

Spontaneous growth mechanism of tin whiskers

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B.-Z. Lee and D.N. Lee, Acta mater. 46 (1998) 3701-3714.

Introduction

Experimental

Results

Discussion

Summary

Experimental method

7 μ m Sn electrodeposit / 70 μ m phosphor bronze sheet from an acid stannous sulfate bath at room temperature

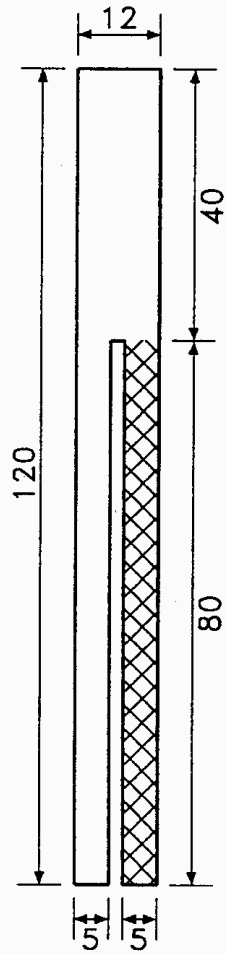
(30g// SnSO₄, 50m// H₂SO₄, and additives; CD 0.5-3.5A/dm²)

The textures of Sn deposits (pole figure device)

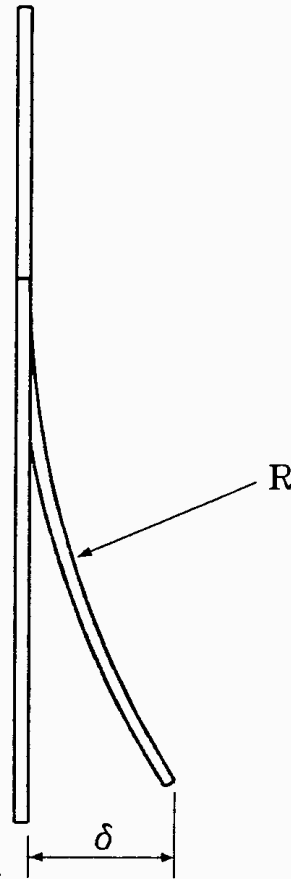
The residual stresses (deflection method)

The growth angle of whisker against surface (SEM)

Specimen for measuring residual stress of Sn film m (unit:mm).



(a)



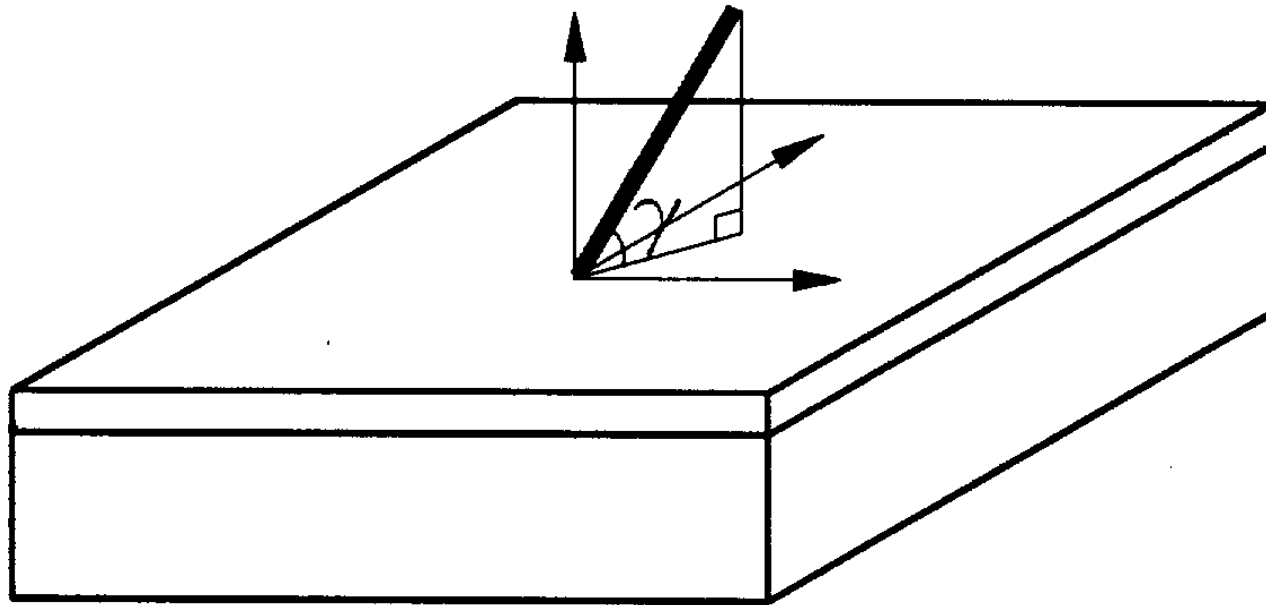
(b)

$$\sigma = \frac{E_s}{6(1 - \nu_s)} \frac{t_s^2}{t_f} \left[\frac{1}{R} - \frac{1}{R_0} \right]$$

