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International Electronics Manufacturing Initiative

Effects of Lead on Tin Whisker Elimination

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Efforts Toward Lead-free and Whisker-free Electrodeposition of Tin

Outline

1. Whisker growth models and actual effects of Pb ?
2. Objectives of the investigation
3. Observations of the effects of Pb on

   - Behavior of electrolytes

   - Characteristics of deposits

   - Growth of Cu-Sn intermetallic compounds (IMC)

   - Internal stress of deposits
4. Summary / Conclusions

Tin Whisker Growth Models

Models (Driving Force)	Prerequisites	Author's Position
Compressive Stress Cu-Sn IMC formation	Cu substrate; uneven IMC; Stress built-up after plating.	It seems to be generally valid.
Compressive Stress Tin Oxide formation	Extremely corrosive environment Low corrosion-resistant deposits	Special cases
Compressive Stress Intrinsic to plating	Intrinsic compressive stress as plated	?
Re-crystallization Energy reduction	Dislocations (Lattice defects)	?
Thermal Mismatch	Significant difference in CTE between deposit and substrate	Special case

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Questions

Fact:

Sn-Pb is one of very few whisker-free electrodeposits.

1. What makes Pb able to prevent tin whiskers completely ?
2. Can Pb-effects confirm the compressive stress growth model ?
3. What can we learn from Pb ?
4. Which effects of Pb are replaceable and which not ?

Objectives of Investigation

Objectives

- Identify the actual effects of Pb on whisker elimination: any possibility to achieve similar effects by using plating bath additives / non-lead metals
- Further understanding the growth mechanism of tin whiskers

Investigations

1. Electrodeposit matte 100Sn, 95Sn-5Pb, 90Sn-10Pb, 60Sn-40Pb
2. Electrochemical behaviors of plating solutions
3. Characterization of the deposits
4. Cu-Sn IMC growth and its morphology
5. Initial internal stress and stress change with time at ambient temperature

Whisker Propensity

Sample	Alloy Composition (% weight, by XRF)	Class of Whiskers (by this study)	Class of Whiskers (data from industrial experience)
a	Sn: 100%	Class 3-4	Class 4
b	Sn/Pb: 95/5	Class 0	Class 1 (occasionally)
c	Sn/Pb: 90/10	Class 0	Class 1 (occasionally)
d	Sn/Pb: 60/40	Class 0	Class 0

Deposit Thickness: 10 µm
Copper substrate: C194

Whisker classification:
Class 0 - no observable whisker growth
Class 1 - infrequent, short length (<5µm)
Class 2 - infrequent, moderate length (5-25µm)
Class 3 - more frequent, short or moderate length (<25µm)
Class 4 - long (>25µm), classic whisker shape, 3-4µm diameter

Electrochemical Study

Test method

1. Electrolyte:

   Matte tin plating solutions contain different concentrations of Pb^{2+} , which were used to prepare deposits of 100Sn, 95Sn-5Pb, 90Sn-10Pb, 60Sn-40Pb.

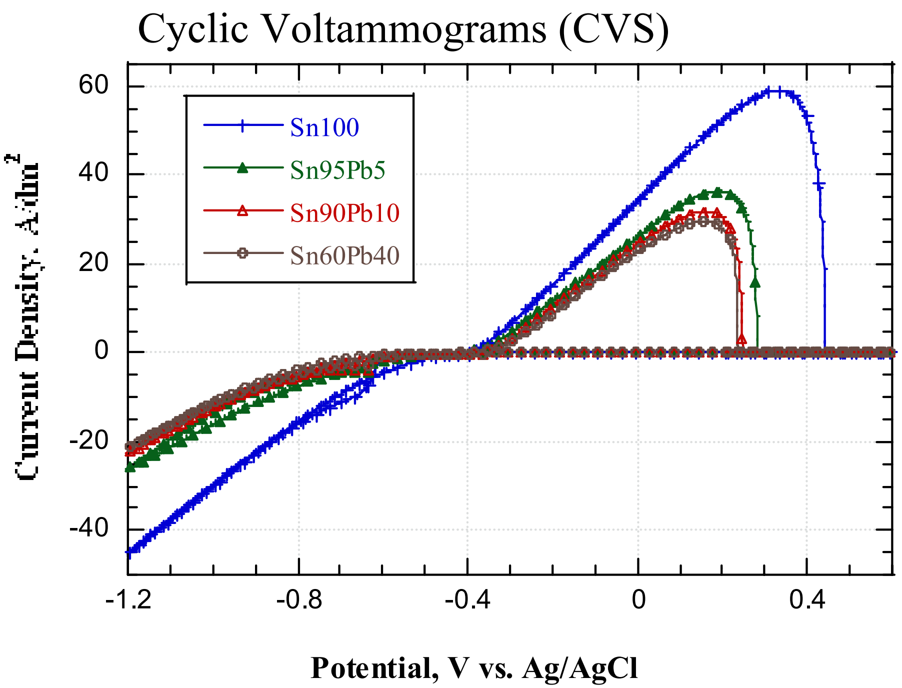
2. Obtaining cyclic voltammograms (CVS) and polarization curves:

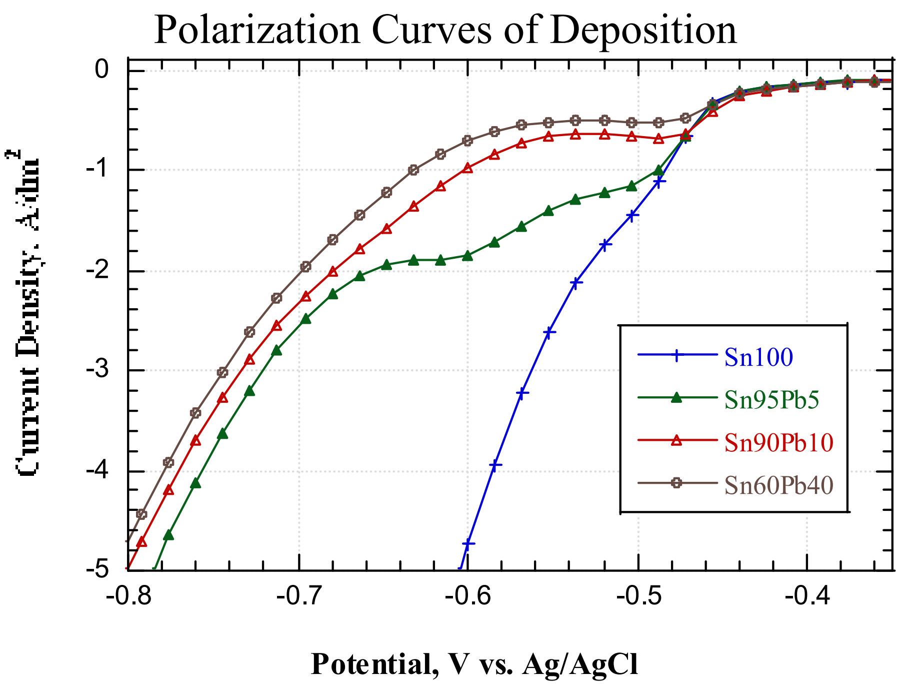
   - a standard three electrode system

   - Ag/AgCl as reference electrode, copper rotating disk as working electrode

   - scan rate: 50 mV/s

Behavior of Electrolytes





Polarization of deposition increases with the increase of Pb-content.

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About Electrochemical Measurements

1. Effect of Pb:

   increasing polarization *or* increasing the overpotential *or* inhibiting/suppressing

   → deposit at the higher potential (higher energy).

2. Activation energy (E_a):

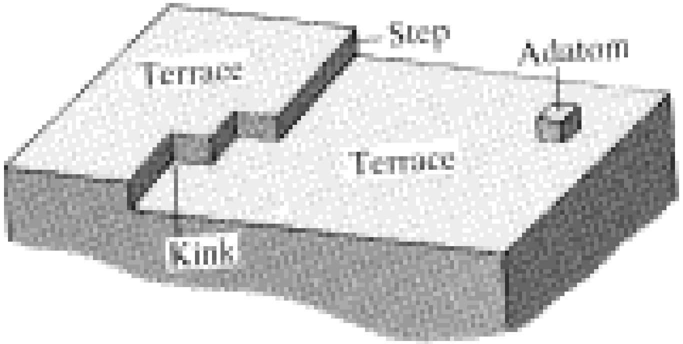
   Generally, E_a for the nucleation of crystals is higher than that for crystal growth.

3. Grain size reduction: either increase overpotential or reduce E_a for the nucleation.

4. More important information can be obtained

   by various electrochemical measurements at the

   lower metal concentrations.



(Important for the plating solution development.)

