
|  |  |  |  |
| 0.288 | 0.358 | 0.402 | 0.487 |
|  |  |  |  |

Surface shape on copper substrate after etching

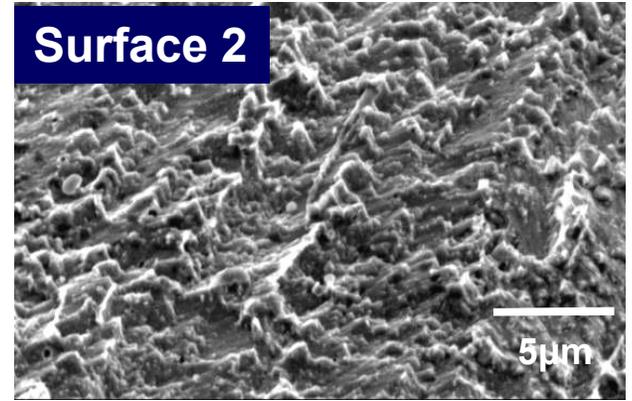
Substrate: CDA19400 leadframe / Etching depth: 2 μm (average)



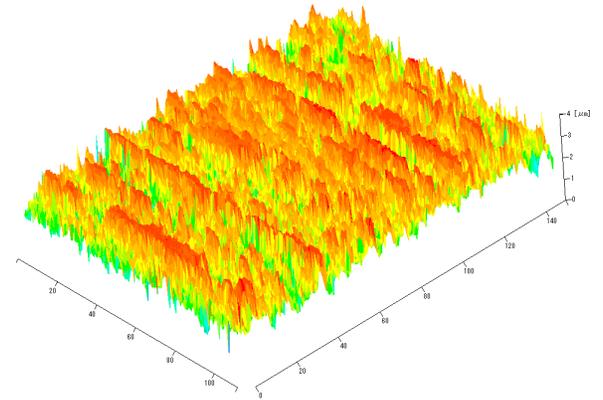
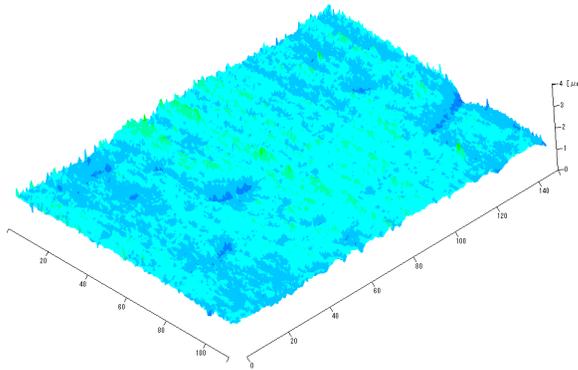
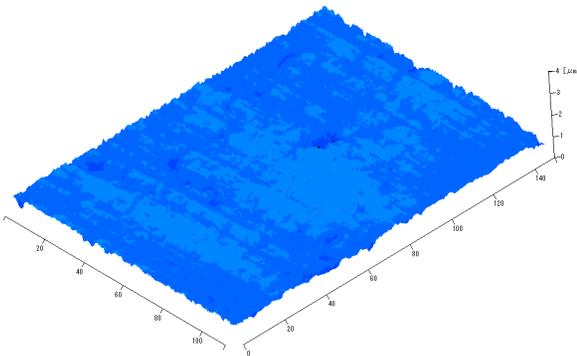
Ra 0.08 μm



Ra 0.15 μm

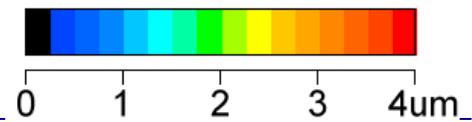


Ra 0.45 μm



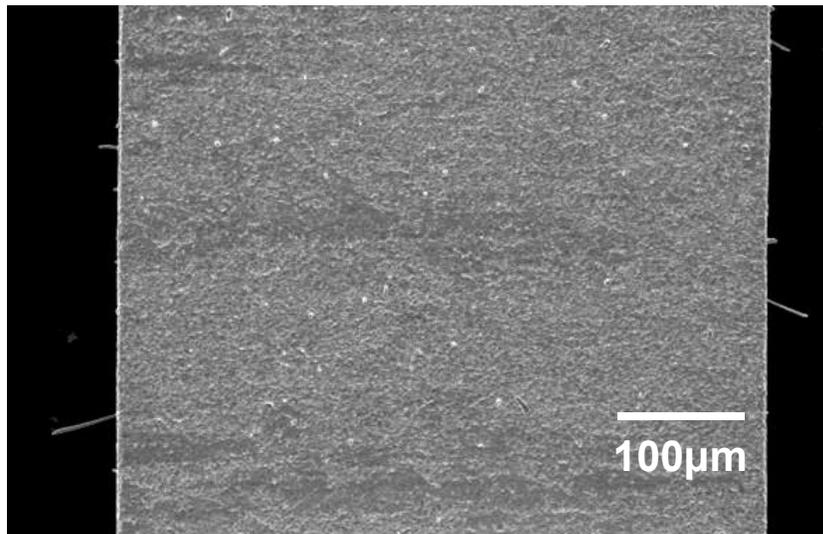
The above 3D roughness map is analyzed by laser microscope.

Ra: arithmetical mean roughness



Observation of tin whisker after test

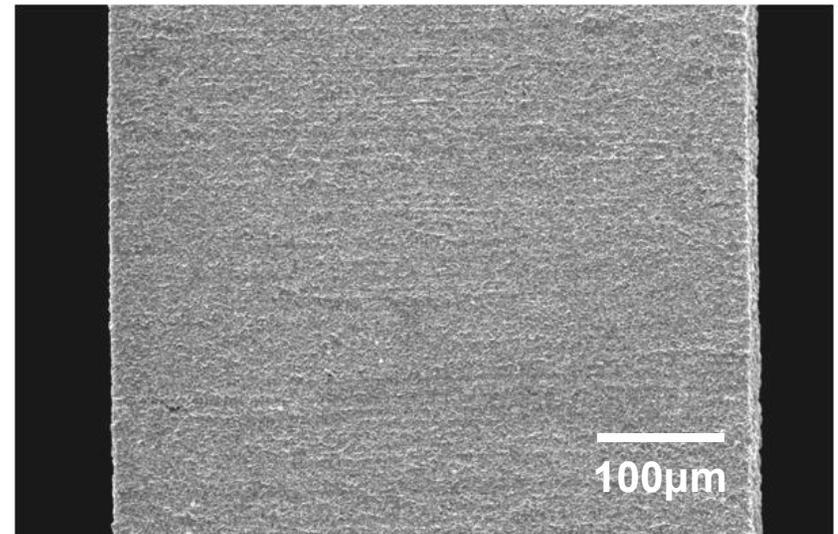
Samples : Tin thickness 3 μ m
Storage condition : 30°C / 60%RH / 1,000hours



Ra 0.13 μ m

Surface roughness
on Cu substrate

Whiskers were observed.