Stoney's equation

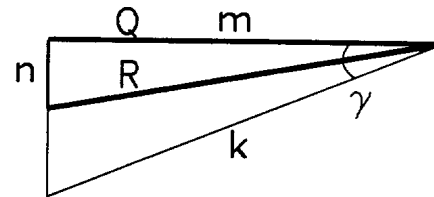
Sn/Cu₆Sn₅/Cu

Definition of growth angle of whisker

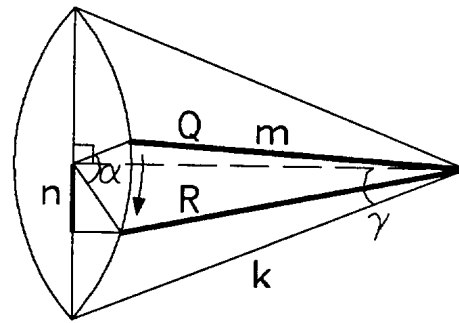


γ : the growth angle of
whisker against surface

Calculation of growth angle using SEM image



(a)



(b)

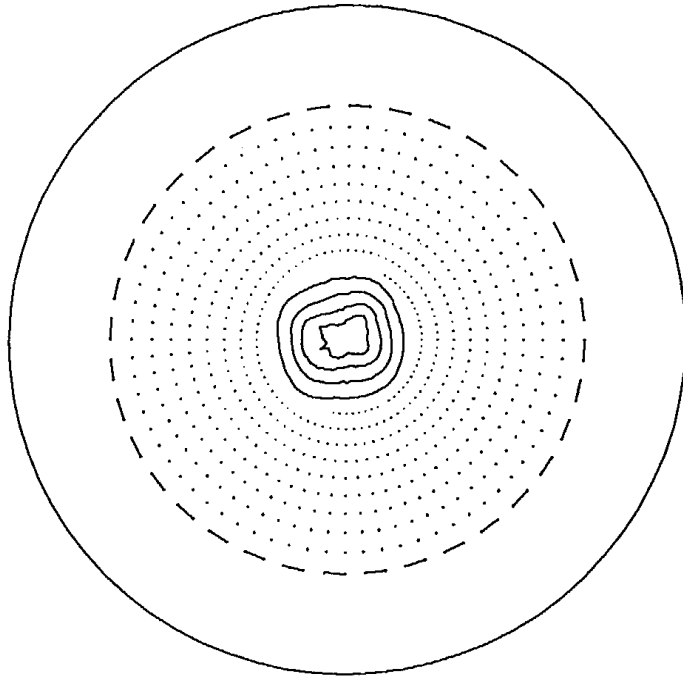
α : tilting angle

γ : the growth angle of whisker against surface

k : length of whisker

$$\begin{aligned} m &= k \cos \gamma \\ n &= k \sin \gamma \sin \alpha \end{aligned} \implies \tan \gamma = \frac{n}{m} \frac{1}{\sin \alpha}$$

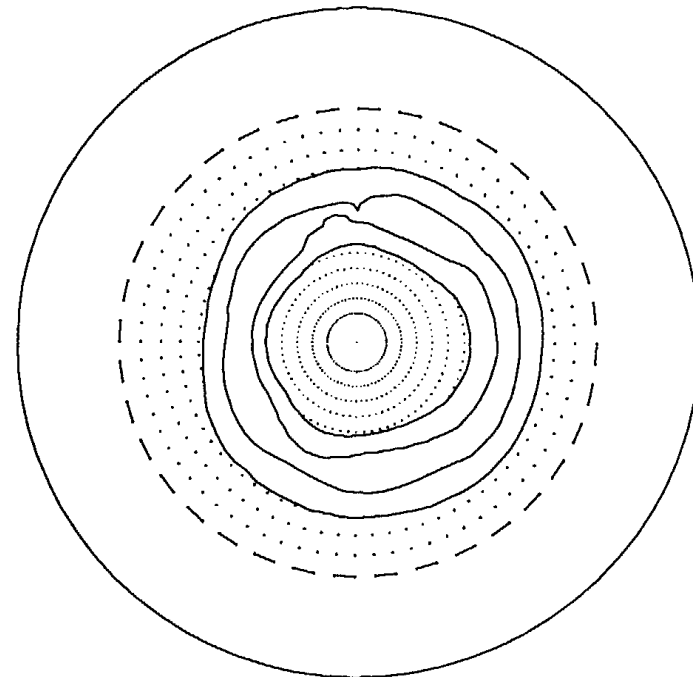
(100) pole figures of Sn electrodeposits