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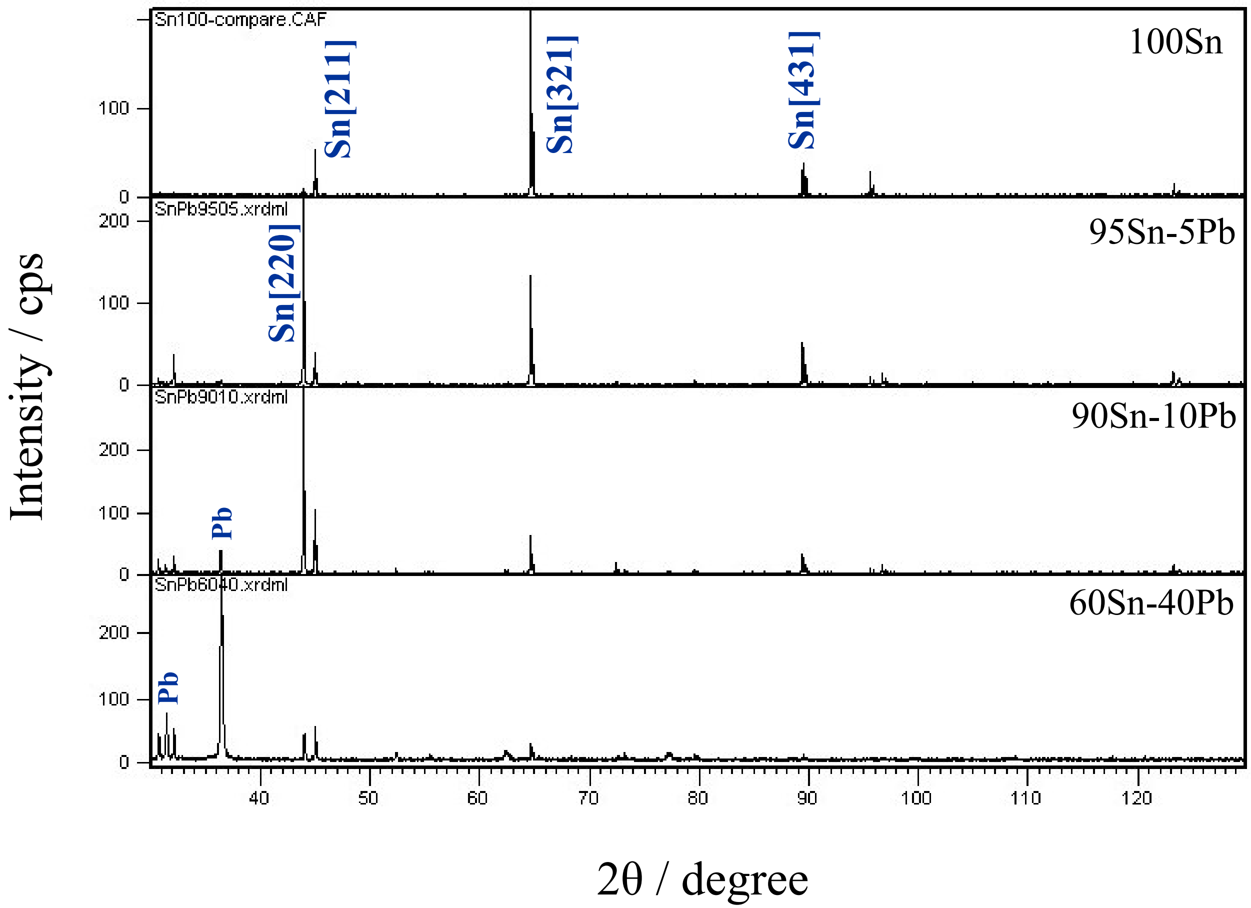
Characterization of Sn and Sn-Pb Deposits

