전자현미경을 이용한 무연솔더/UBM 계면반응 분석

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Characterization of the interface between lead-free solder/UBM using electron microscopy

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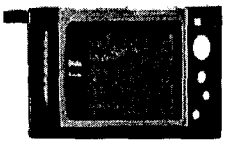
Contents

- Introduction
- Objective
- Experimental procedure
- Result
  - ***SEM (Scanning Electron Microscopy)***
  - ***TEM (Transmission Electron Microscopy)***
    - **Image analysis**
    - **Chemical analysis**
    - **Crystallographic analysis**
- Summary

Introduction

Packaging Trend

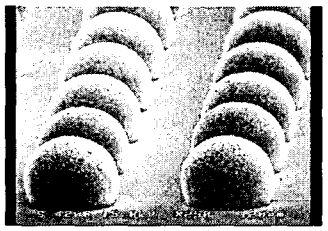
Cell Phone



Palm-Based PDA

Fine pitch assembly

- ➢ High I/O – density
- ➢ Greater performance
- ➢ Miniaturization



Area Array Packaging

- ➢ Ball Grid Array (BGA)
- ➢ Chip Scale Package (csp)
- ➢ Flip Chip Technology

Introduction

1. Fine pitch assembly ⟹ Area array package

: BGA, μBGA, CSP, *Flip chip*

2. Successful implementation of Flip chip technology ⟹ Cost reduction

New Bumping Technology for Low Cost Flip Chip Technology

⇩

Electroless Ni/Au Bumping

3. Pb - free solders ⟹ Sn-based alloys with Ag, Bi, In, Sb, Zn etc.

Introduction

Why Use Electroless Ni/Au Bump

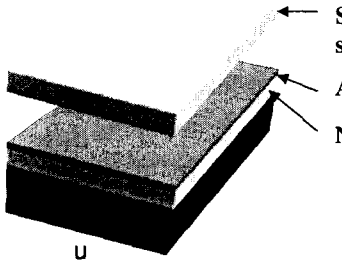
1. Ni is a good diffusion barrier in the Au/Cu metallization because Ni-Sn compounds show a very slow IMC growth rate and Ni has a relatively low diffusion rate through Au and Cu.
2. Simplicity of process and low cost
3. Many good properties such as high hardness, uniform thickness, remarkable wear resistant and excellent corrosion resistance.
4. Applicable to all flip chip package assembly process
   - Solder-bumped Flip Chip
   - Anisotropic Conductive Adhesive
   - Polymer Flip Chip (Conductive Adhesive)
   - Non Conductive Adhesive

Objective

Sn-3.5Ag and Sn-58mass%Bi solder
Ni/Au UBM

- understand the mechanism of interfacial reaction during reflow
- clarify interfacial compounds formed at solder joint
- identify various Ni-Sn IMCs(Intermetallic Compounds) and Ni-P IMCs exist at the interface after reflow soldering.

Experimental



Sn-3.5Ag / Sn-58mass%Bi solder foil

Au (0.5 ㎛)

Ni-15at%P (5 ~ 7 ㎛) } Electroless plating

U

reflow soldering

- SEM / EPMA
- XRD
- TEM

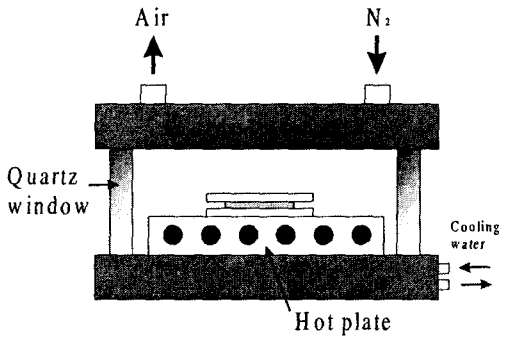
} poor spatial resolution

Experimental

Reflow temperature : 220 (℃) / 260 (℃)

Reflow time : 10, 30, 60,120, 300 (s) / 60 (s)