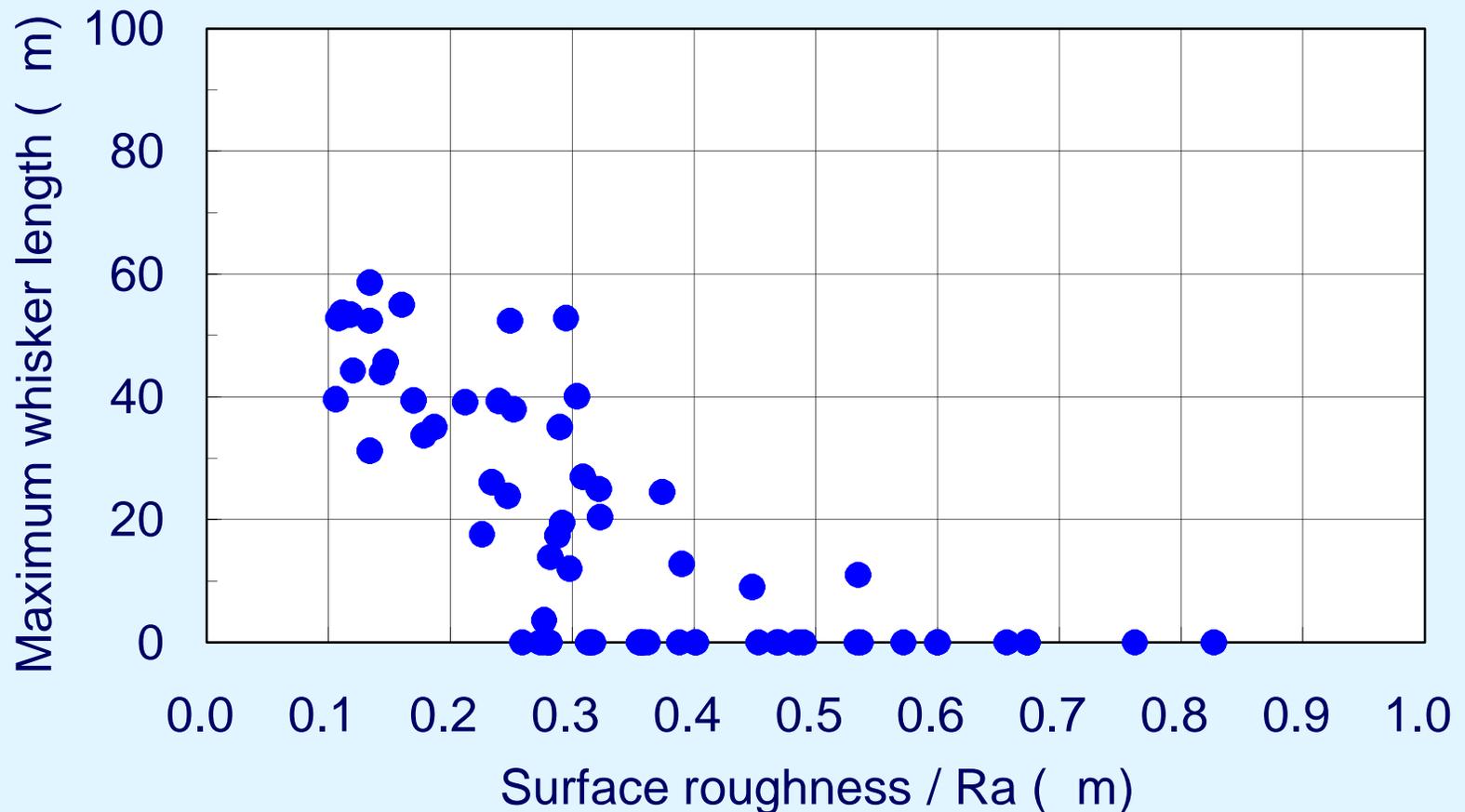
Ra 0.45 μ m

No whiskers

Maximum Whisker Length on 3 μ m thickness tin deposit

Samples : Tin thickness 3 μ m

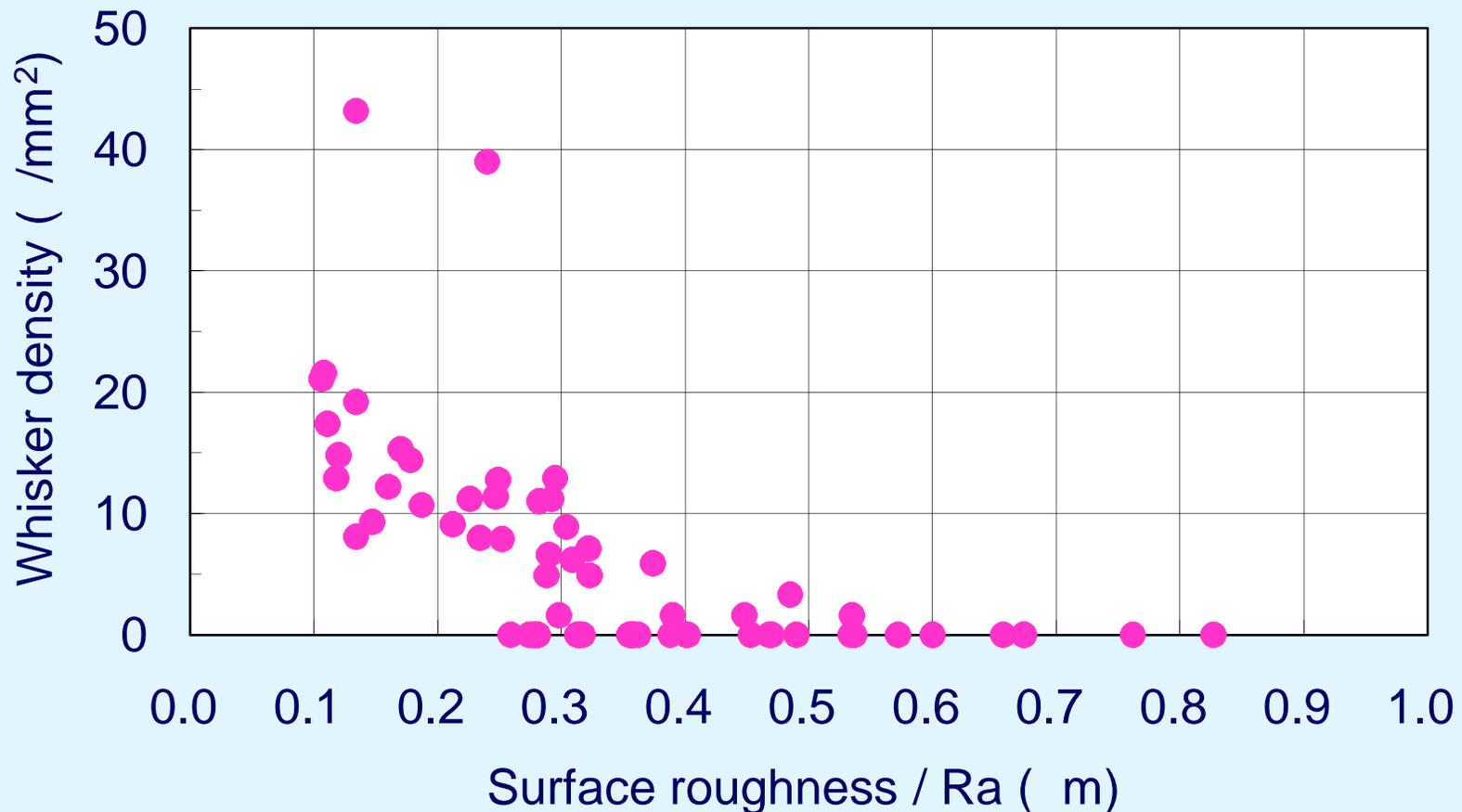
Storage condition : 30°C / 60%RH / 1,000hours