Texture

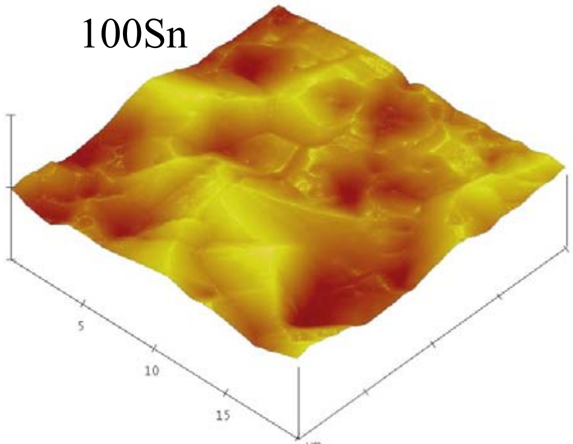
XRD Patterns of Deposits



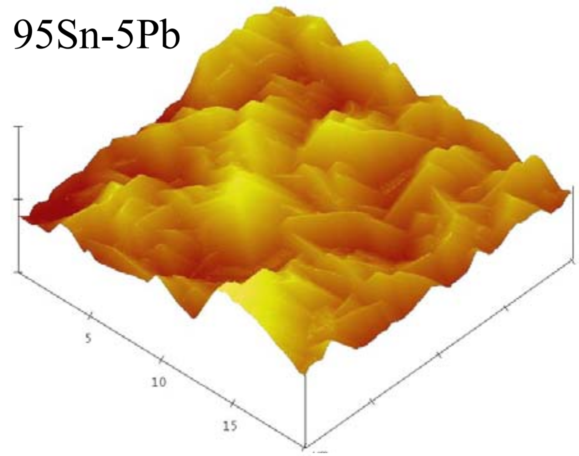
Surface Morphology

3-D AFM Images of Deposits

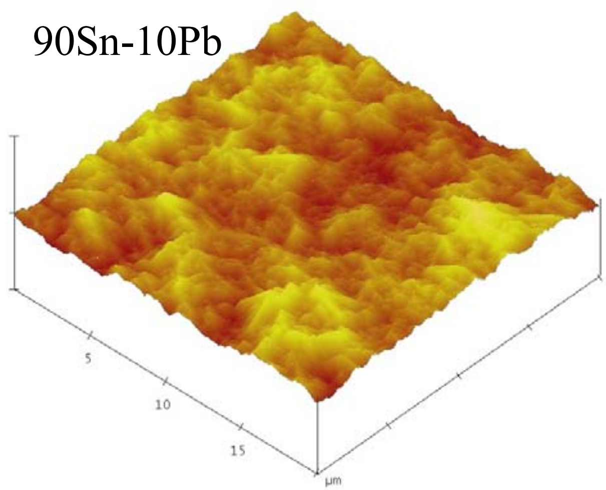
100Sn



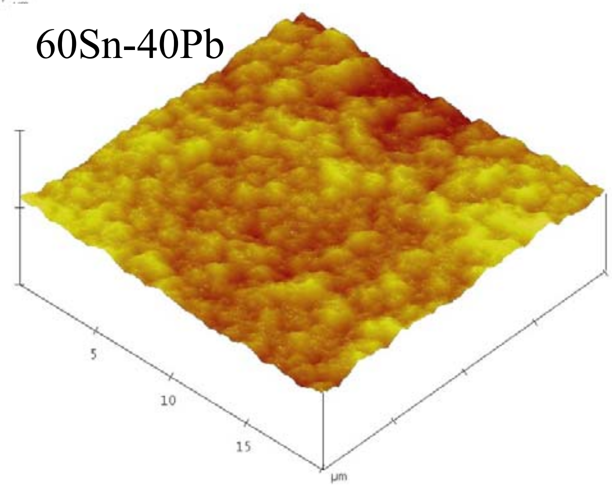
95Sn-5Pb



90Sn-10Pb



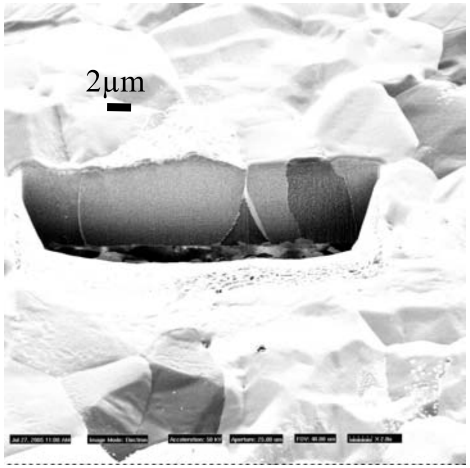
60Sn-40Pb



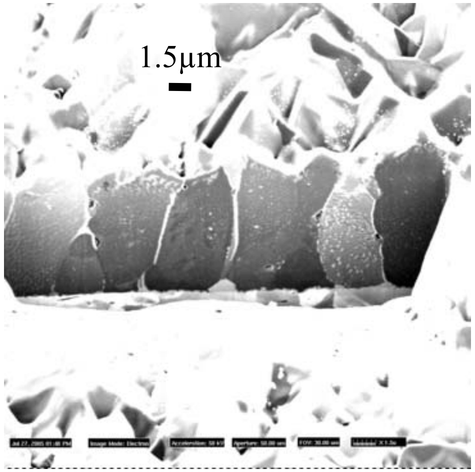
Grain Structure

FIB-SIM Cross-sectional Images of Deposits

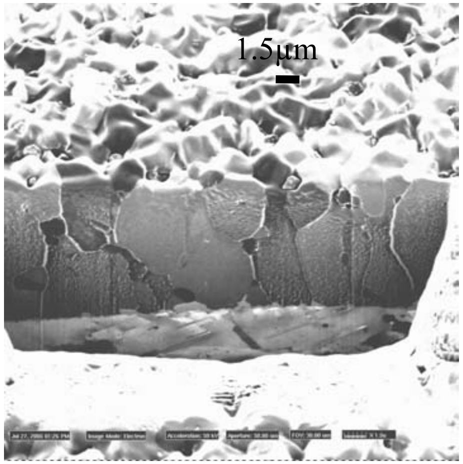
100Sn



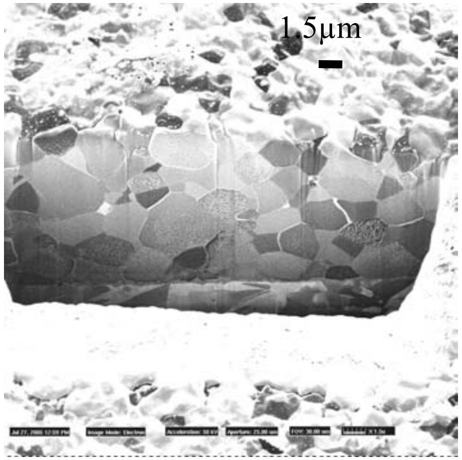
95Sn-5Pb



90Sn-10Pb



60Sn-40Pb



columnar → equiaxed

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Effects of Pb on Deposits

With increased Pb-content in deposits (0 - 40% wt)

1. Texture of Sn:

   [321] → [220] → weak texture (200, 101, 220, 211,)