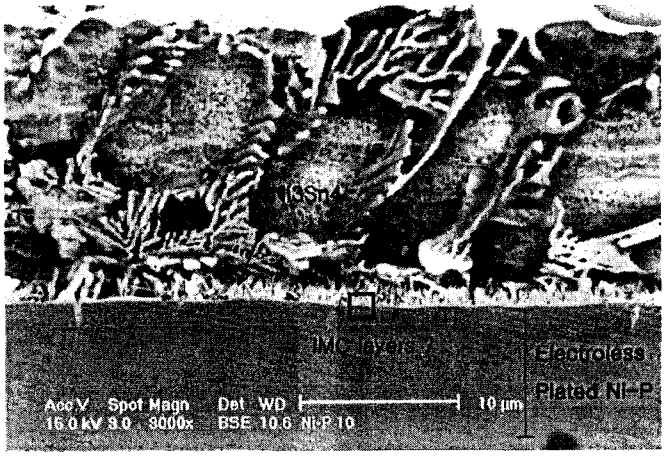
RMA flux



SEM Analysis - Cross-sectional view 1

Sn-3.5Ag

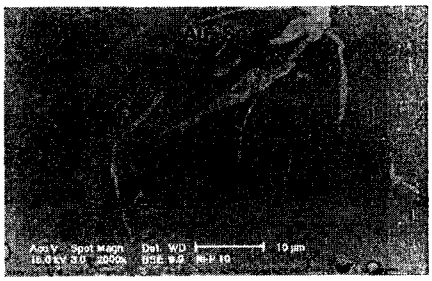
After reflow for 10 sec.

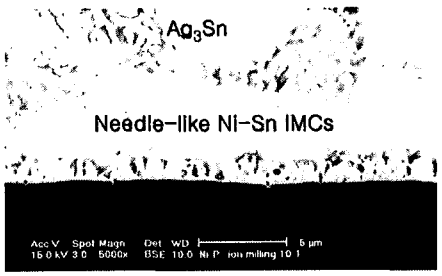


SEM Analysis - Cross-sectional view 2

Sn-3.5Ag

After reflow for 10 sec.

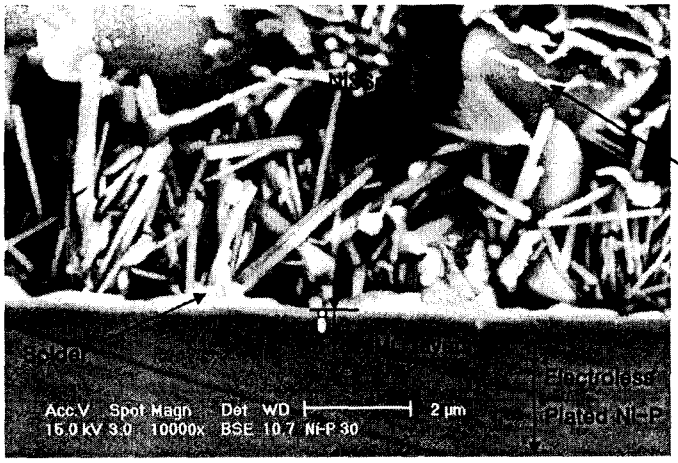




SEM Analysis - Cross-sectional view 3

Sn-3.5Ag

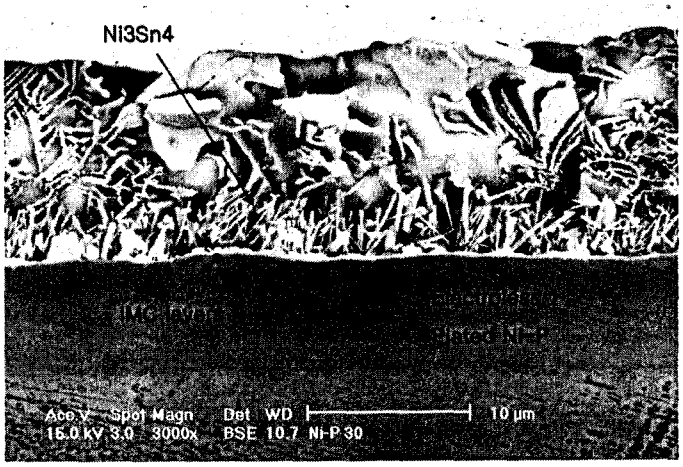
After reflow for 30 sec.



SEM Analysis - Cross-sectional view 4

Sn-3.5Ag

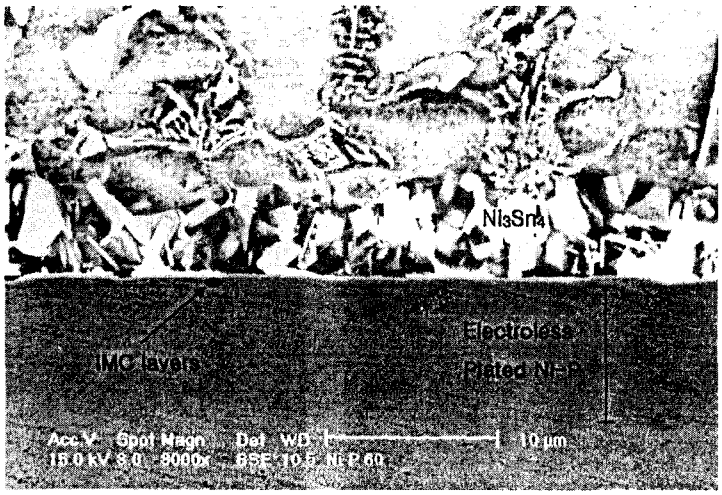
After reflow for 30 sec.