Maximum 9.9
contour level 2.0 4.0 6.0 8.0

0.5 A/dm²

<100>

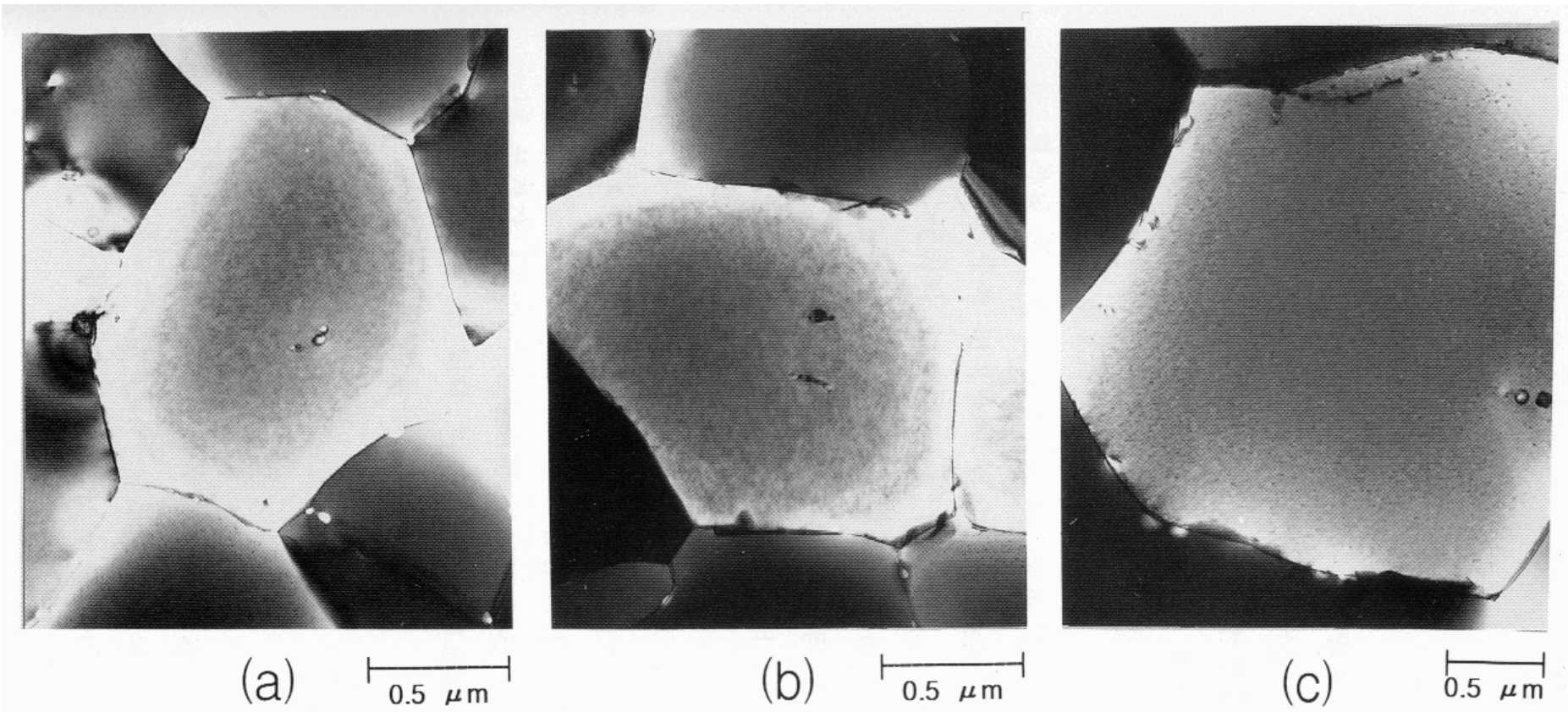


Maximum 2.7
contour level 1.0 2.0

3.5 A/dm²

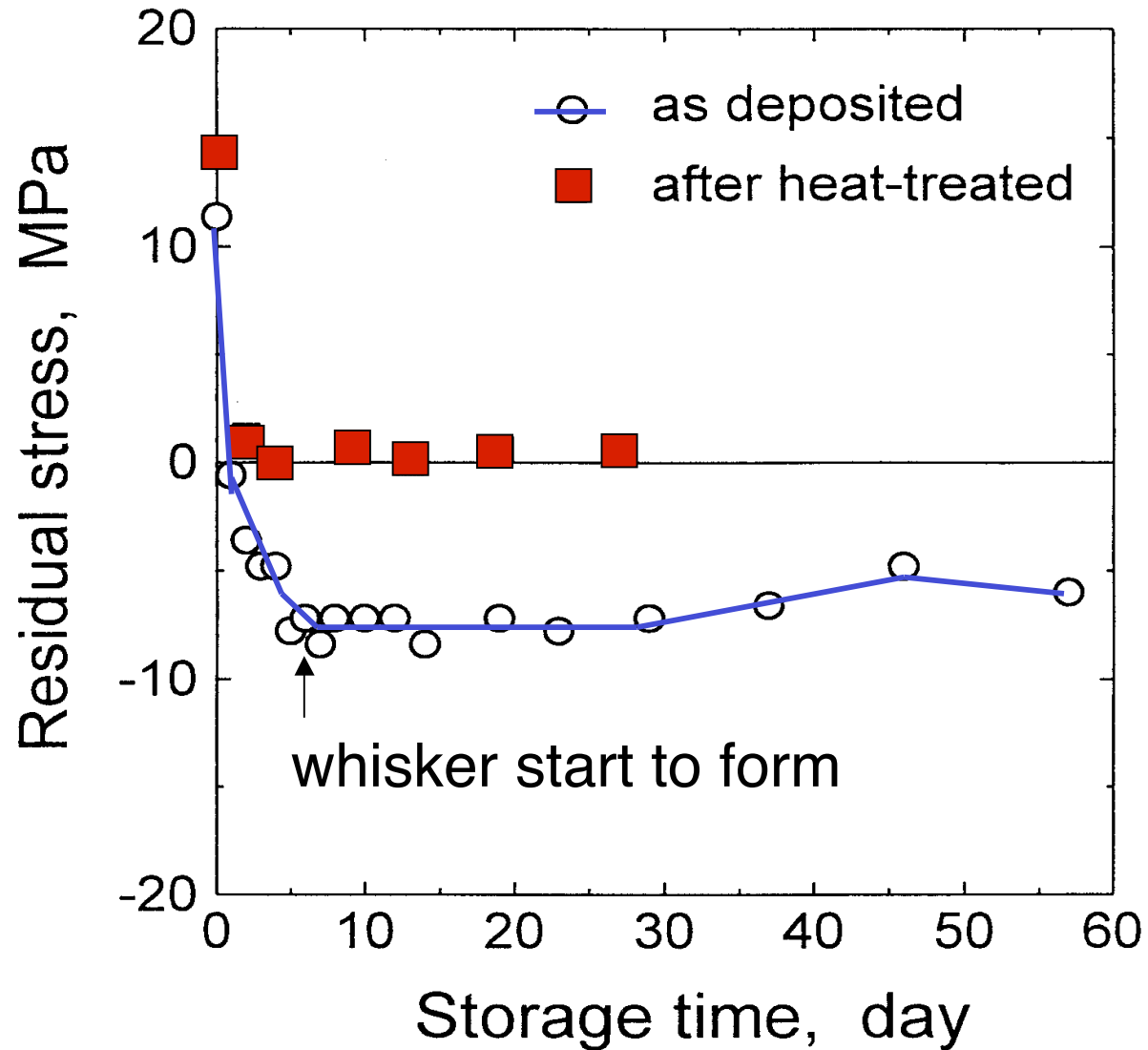
<110>

TEM micrographs of tin electrodeposits on copper substrate



(a) 3.5 A/dm^2 , as deposited; (b) 3.5 A/dm^2 , annealed at 150°C for 1 h;
(c) 1 A/dm^2 , as deposited

Residual stress of Sn deposit obtained at 3.5 A/dm²