Whisker Density on 3 μ m thickness tin deposit

Samples : Tin thickness 3 μ m

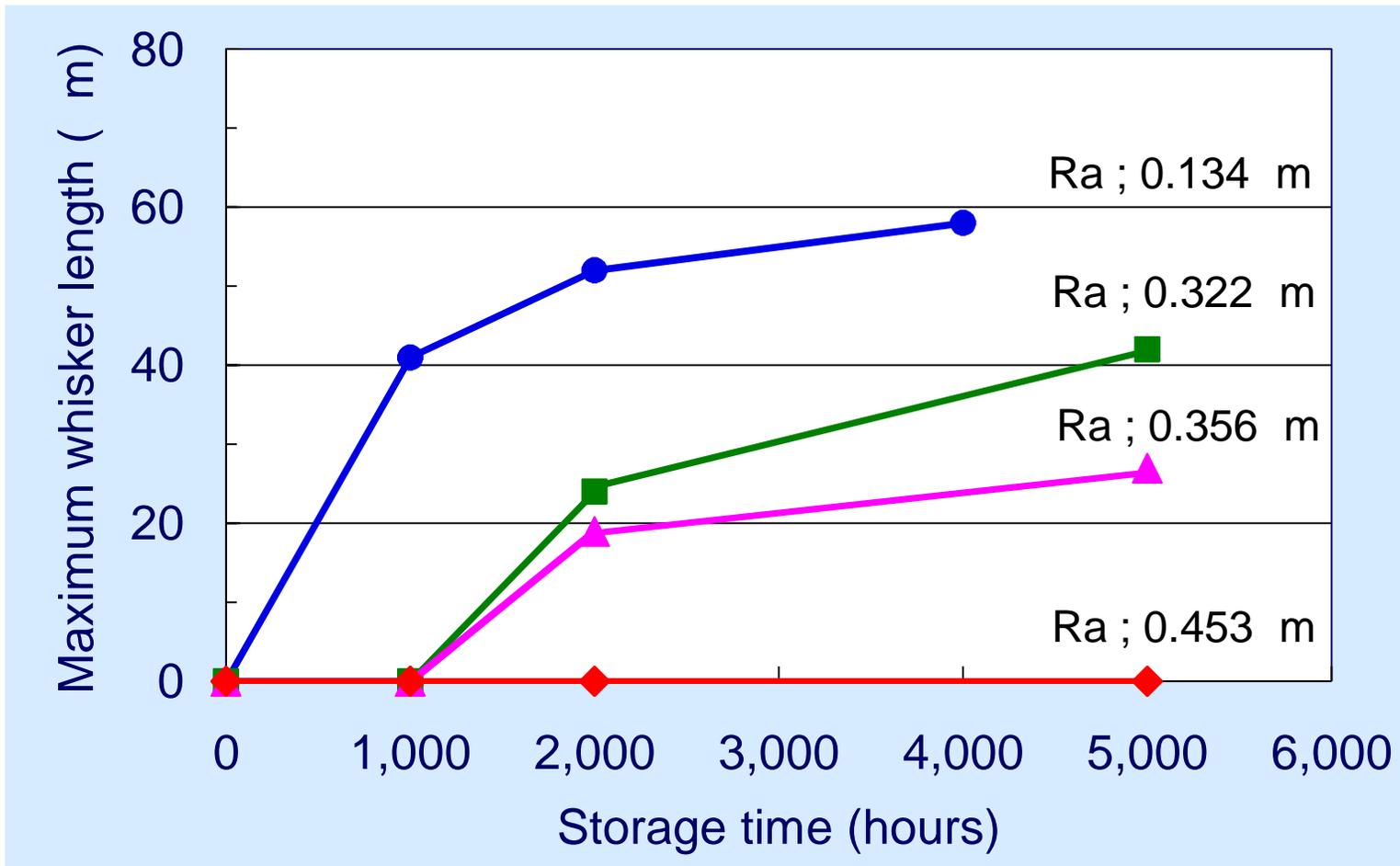
Storage condition : 30°C / 60%RH / 1,000hours



The relation of Maximum whisker length vs. surface roughness

Samples : Tin thickness 10 m

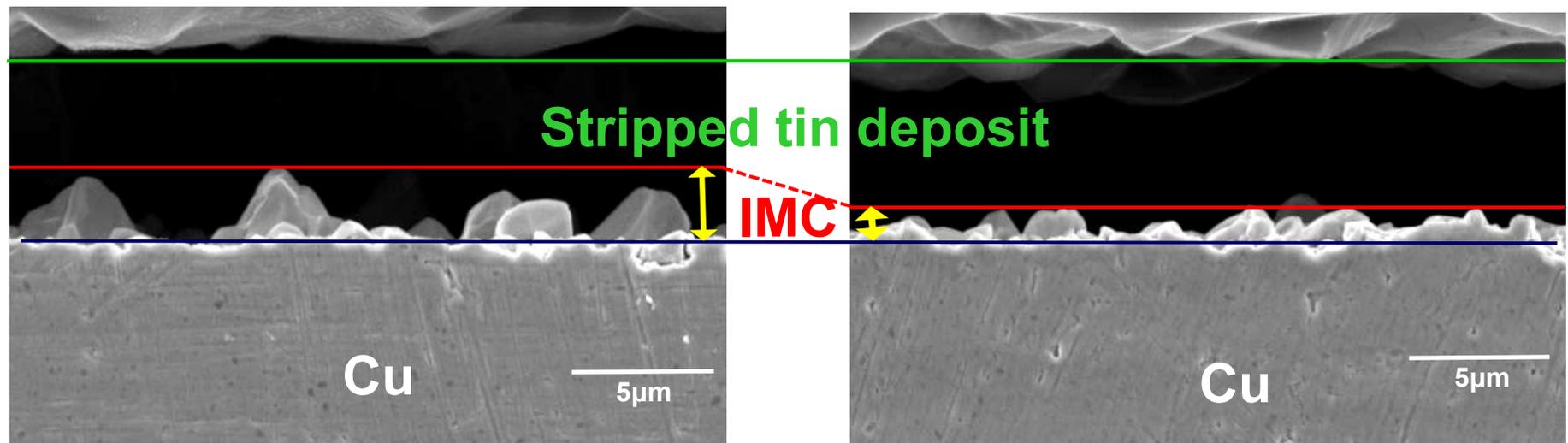
Storage condition : 30°C / 60%RH / 5,000hours



Comparison of the IMC with surface roughness after stripping tin deposit by cross section

Samples : Tin thickness 10 μm

Storage condition : 30°C / 60%RH / 7,000hours



Ra 0.13 μm

Surface roughness on copper substrate

Ra 0.47 μm

- Large IMC grain
- Localized

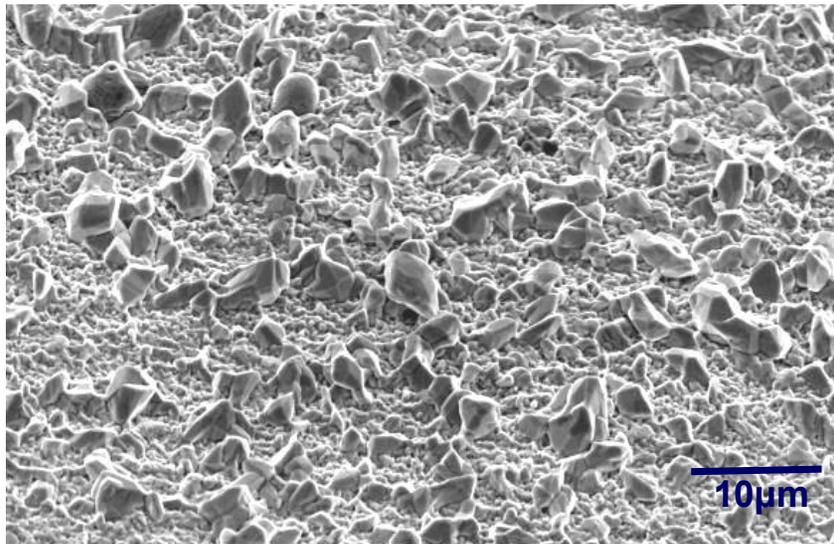
- Small IMC grain
- Comparatively dispersed and uniform

Comparison of the IMC with surface roughness after stripping tin deposit by surface SEM

Samples : Tin thickness 10 μm

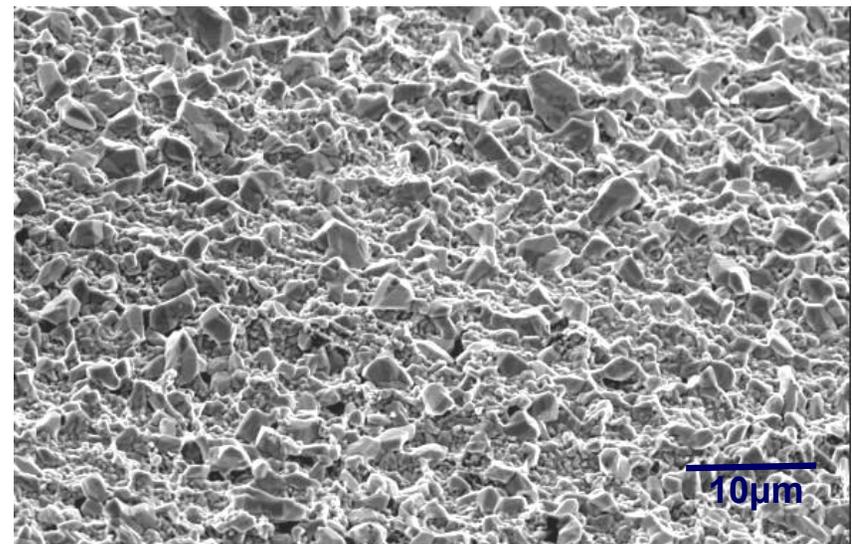
Storage condition : 30°C / 60%RH / 7,000hours