SEM Analysis - Cross-sectional view 5

Sn-3.5Ag

After reflow for 60 sec.



SEM Analysis - Cross-sectional view 6

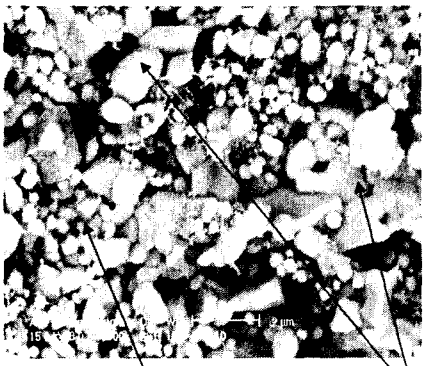
Sn-3.5Ag

After reflow for 60 sec.

SEM Analysis - Plan-view

Sn-3.5Ag

After reflow for 10 sec.



Plan-view image of needle-like Ni_3Sn_4

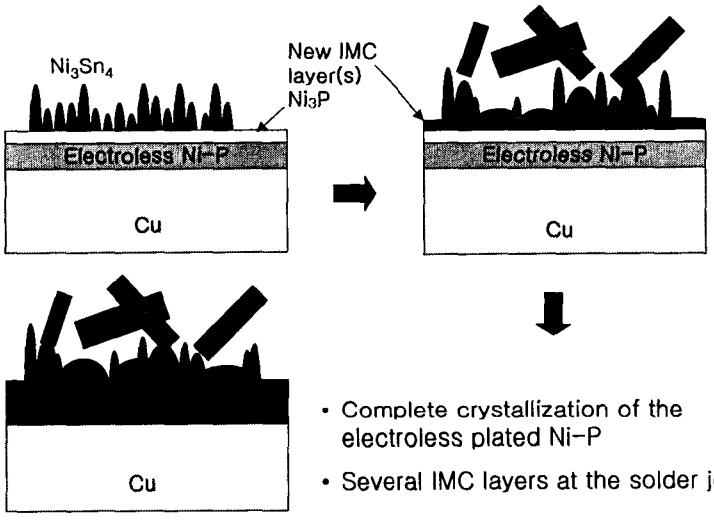
Ag_3Sn

After reflow for 60 sec.