Deposit heated at 150°C for 1h



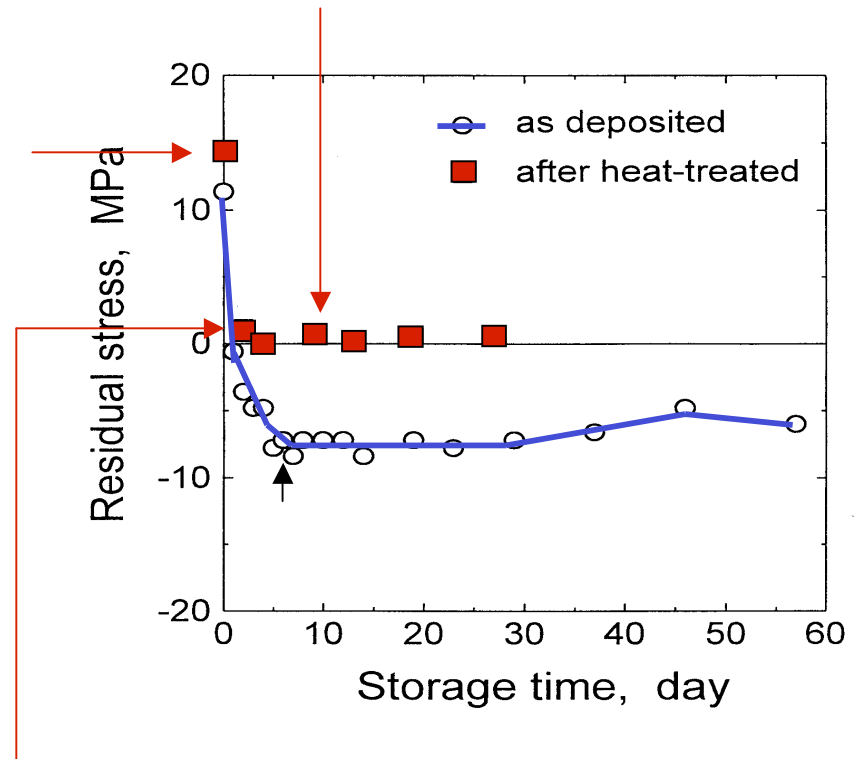
Thermal stress

due to thick Cu_6Sn_5 layer

$$\sigma_{th} = \frac{E_f}{1 + \nu_f} \left(\alpha_s - \alpha_f \right) \int_{T_0}^{T_1} dT$$

=51 MPa

The yield strength of commercially pure tin (>99.8%) is 11 MPa



Creep of Sn; Room $T=0.6 T_m$ of Sn

Thermal stress

$$\sigma_{th} = \left(\frac{E_f}{1 - \nu_f} \right) \int_{T_0}^{T_1} (\alpha_s - \alpha_f) dT$$