45° tilt in SEM



Ra 0.13 μm

- Large IMC grain
- Localized



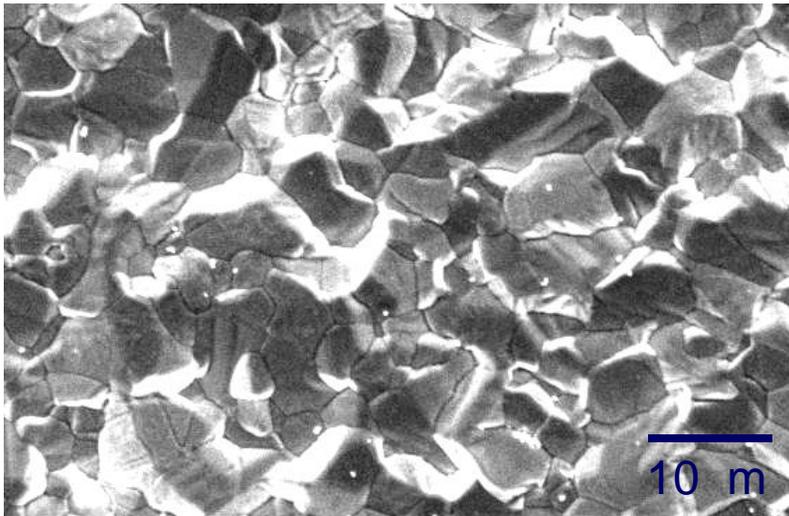
Ra 0.47 μm

- Small IMC grain
- Comparatively uniform

Surface roughness on copper substrate

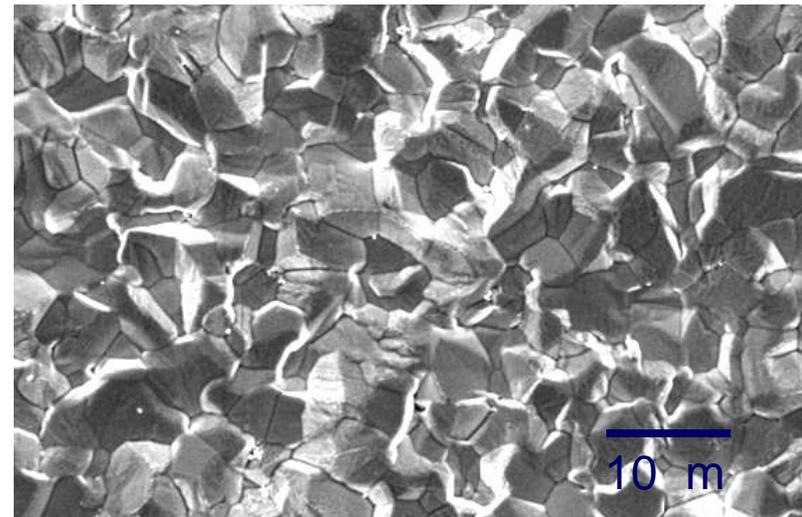
Comparison of the tin surface morphology with copper surface roughness

Tin thickness: 10 μm



Ra 0.13 μm

Surface roughness
on copper substrate



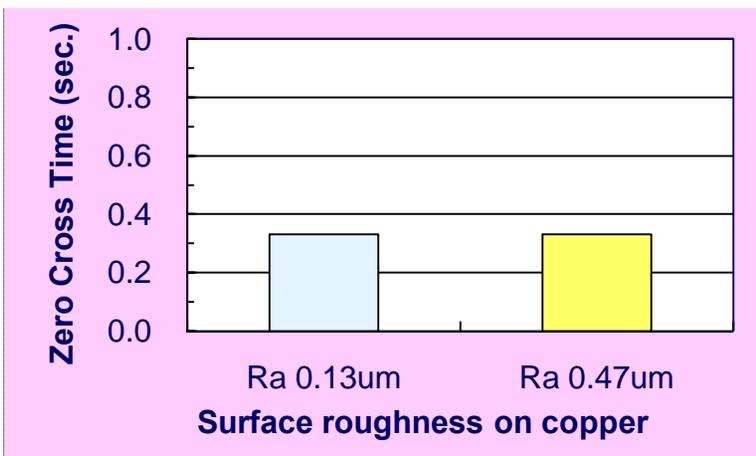
Ra 0.47 μm

- ✓ Tin deposits on two different copper surfaces had same surface morphology.

Comparison of the tin deposit characters with copper surface roughness

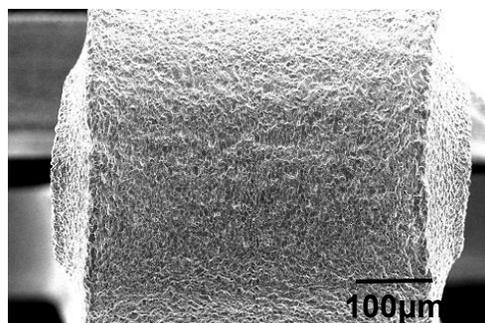
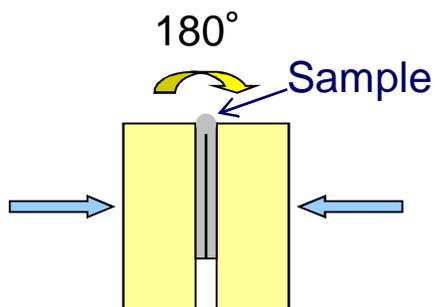
Solderability of tin deposits

Tin thickness: 10 μm

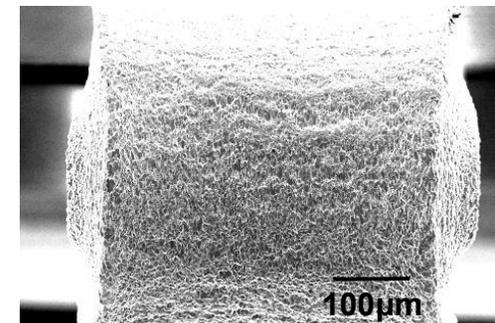


Instrument: SWET-2100 (Tarutin Kester)
 Method: Wetting Balance Method
 Solder: Sn-3Ag-0.5Cu (Senju Metal Industry / M705)
 Flux: CF-110VH-2A (Tamura Kaken)
 Temperature: 255°C
 Immersion Depth: 2mm, Immersion Speed: 2mm/sec.

Bending test (ductility)



Ra 0.13 μm



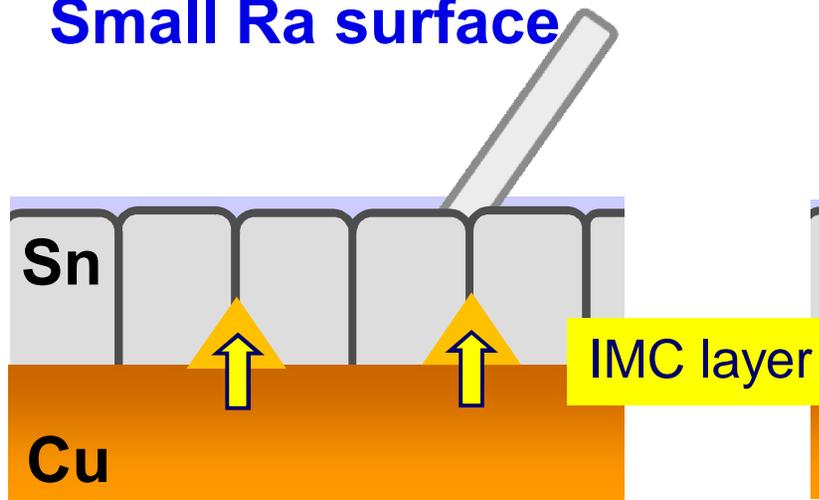
Ra 0.47 μm

Surface roughness on copper substrate

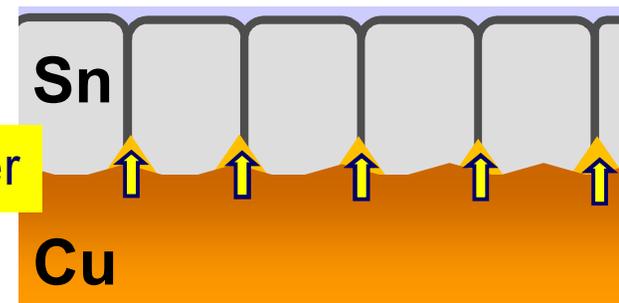
✓ Solderability and ductility of tin deposits on two different copper roughness were excellent. Surface roughness on copper substrate didn't affect properties of tin deposits.