Plan-view image of plate-like Ni_3Sn_4

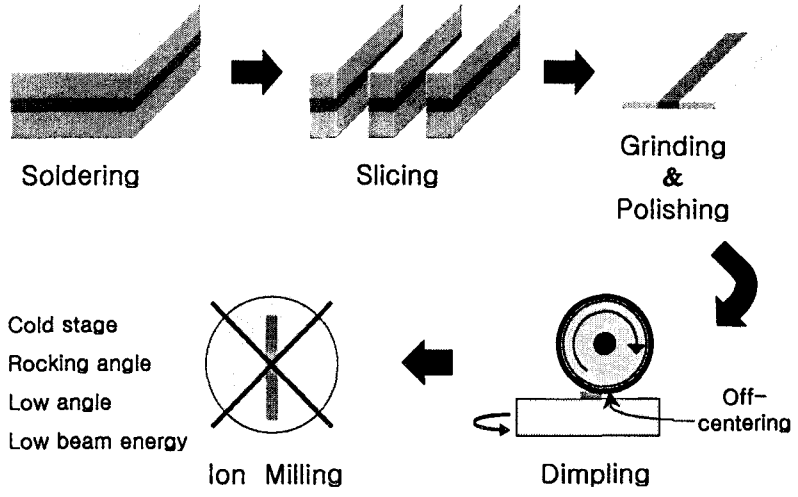
What we learn from the SEM results

Sn-3.5Ag

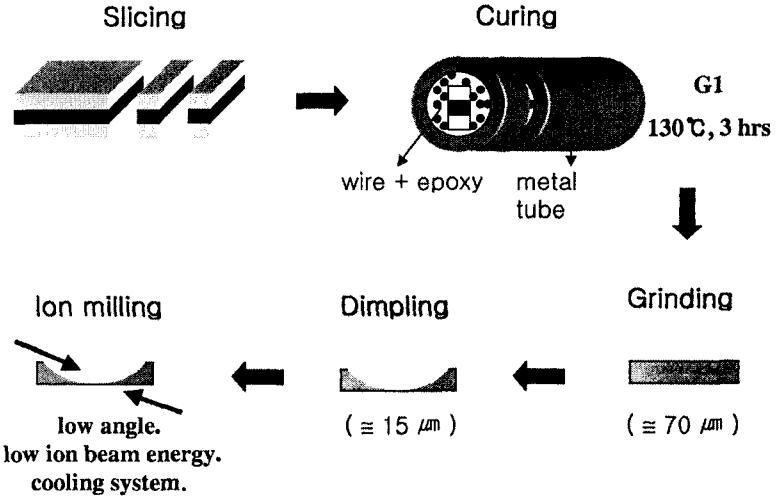


- Complete crystallization of the electroless plated Ni-P
- Several IMC layers at the solder joint

TEM Specimen Preparation for Solder (1)

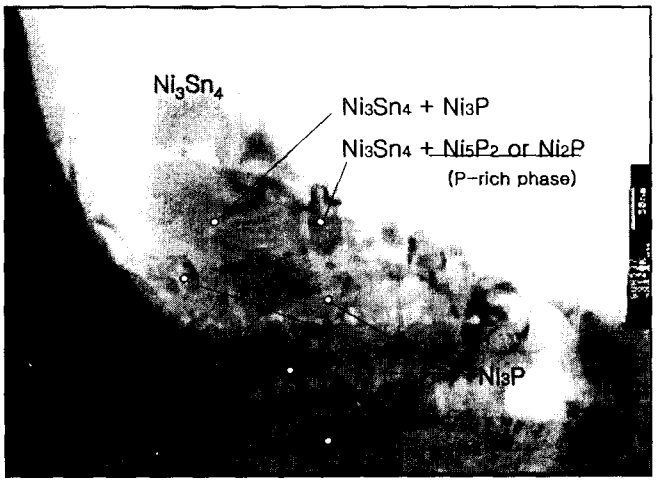


TEM Specimen Preparation for Solder (2)