2. Grain size:

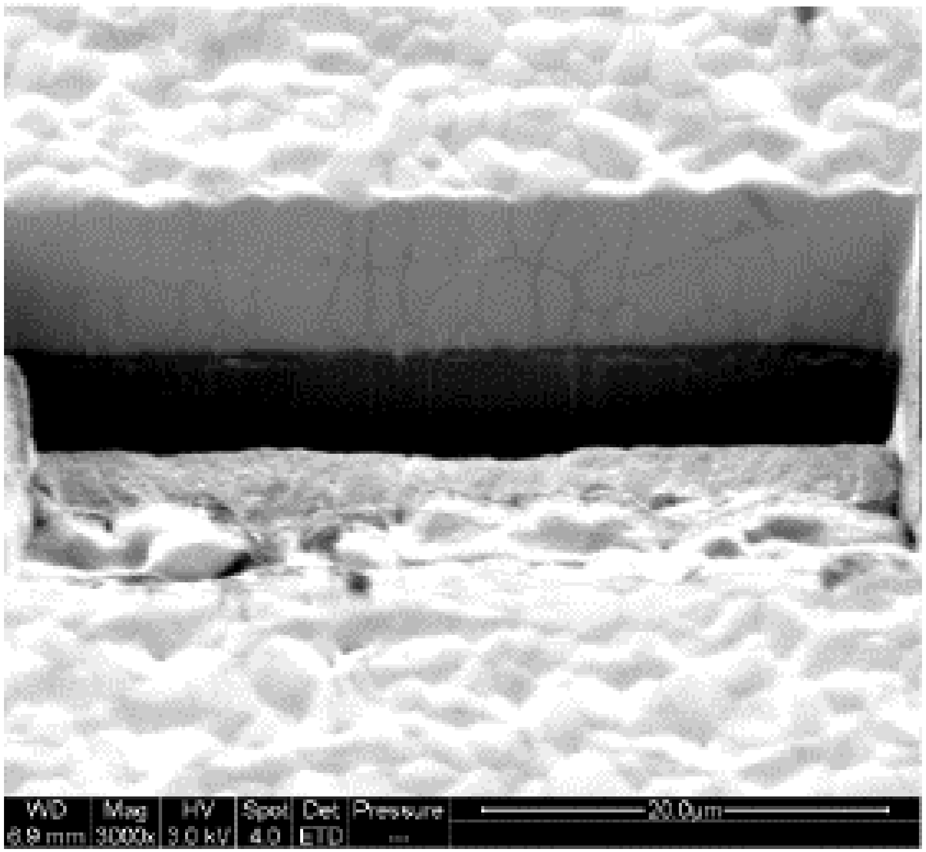
   average 5-6 μm → average 2-3 μm

3. Cross-sectional microstructure:

   columnar → equiaxed

Feasible Without Pb

A matte pure tin deposit (FIB)



Process Solderon ST-380:

- [220] predominant texture
- equiaxed grain structure
- grain size 1-2 µm
- low whiskering (class 1)

Cu-Sn Intermetallic Compounds

Test methods

1. Sn and Sn-Pb samples were stored under ambient condition
2. To expose IMC layer, Sn and SnPb deposits were selectively stripped
3. IMC growth rate: weight gain
4. Texture of IMC: XRD
5. Surface morphology of IMC layers: AFM images
6. FIB cross-sectional images of IMC (two cases):

   100Sn (whiskering) and 60Sn-40Pb (whisker-free)

Cu-Sn IMC Growth Rate

Two months after plating

Deposit	100Sn	95Sn-5Pb	90Sn-10Pb	60Sn-40Pb
IMC found (mg/dm^2)	**13.6**	**13.6**	**11.8**	**12.7**

Determined by weight gain method

Minimum uncertainty: $\pm$ 0.5 mg/dm^2

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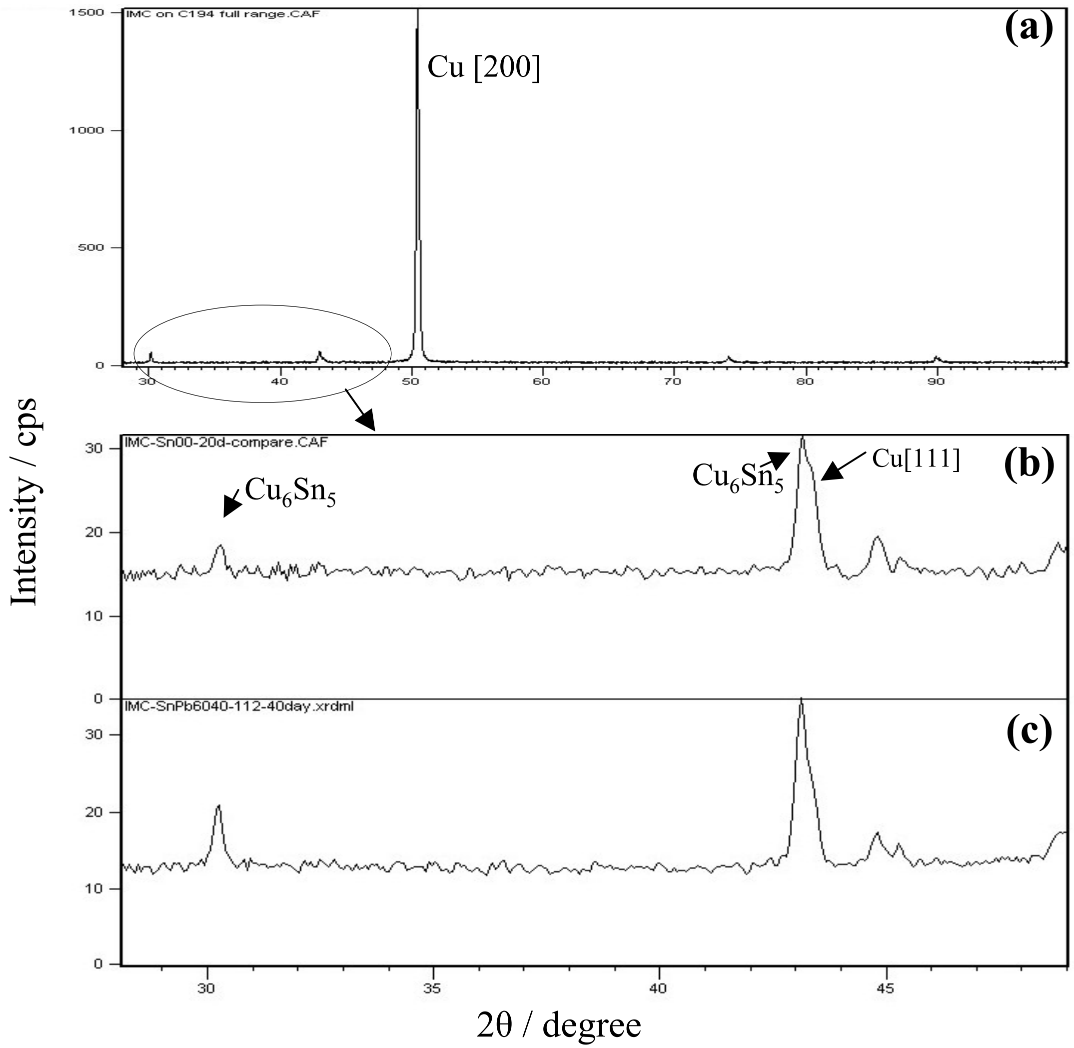
Texture of IMC