Consideration of tin whisker mitigation by copper substrate roughness

Small Ra surface



Large Ra surface



General understanding

- Large IMC
- Localization



Localized compressive stress is generated in tin deposit.

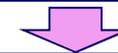


Tin whisker is formed.

- Small IMC
- Comparatively dispersed and uniform IMC layer



Localized compressive stress in tin deposit is relieved.



Tin whisker is reduced.

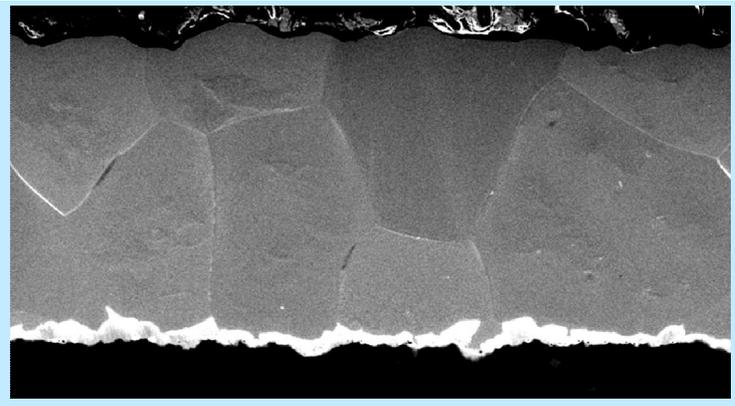
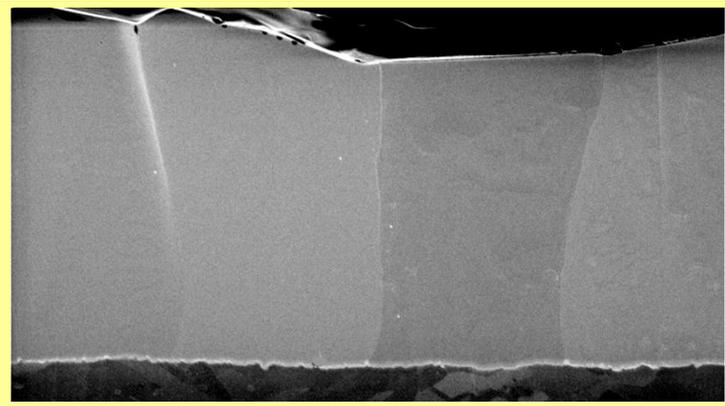
**Study of
The Crystal Structure of Tin Deposit
vs.
Tin Whisker formation**

Checked the different crystal structure of the tin deposit and tin-lead alloy deposit

Whisker formation
Typical tin deposit

Whisker prevention
Tin-lead alloy deposit

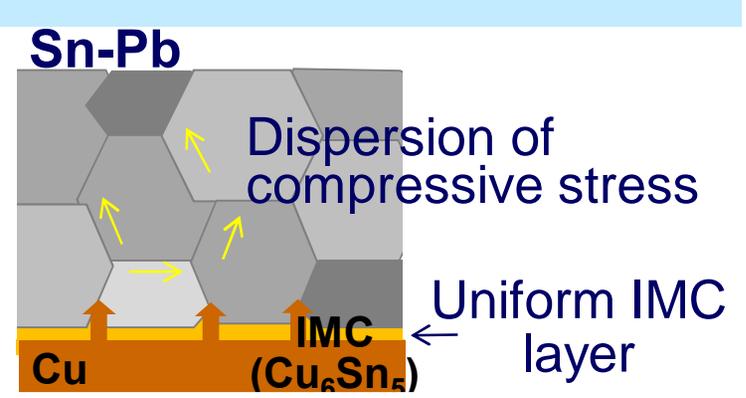
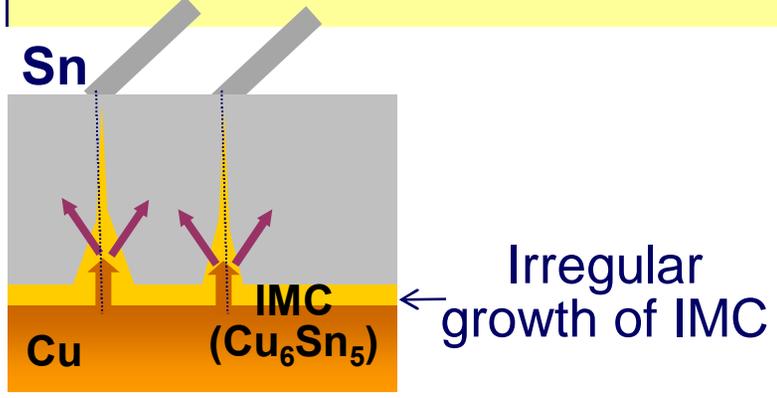
Cross section



Crystal structure

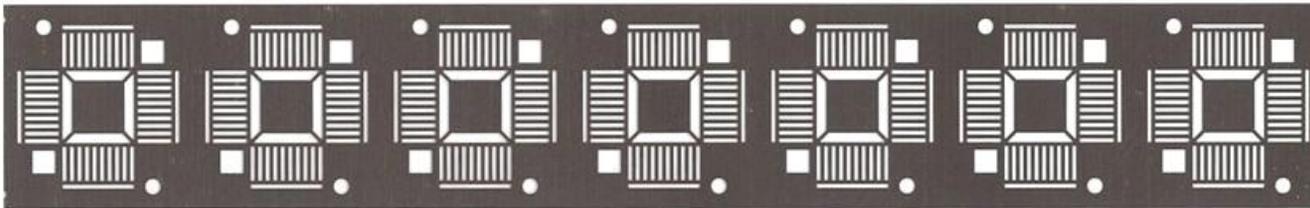
Column structure

Equiaxed structure



Test vehicle

- CDA19400 (Cu-2.3Fe-0.03P-0.12Zn) leadframe
(Original leadframe)



Tin plating

- Plating bath : MSA matte tin plating bath
 - : Three tin plating baths with different additives
- Cathode current density : $10\text{A}/\text{dm}^2$
- Thickness ; $10\mu\text{m}$ (typical thickness for leadframe)



The evaluation method of tin whisker formation

Whisker test

- Storage condition : 30°C / 60%RH
- Storage time : more than 4,000hours
- Parameter : Maximum whisker length
Whisker density
- Definition of whisker
Aspect ratio (long/diameter); more than 2
Whisker length; more than 10um
- Measurement method of whisker length; JEITA ET-7410
The straight line distance from the point of emergence of the whisker to the most distant point on the whisker.