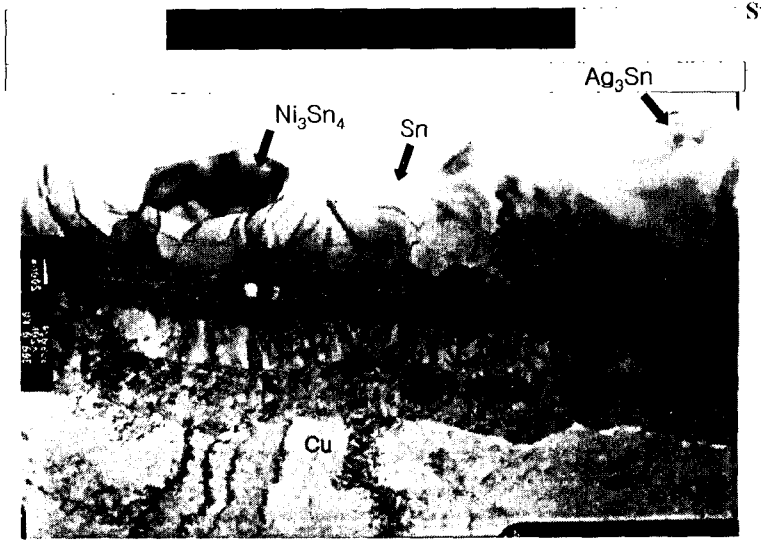
TEM Analysis 1

Sn-3.5Ag



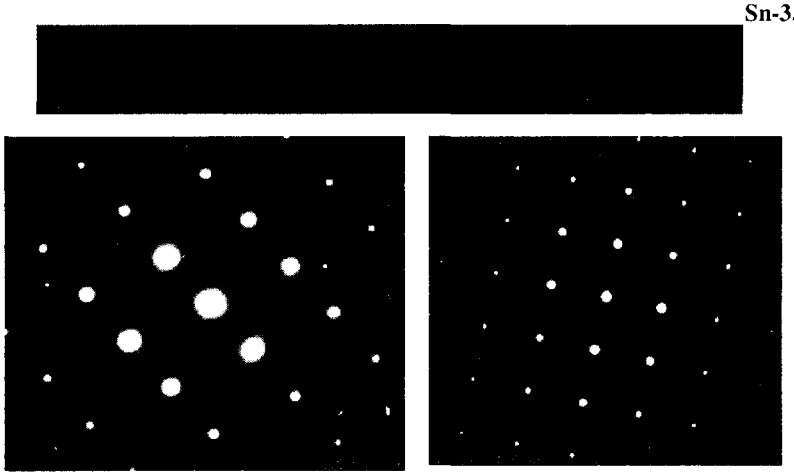
TEM Analysis 2

Sn-3.5Ag



TEM Analysis 3

Sn-3.5Ag

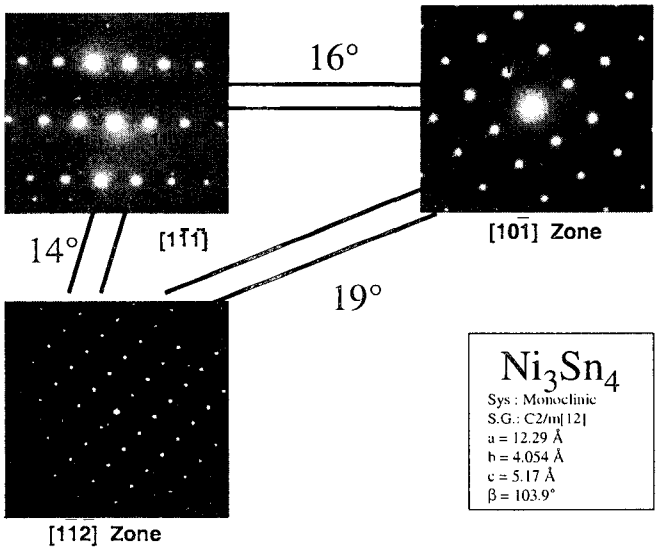


Ag_3Sn phase
<12$\bar{1}$> ZAP

Sn-rich(βSn) phase
<100> ZAP

TEM Analysis 4

Sn-3.5Ag



Ni_3Sn_4
Sys : Monoclinic
S.G.: C2/m[12]
a = 12.29 Å
b = 4.054 Å
c = 5.17 Å
β = 103.9°

What we learn from the c-TEM results

During reflow soldering reaction,

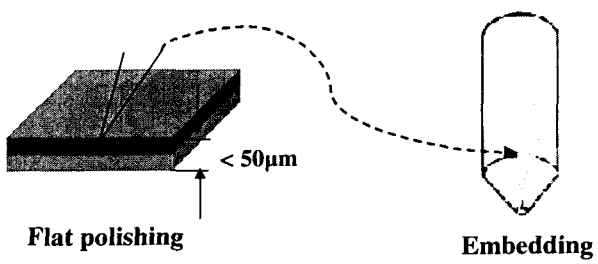
- Ni-Sn IMC, identified as Ni_3Sn_4 by TEM analysis, was formed at the solder joint and amorphous Ni-P was crystallized into Ni_3P as shown in many previous works.
- Several Ni-Sn-P IMCs layers were formed near the Ni_3P layer ; these IMCs seem to be nanocrystalline structure and mixture phase of Ni-Sn crystals such as Ni_3Sn_4, Ni_3Sn_2 or Ni_3Sn and Ni-P crystals such as Ni_3P, Ni_2P, Ni_5P_4 or NiP_2.

TEM Specimen Preparation for Solder (3)

Ultramicrotomy

1. **Self-Supporting Specimen(embedding)**

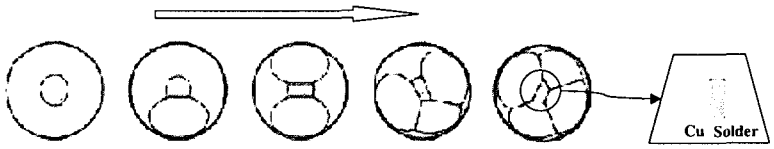
   Flat polishing & shape to a "pencil stub"
   Embed in "Epofix" epoxy(hardner 3: resin 10 ; weight ratio)
   Cure – Vacuum oven @ 35℃ overnight



TEM Specimen Preparation for Solder (3)

2. Trimming

Trim to a fine facet with glass knife



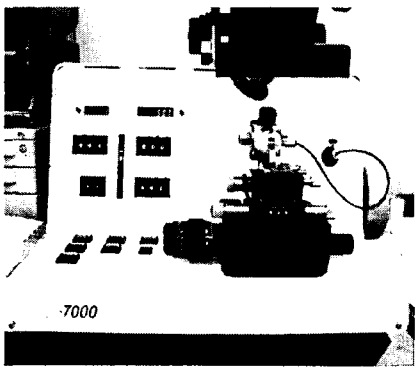
3. Section

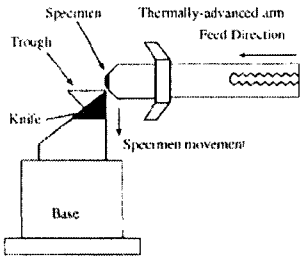
Section at 0.4mm/sec and 5° bevel angle, 70nm thick
using RMC MT-7000, Diamond knife(Druker, 45 °knife)