Sn or SnPb was completely stripped off;

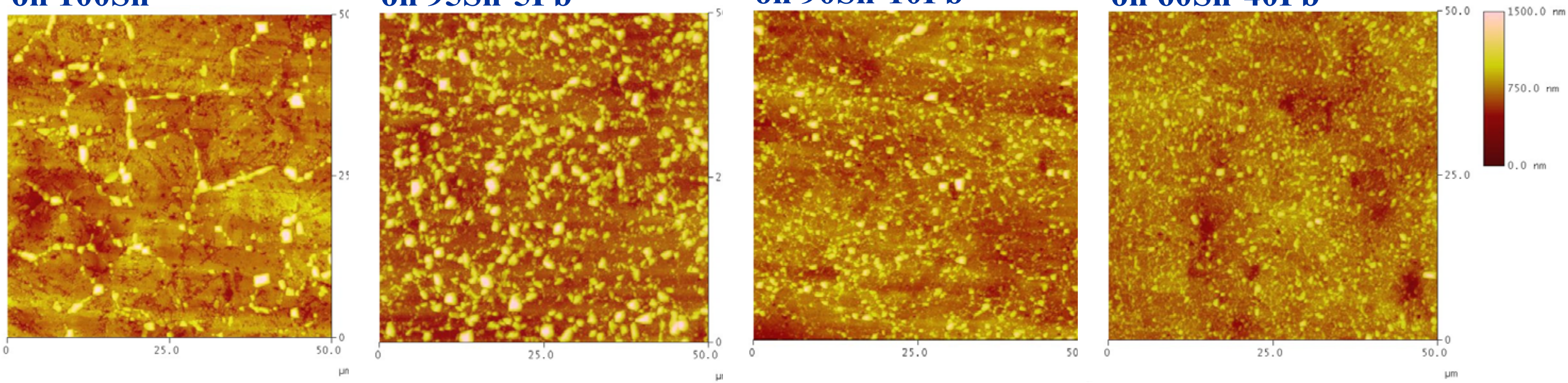
on 100Sn deposit

on 60Sn-40Pb deposit

AFM Images of IMC

After 10-day Ambient

on 100Sn **on 95Sn-5Pb** **on 90Sn-10Pb** **on 60Sn-40Pb**



Height Images: 50 μm x 50 μm

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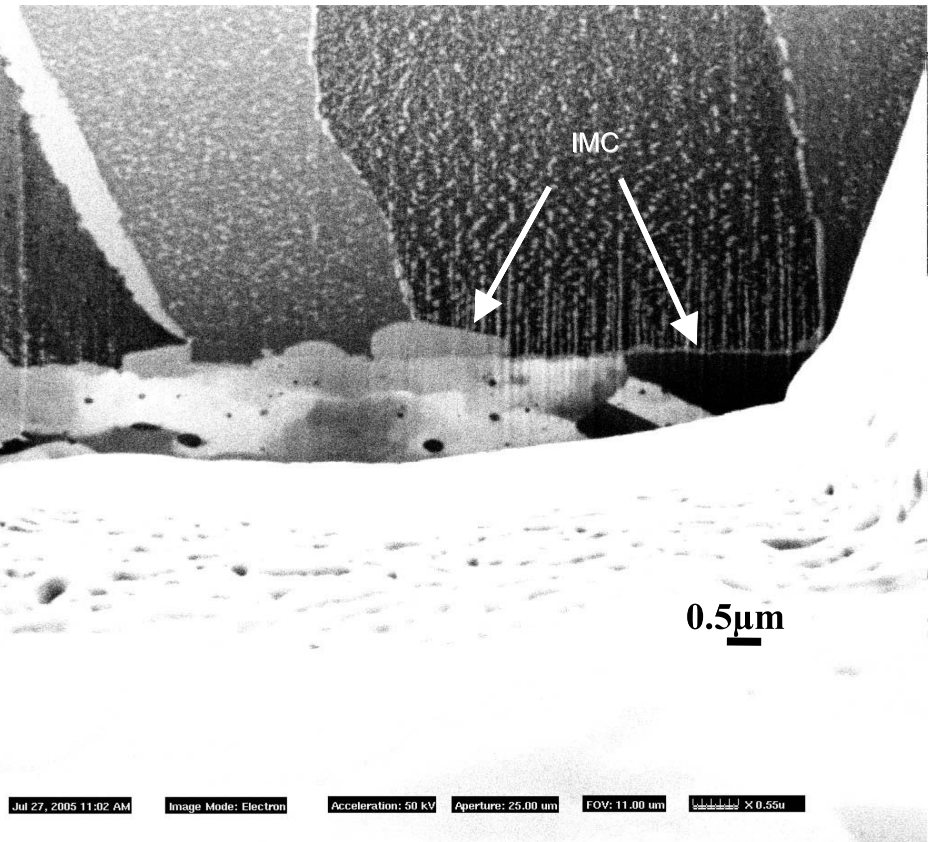
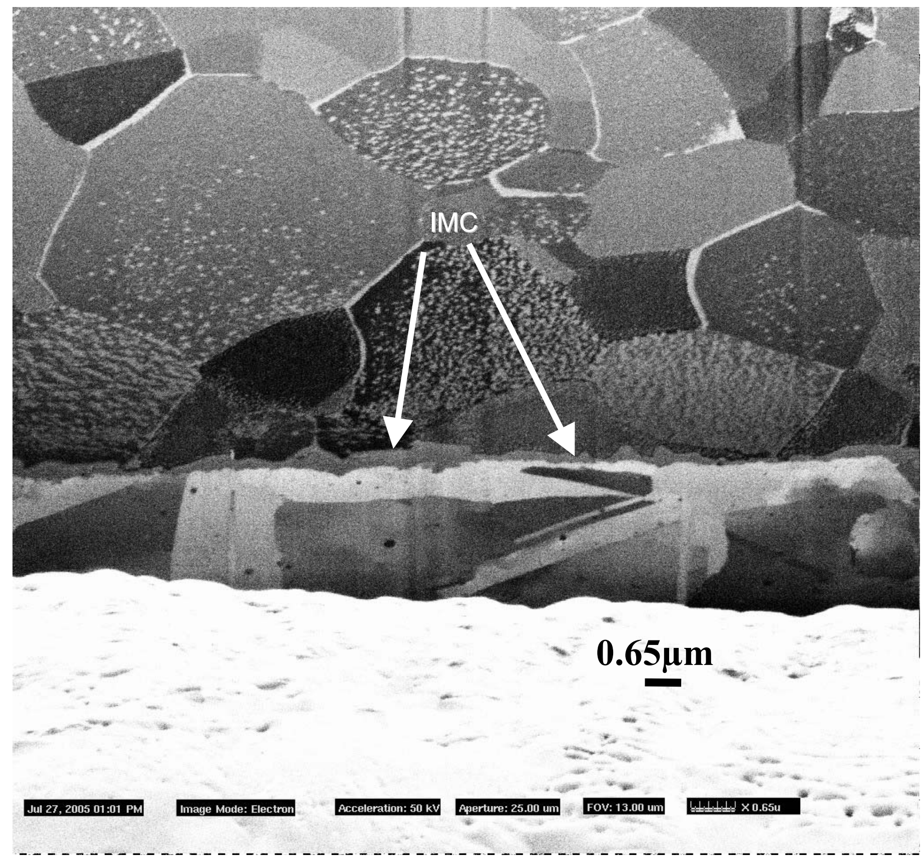
FIB Images of IMC

After Two-Month Ambient

100Sn



60Sn-40Pb



Effects of Pb on IMC Formation

1. Similar amount of Cu-Sn IMC was found on all samples (Note: Pb does not form IMC with Cu) → Pb accelerates the Cu-Sn IMC formation;
2. Similar XRD patterns of Cu_6Sn_5 were exposed on all deposits;
3. IMC grains become denser and finer with increase of Pb;
4. Similar XRD patterns of Cu6Sn5 were exposed on all deposits
5. On 100Sn deposit, IMC is formed mainly through grain boundary diffusion of Cu;
6. On 60Sn-40Pb deposit, IMC is formed equally through grain boundary and bulk diffusion of Cu.

Some Assumptions

Possible explanations for Bulk Diffusion ↑ and GB Diffusion ↓

1. Looser packing of atoms in grains (on crystal planes and between crystal planes):

   - due to crystal growth orientations (XRD only is not sufficient)

   - due to alloying effect

2. Grain boundary segregation of Pb: (unstable eutectic structure ?)

   - reduces the tendency for Cu diffusing through GB (no formation of IMC)

   - facilitates diffusion of Cu through bulk (make space free for Cu ?)