Three kinds of tin deposit

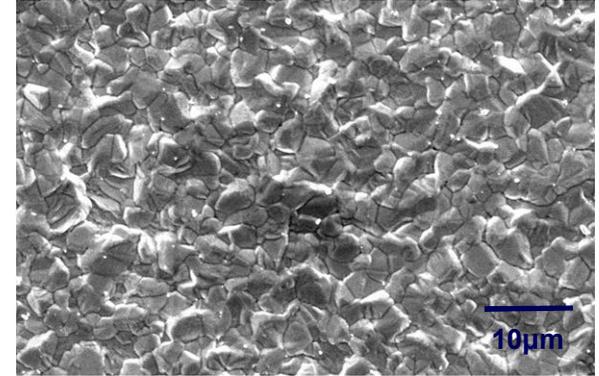
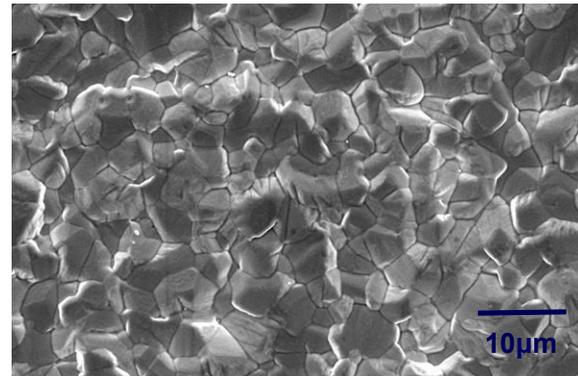
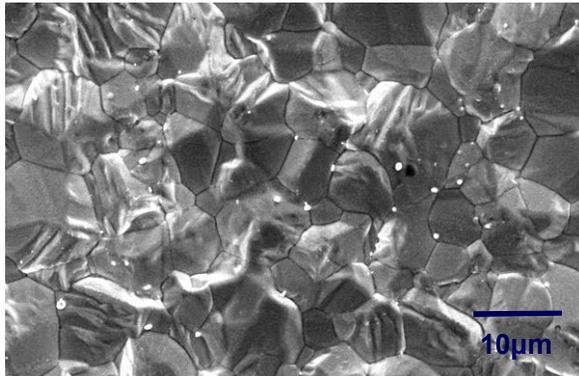
| Kind of tin deposit | | Type A | Type B | Type C | |
|---------------------------------|-------|--------|--------|-------------------|-------|
| Grain size | Large | > | > | | Small |
| Crystal structure | | Column | Column | Column + Equiaxed | |
| Appearance of deposit | | matte | matte | matte | |
| Carbon content in deposit (wt%) | | 0.001 | 0.001 | 0.001 | |

Surface morphology - Grain size -

Type A

Type B

Type C



Large



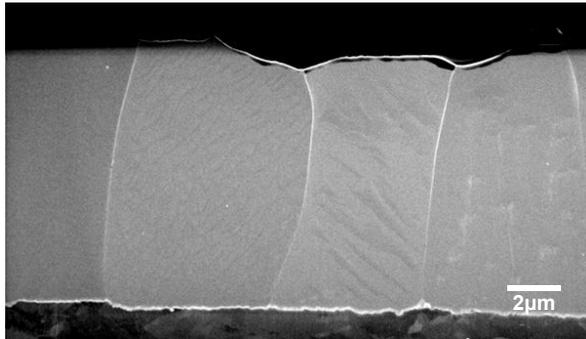
Small

Crystal structure - Cross section -

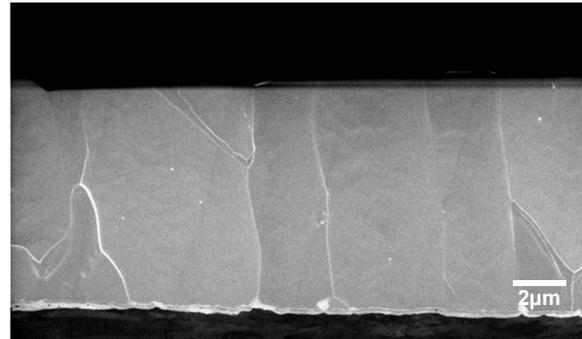
Type A

Type B

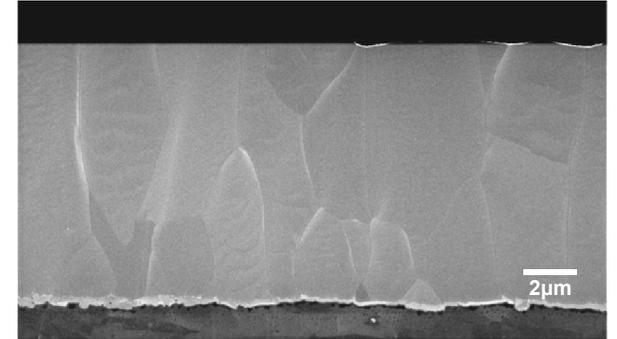
Type C



Column structure



Column structure

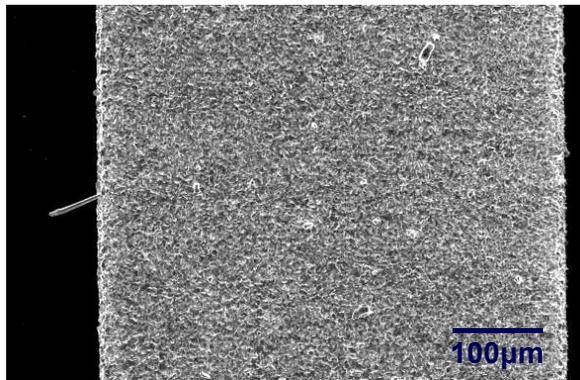


Column + Equiaxed structure

Observation of tin whisker after test

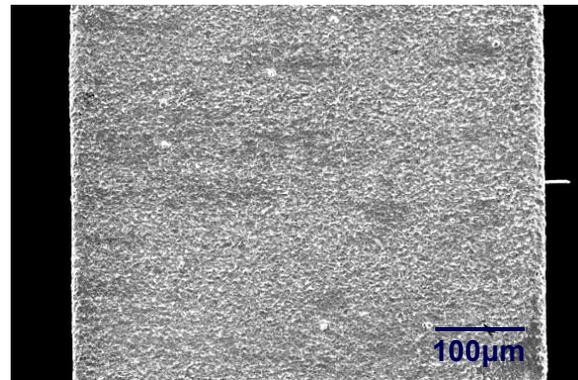
Samples : Tin thickness 10 m
Storage condition: 30°C / 60%RH / 4,000hours

Type A



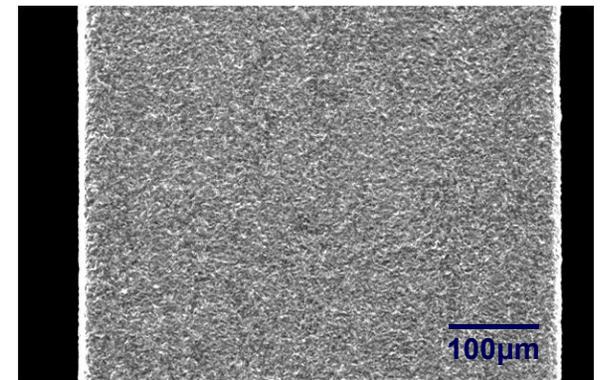
Whiskers were found.

Type B



Whiskers were found.
Whiskers were shorter than Type A.