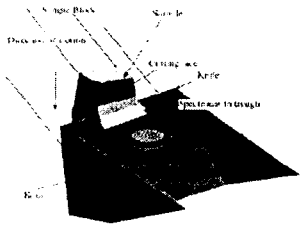
4. Collect section onto TEM Grid

Onto formver coated grid (200mesh Cu grid)

TEM Specimen Preparation for Solder (3)







Accessory

1. Resin for embeding
2. Knife (glass or diamond)
3. Loop for removing sectioned film
4. Brush made of Eye-lash

TEM Specimen Preparation for Solder (3)

Ion-milling Artifacts

Sn-Ag solder

Thermal damage

Milling time : very long(over 4hr)

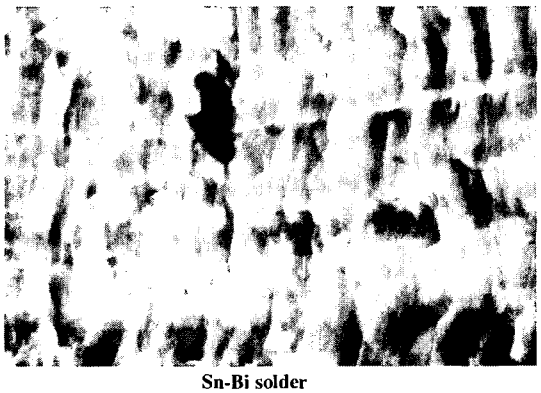
Grid(Mo) & Cu(Sub.) contamination

Differential milling rate (solder, Cu plate)

TEM Specimen Preparation for Solder (3)

Ultramicrotomy Artifacts

High strain rate, shear lamellae, dislocations, fracture, Compression, chatter, knife marks, etc.



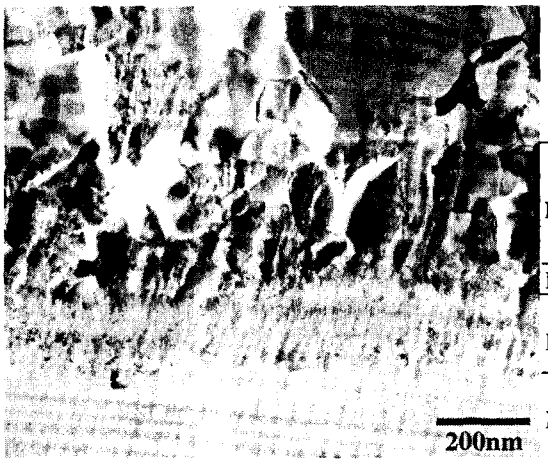
Sn-Bi solder

Sectioning Direction

TEM Analysis 5

Cross-Sectional BF-TEM micrographs

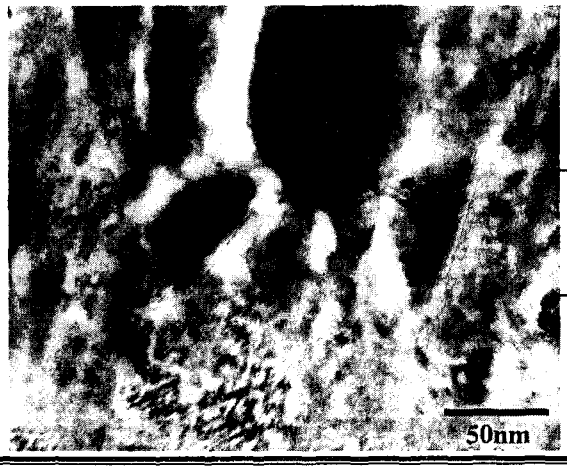
- low magnification image showing Ni30at.%P/Ni_3Sn/Ni_3Sn_4 structure