E_f Young's modulus

ν_f Poisson's ratio

α thermal expansion coefficient

The subscript **f** stands for the tin film

and **s** stands for the bronze substrate

T_1 initial temperature

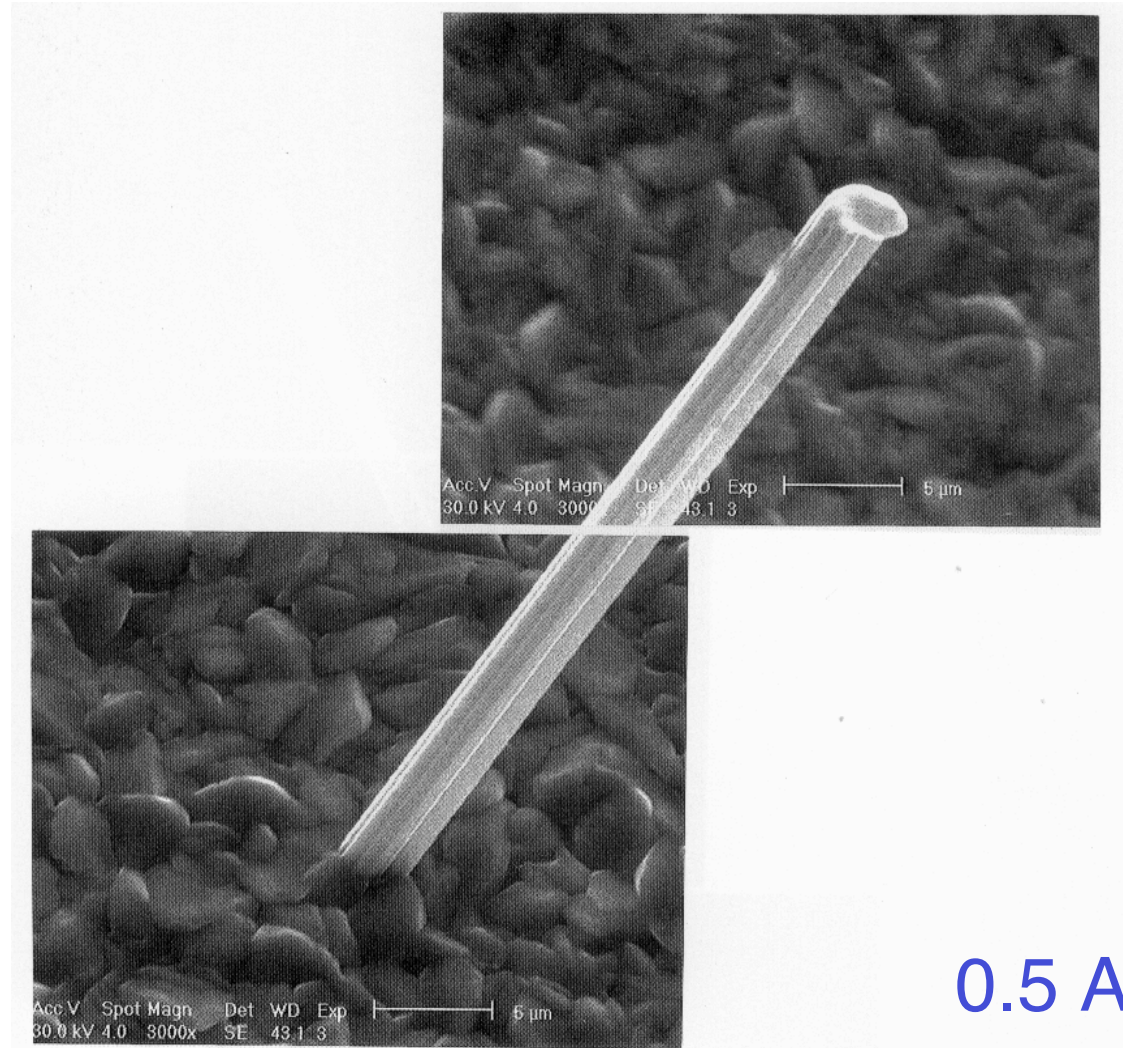
T_0 final temperature

Setting $E_f = 50 \text{ GPa}$, $\nu_f = 0.33$, $\alpha_s = 18 \times 10^{-6} \text{ K}^{-1}$, $\alpha_f = 23.5 \times 10^{-6} \text{ K}^{-1}$