3. Bonding and energy: Sn-Sn, Sn-Pb, Sn-Cu (more information)

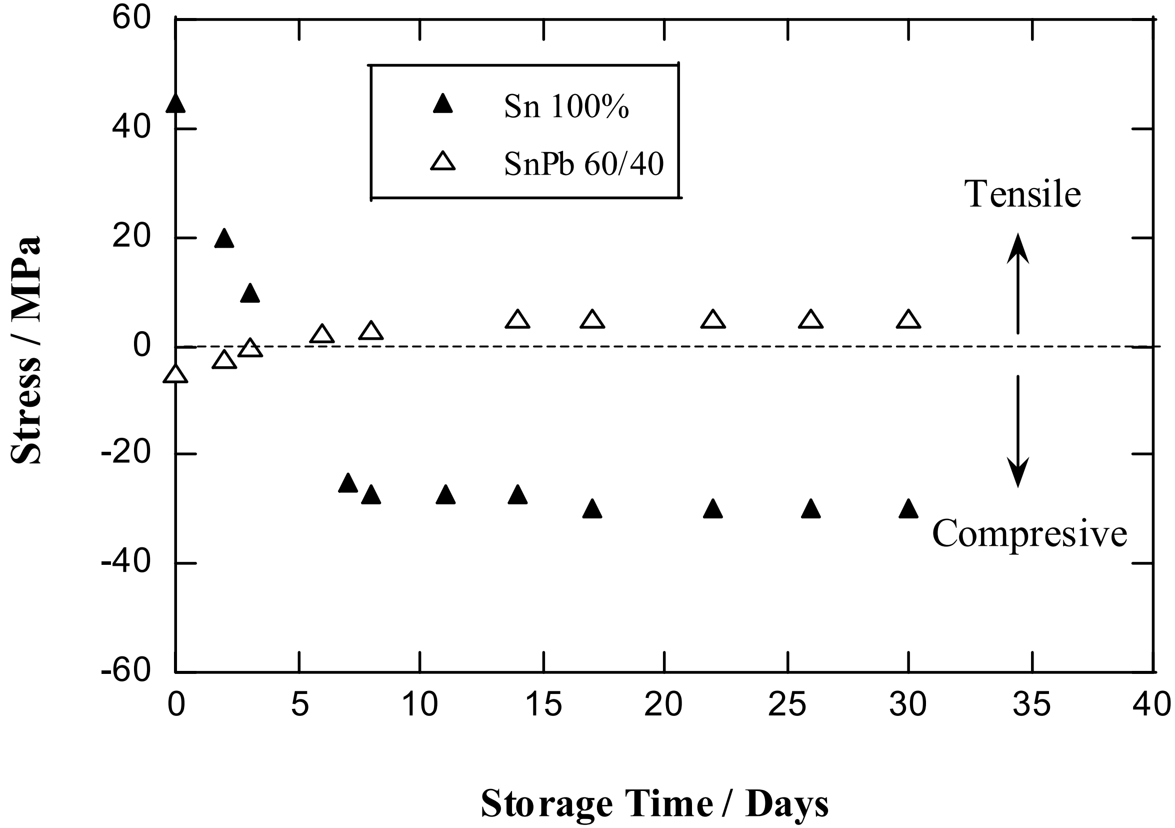
Stress Measurements

Test methods

1. Method: bent strip;

   Substrate: C194 (from Specialty testing & Development Co.)
2. Two samples: 100Sn (whiskering) and 60Sn-40Pb (whisker-free)
3. Same plating condition as for other sample preparation
4. Measure the internal stress as plated and the change during ambient storage

Effect on Internal Stress



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Stress and Whiskers

1. Whiskering deposit (100Sn) showed a tensile stress as plated;

2. Whisker-free deposit (60Sn-40Pb) showed a slightly compressive stress as plated; (Q: any relationship between intrinsic compressive stress and less GB diffusion of Cu ?)

3. During storage, whisker-free deposit showed a constant low tensile stress → indicating that no compressive stress was ever built-up.
(Threshold compressive stress for whisker here is ca. 30 MPa; Threshold stress for creep ?)

Note: A very similar picture was also obtained on two bright tin deposits (whiskering vs. whisker-free), but with much higher tensile and compressive scales. (some unwanted properties of the deposit; investigation is under way)

Summary

	Deposit with Pb	Critical for whisker-free ?
Texture of deposit	relatively intensive [220] peak, and a weak texture	Likely influence Cu-diffusion and stress relief
Grain size	reduced grain size	no
Grain structure	tendency from columnar to equiaxed	?
IMC growth rate	tendency of increasing	no
Texture of IMC	no effect	
Diffusion of Cu	reduce GB diffusion increase bulk diffusion	matte deposits: yes bright deposits: ?
Morphology of IMC layer	even	
Intrinsic stress as plated	slightly compressive	?
Compressive stress built up	no built-up of compressive stress with time	yes
Compressive stress relief	no need (for higher Pb-content)	only when there is stress

A Whisker-free Deposit

1. No source for compressive stress

Cu diffusion: GB ~ Bulk

→ Even growth of Cu-Sn intermetallic compounds

2. No driving force for whiskers

as plated: nearly zero internal stress as plated

with time: no tendency towards more compressive

Ambient condition; Early judgment for the plating solution development

Thank You !

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