Type C

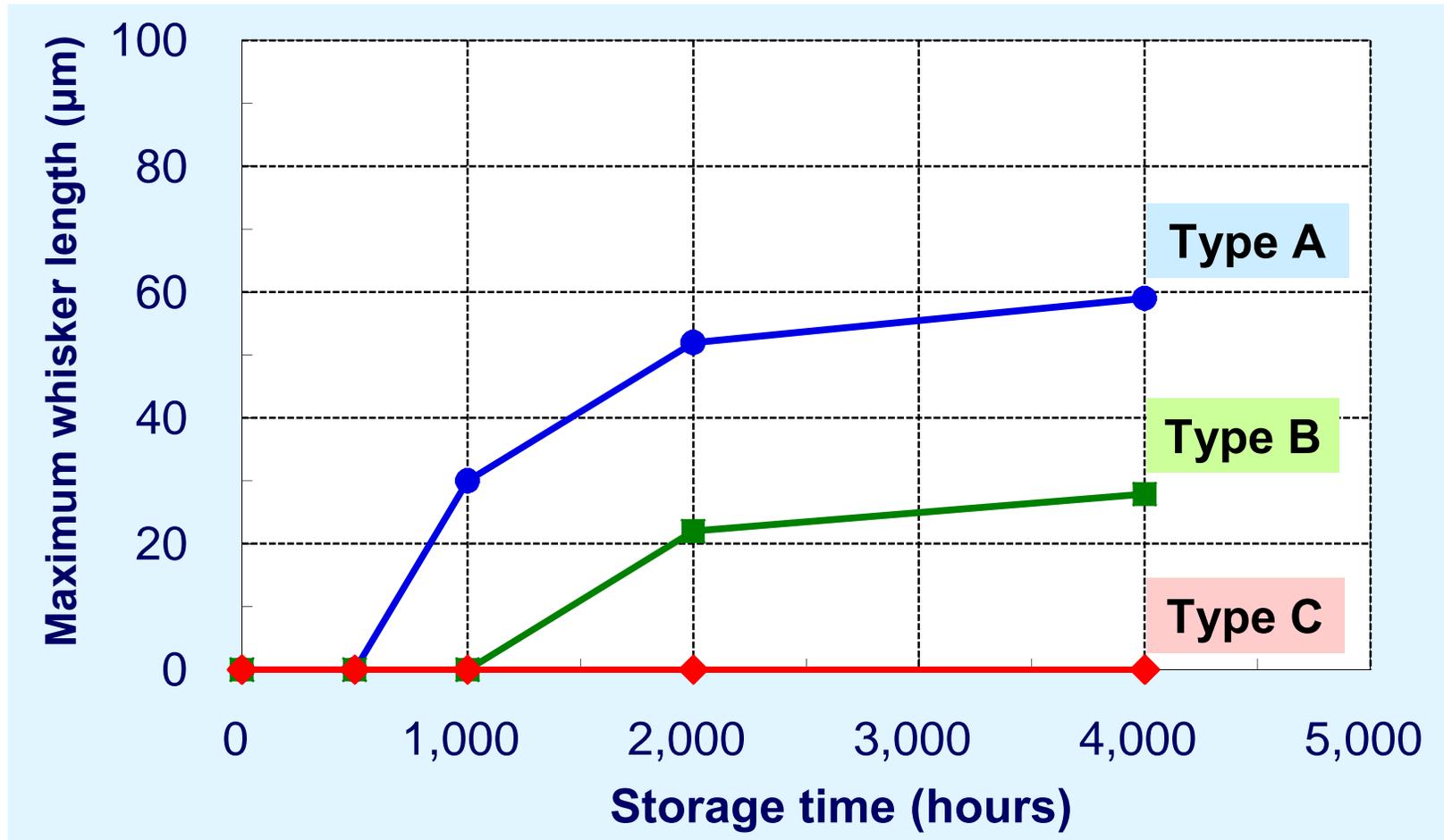


No whiskers

Maximum whisker length

Samples : Tin thickness 10 m

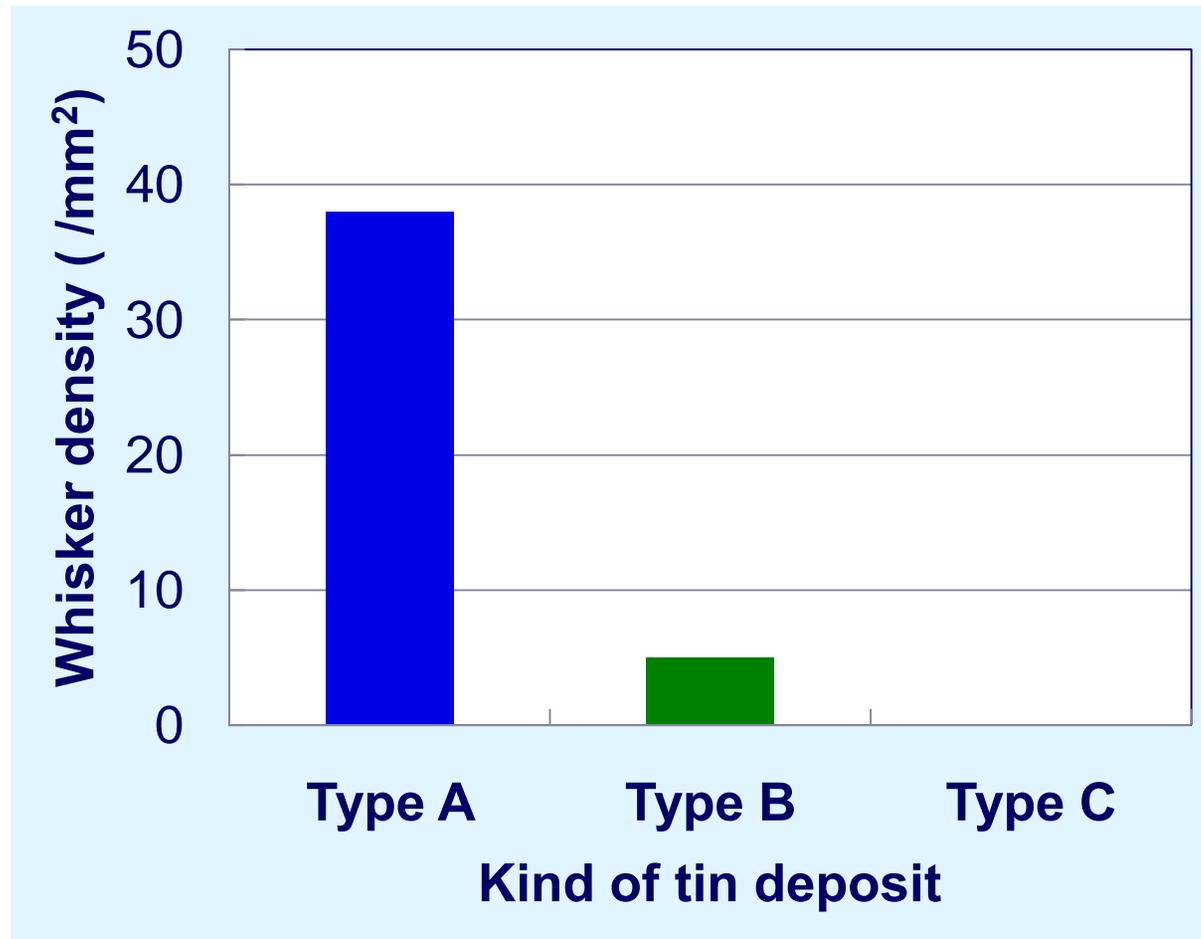
Storage condition: 30°C / 60%RH / 4,000hours



Whisker density

Samples : Tin thickness 10 m

Storage condition: 30°C / 60%RH / 4,000hours

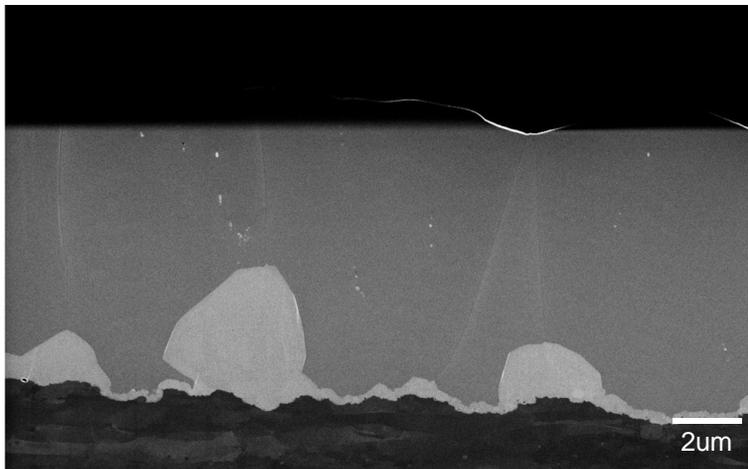


Cross-section after 22,000hours at 30°C / 60%RH

Samples : Tin thickness 10 μ m

Storage condition: 30°C / 60%RH / 22,000hours

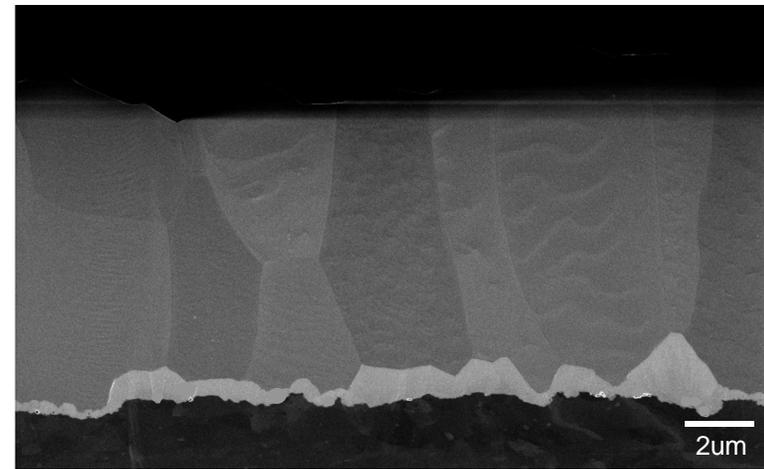
Type A



Whiskers were found.