TEM Analysis 6

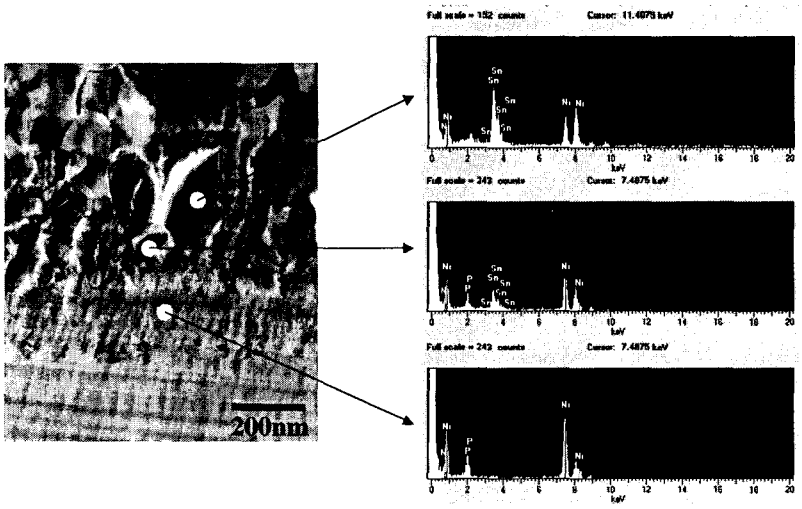
Cross-Sectional BF-TEM micrographs

- high magnification image
- Ni_3Sn is formed between Ni_3Sn_4 and Ni30at.%P layer



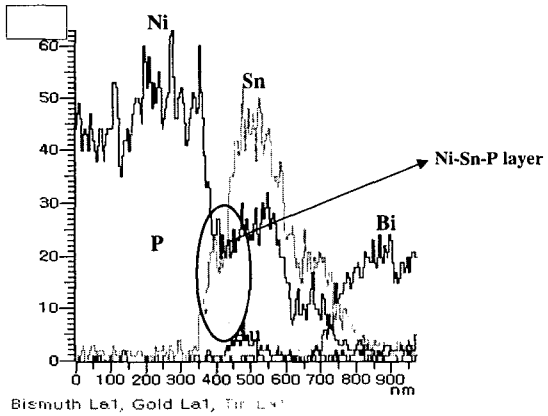
TEM Analysis 7

STEM/EDS spot analysis



TEM Analysis 8

STEM/EDS line analysis

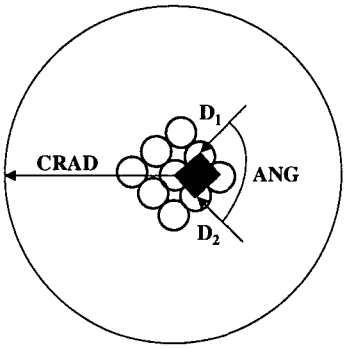


STEM/EDS line profile of the interface in the Sn58Bi/NiP/Cu joints when reflowed for 60sec. Constant Ni-Sn-P composition is present at the Ni_3Sn_4/NiP interface.

TEM Analysis 9

Phase Identification method by CBED pattern

- **ZOLZ(Zero Order Laue Zone) disc**
  : the area of projection(**A**) in the ZA[UVW]
- **HOLZ(High Order Laue Zone) ring radius (CRAD)**
  : the reciprocal lattice spacing(**H**) in the ZA[UVW]



$$Cellvol. = \frac{CL^2 \cdot \lambda^3}{D_1 \cdot D_2 \cdot \sin(ANG) \cdot \left[1 - \cos\left\{\tan^{-1}\left(\frac{CRAD}{CL}\right)\right\}\right]}$$

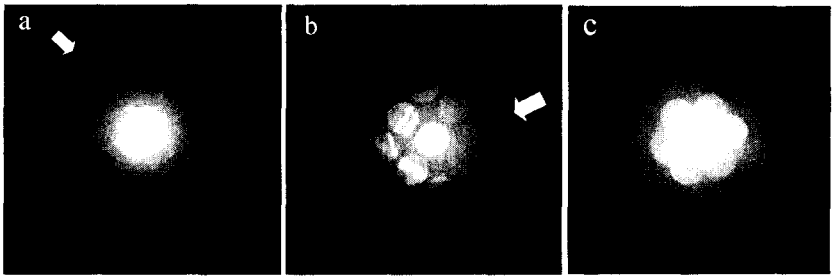
TEM Analysis 10

The crystallographic data and Primitive Cell Volume(PCV) of each possible phase

Phase	Structure	Space group (no.)	Lattice parameters (ang.)		Primitive cell vol. (ang.^{3})
Ni_3Sn_4	Monoclinic	C2/m (12)	a=12.290 b=4.054 c=5.17 β=103.9		125.02
Ni_3Sn_2	Hexagonal	$P6_3/mmc$ (194)	a=b=4.07	c=4.09	73.88
Ni_3Sn	Hexagonal	$P6_3/mmc$ (194)	a=b=5.2961	c=4.2481	103.19
Ni_3P	Tetragonal	I4 (82)	a=b=8.952	c=4.388	175.82
Ni_2P	Hexagonal	P321 (150)	a=b=5.86	c=3.37	100.22
Ni_2PSn	Orthorhombic	Pnma (62)	a=12.86 b=3.594	c=5.0896	235.24
$Ni_{12}P_5$	Tetragonal	I4/m (87)	a=b=8.646	c=5.07	189.50