$\sigma_{th} = 51 \text{ MPa}$

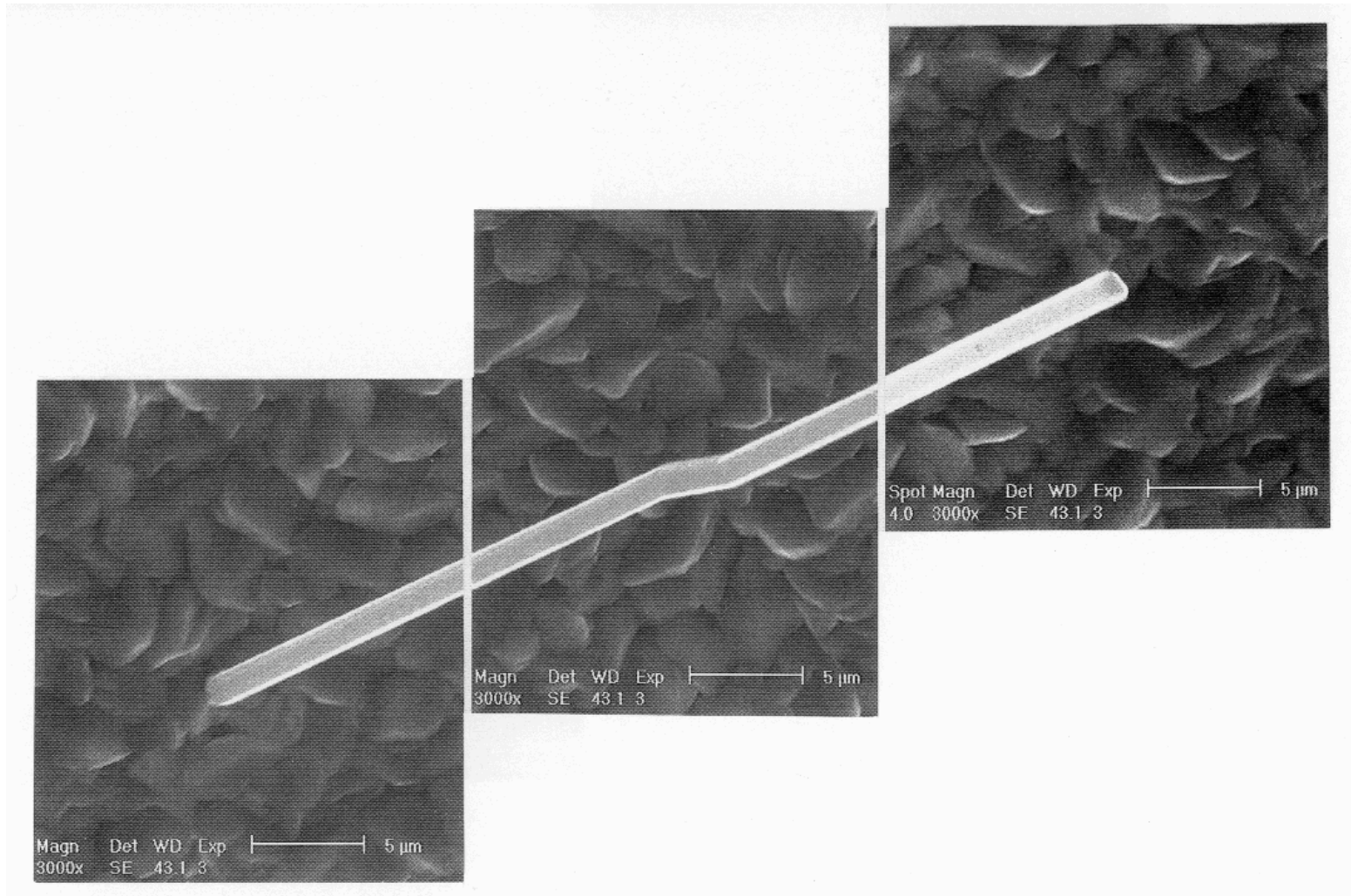
yield strength of commercially pure tin (> 99.8%) is 11 MPa at 23 °C