- Large IMC grain
- Localized

Type C



No whiskers

- Uniform IMC layer

Observation of surface of IMC layer after stripping tin deposit

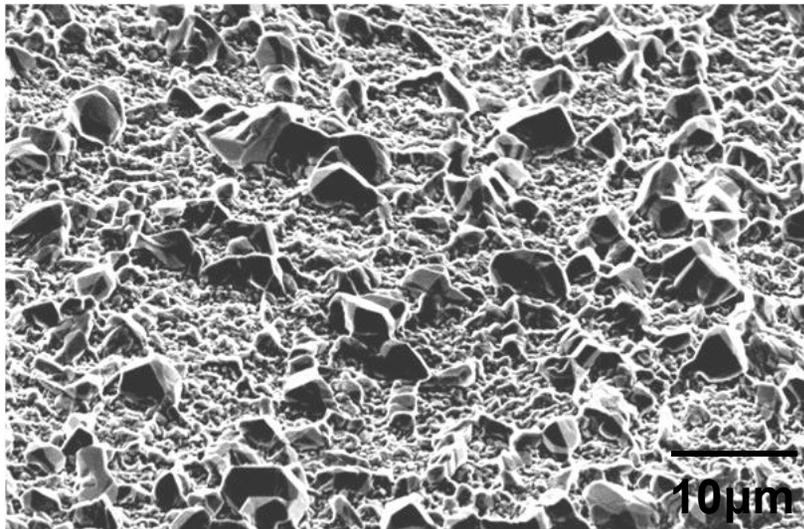
Sample : Tin thickness 10 μ m

Storage condition : 30°C / 60%RH / 22,000hours

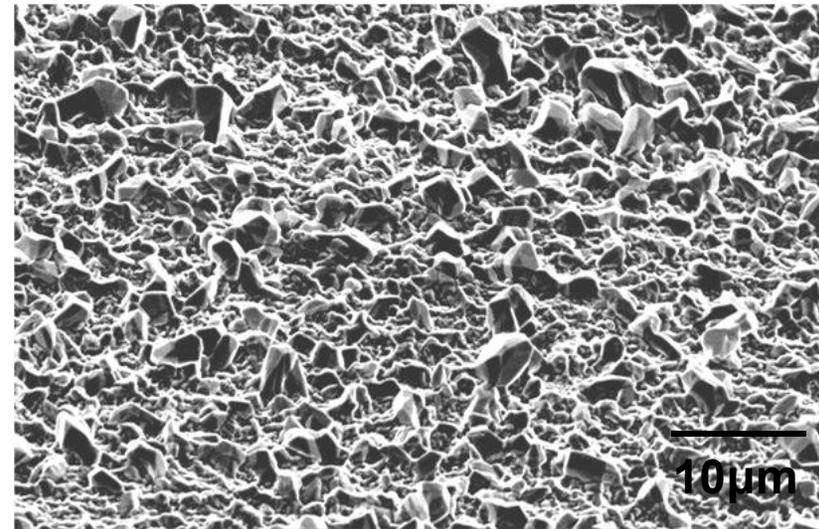
Type A

45° tilt in SEM

Type C



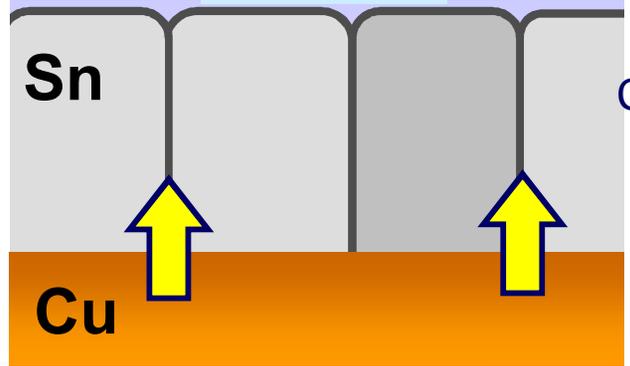
- Large IMC grain
- Localized



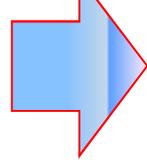
- Small IMC grain
- Comparatively uniform

Consideration of the tin whisker mitigation - Type B -

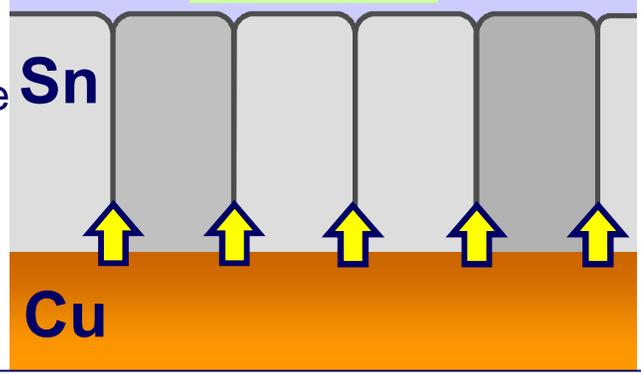
Type A



Countermeasure



Type B



General understanding

Tin grain size is large.
>> a few grain boundaries

Large IMC grow into grain boundaries at local places.

Localized compressive stress is generated in tin deposit.

Tin whisker growth

Tin grain size is small.
>> many grain boundaries

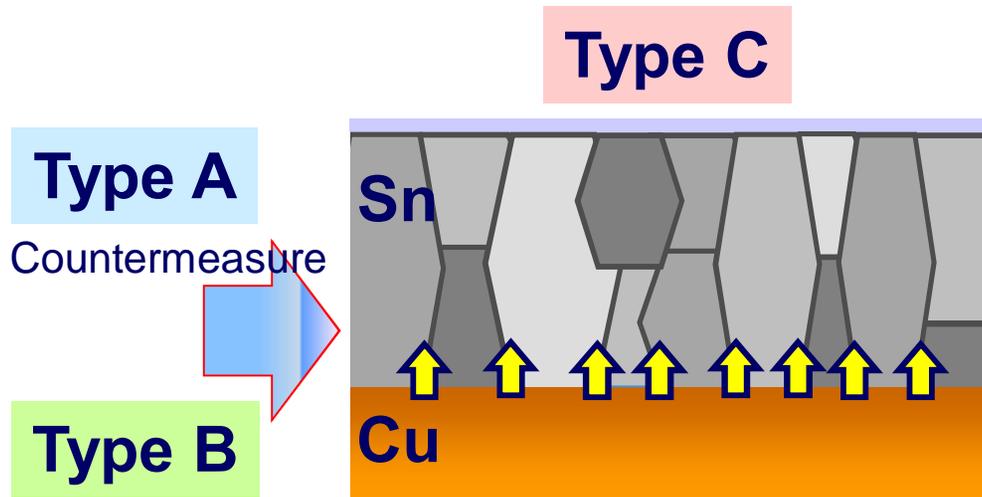
Dispersion of copper diffusion

Small and uniform IMC layer

Low compressive stress in tin deposit

Tin whiskers are reduced.

Considering of the tin whisker mitigation - Type C -



Tin grain size is smaller.
>> many grain boundaries
+
Equiaxed and column structure

Dispersion of copper diffusion

Small and uniform IMC layer

Grain boundary diffusion
of tin disperses and slows.

Compressive stress in tin
deposit is relieved more.

**Tin whiskers
are restrained.**

Summary

Effect of Copper Substrate Roughness

- Tin deposits on rough copper (higher Ra values) reduced whisker formation at ambient conditions. Rougher copper forms a uniform IMC layer, and prevents the localization of internal stress.

Effect of Tin Deposit Crystal Structure

- Compared with large grain size tin deposit, tin deposit that had small grain size reduced tin whisker formation at ambient conditions.
- Tin deposit which had crystal structure similar to tin-lead deposit restrained tin whisker formation effectively.
- Crystal structure in tin deposit is one of the most important factors to restrain tin whiskers.



Thank you

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