TEM Analysis 11

Phase Identification by CBED patterns

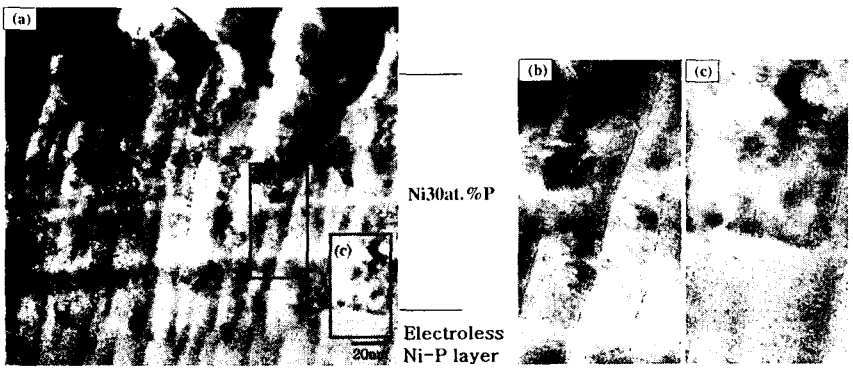


the arrow indicates HOLZ(High Order Laue Zone) line

	a	b	c
the measured PCV	128.37ang^3	104.10ang^3	
the possible phase (the theoretical PCV)	Ni_3Sn_4 (125.02ang^3)	Ni_3Sn (103.19ang^3) or Ni_2P (100.22ang^3)	*Ni30at.%P layer (6-fold symmetry)*

TEM Analysis 12

Columnar voids



Cross-sectional BF-TEM micrographs of Sn-58Bi/Au/NiP/Cu reflowed for 60sec at 220℃.
(a) Crystallized Ni-P layer because Ni is consumed to form Ni3Sn4 or Ni3Sn. Columnar voids are present in the crystallized Ni-P layer. (b), (c) magnified columnar voids.

Discussion(1)

Ni_3Sn compound formation

- From the CBED pattern
  Measured value of 104.10ang^3 well corresponds to Ni_3Sn PCV of 103.19ang^3.
  But, Ni_2P's PCV (100.22ang^3) is also close to the measured value.
  Also, the theoretic PCV of Ni_2SnP is 235.24ang^3.

  This phase is Ni_3Sn or Ni_2P rather than Ni_2SnP.

- The result of EDS analysis
  Gives a composition of *47.99 at.% Ni, 43.04 at.% Sn, 8.96 at.% P*
  If probe size of electron beam is about 5nm, however, beam broadening will occur up to 100nm which is larger than the size of the phase (40~60nm) interested in.
  It implies that surrounding elements of Sn and P can be detectable and contribute to the EDS spectra.

- The diffusion of Sn through Ni_3Sn_4 is known to be much faster than Ni through Ni_3Sn_4. Below the coarse Ni_3Sn_4 grain, the Sn diffuses into the P-rich Ni layer. Consequently, beneath the coarse Ni_3Sn_4, fine Ni_3Sn compound is formed.

  Ni_3Sn : Slow growth kinetics and Fine Structure

Discussion(2)

Ni30at.%P layer

- The result of EDS analysis
  The composition of P-rich Ni layer was measured to be Ni-30at.%P.
  According to the phase diagram of Ni-P system, Ni-30at.%P is corresponding to a mixture of $Ni_{12}P_5$ and Ni_2P.

- From the CBED pattern
  CBED pattern shows that 6-fold symmetry is present.
  Among the possible Ni-P compounds, only the Ni_2P has the 6-fold symmetry.

  Although we could not measure the primitive cell volume of P-rich layer, it was confirmed that at least Ni_2P is present in the P-rich layer from EDS and CBED pattern.

Conclusion

In this study, interfacial reaction between electroless plated Ni-P/Au UBM and eutectic Sn-58mass%Bi solder was investigated by using various AEM techniques (STEM/EDS and CBED) and Ultramicrotomy.

- Cross-sectional TEM samples were prepared by **Ultramicrotomy.**

  The advantages of Ultramicrotomy over Ion-milling
  : no irradiation damage, no chemical mixing, no differential thinning rates
  : the ease of preparation of many serial sections with large, thin areas of uniform thickness in a relatively short time.

- At the interface of Ni_3Sn_4/P-rich Ni layer, ***we found the Ni_3Sn phase using CBED phase identification.*** The measured primitive cell volume(104.10ang^3) of this phase is close to the **Ni_3Sn(103.19ang^3)** rather than Ni_2SnP(235.24ang^3).

- In addition, it was confirmed that at least **Ni_2P** is present in the P-rich layer from EDS and CBED pattern.