Sn whisker



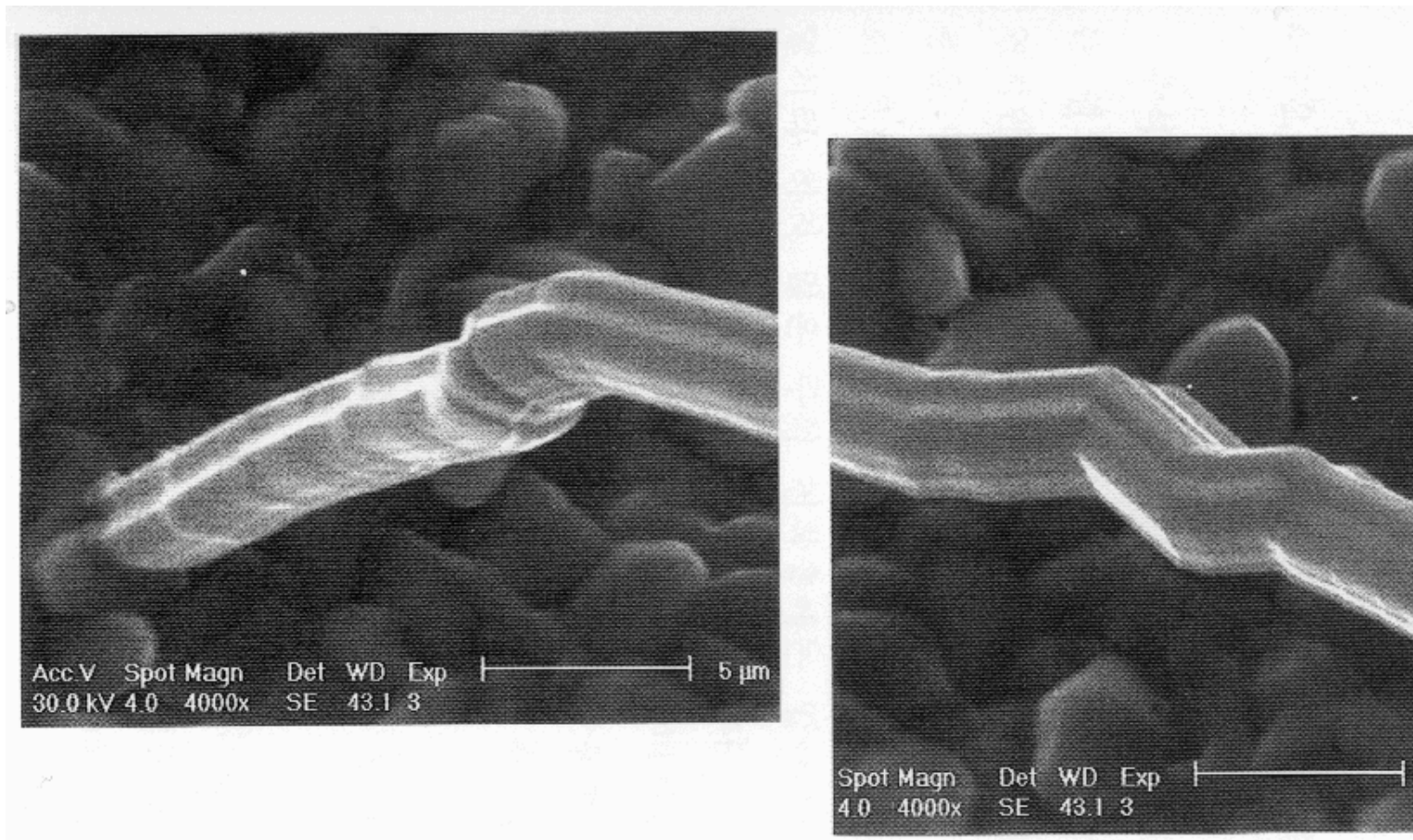
0.5 A/dm²

Sn whisker



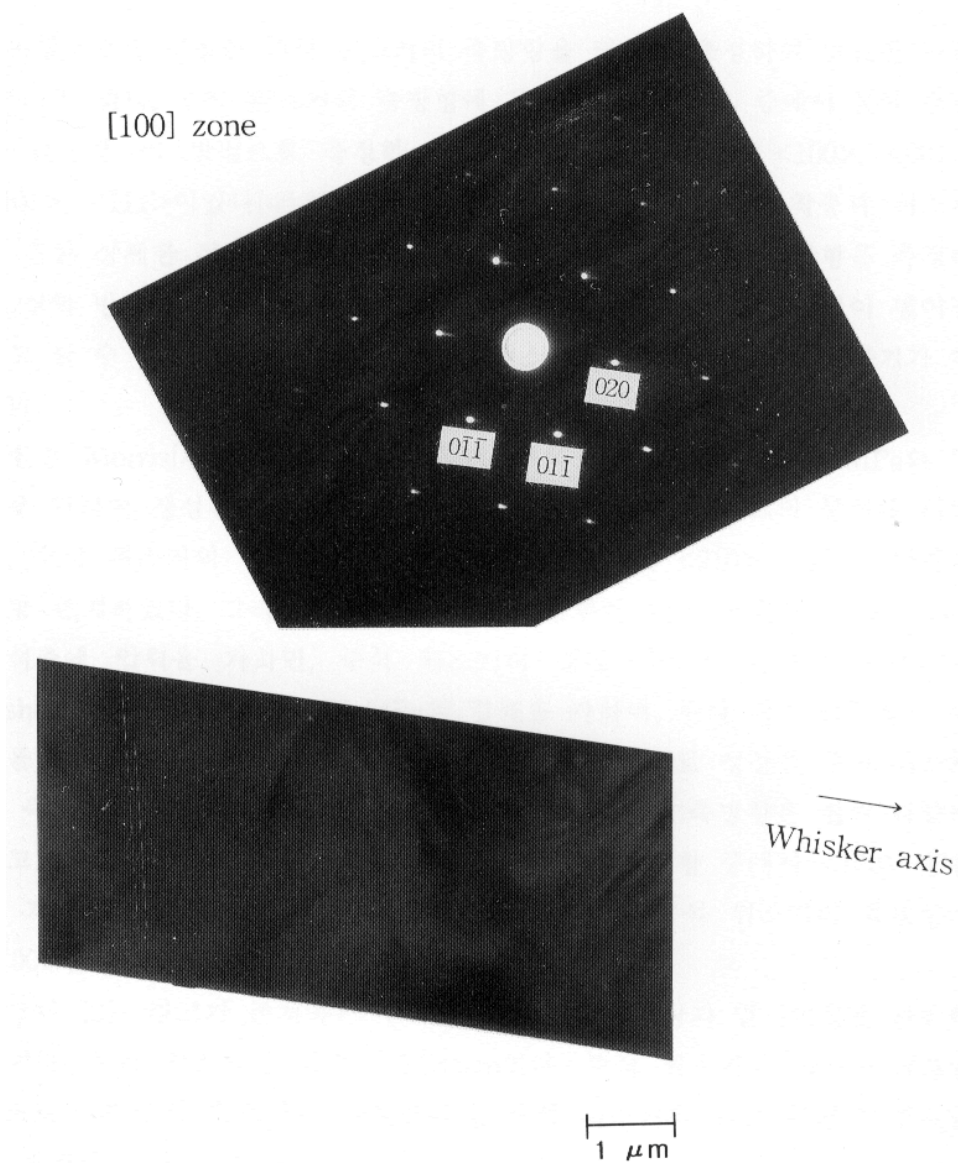
1 A/dm²

Sn whisker



3.5A/dm²

TEM micrographs of tin whisker to measure growth direction

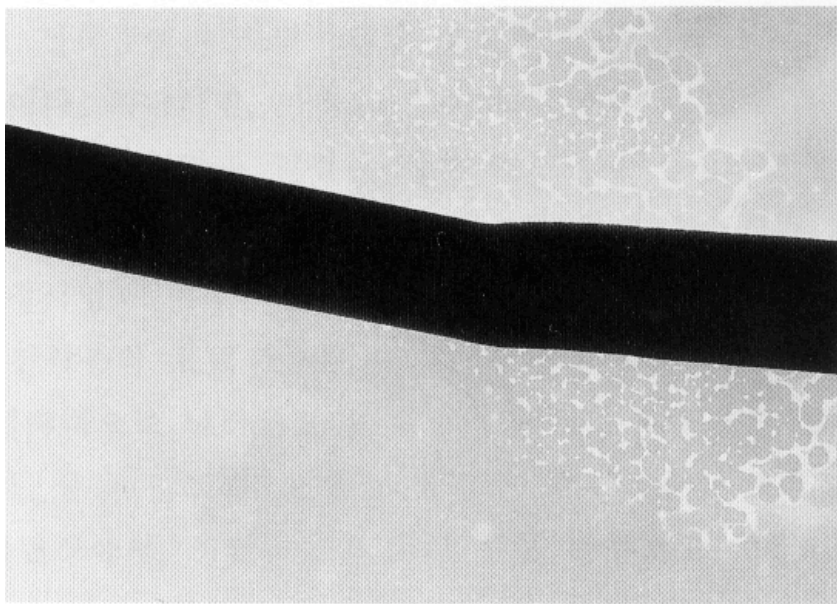


Growth angle of Sn whisker and orientation of grain from which Sn whisker grows

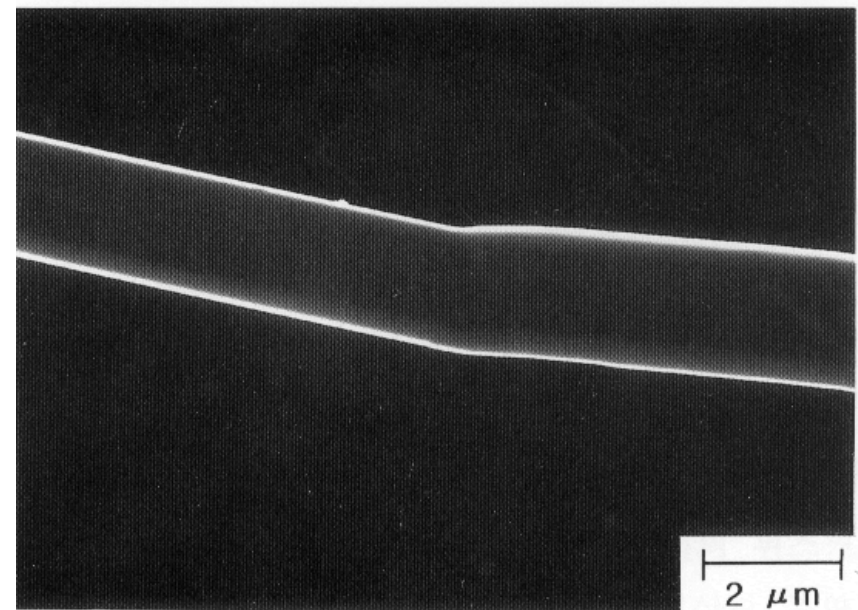
Current density (A/dm ²)	Texture of Sn deposit	Growth angle of Sn whisker : number of whisker	Orientation of grain from which Sn whisker grows
0.5	(200)	45~52°: 4 57~66°: 3 71~74°: 2	(220) (420) (620)
3.5	(220)	59~67°: 8 71~76°: 3 49~53°: 2 37° : 1 25~29°: 2	(420) (501) (321) (321) (420) or (321)

TEM micrographs of Sn whisker showing kink

When the kinked whisker is viewed in the dark field, the slight differences in orientation of the grains result in diffraction contrast effects which cause individual crystallites to be delineated. No diffraction contrast is seen in Fig. 13.1.9. Therefore, the kinked whisker is single crystal.

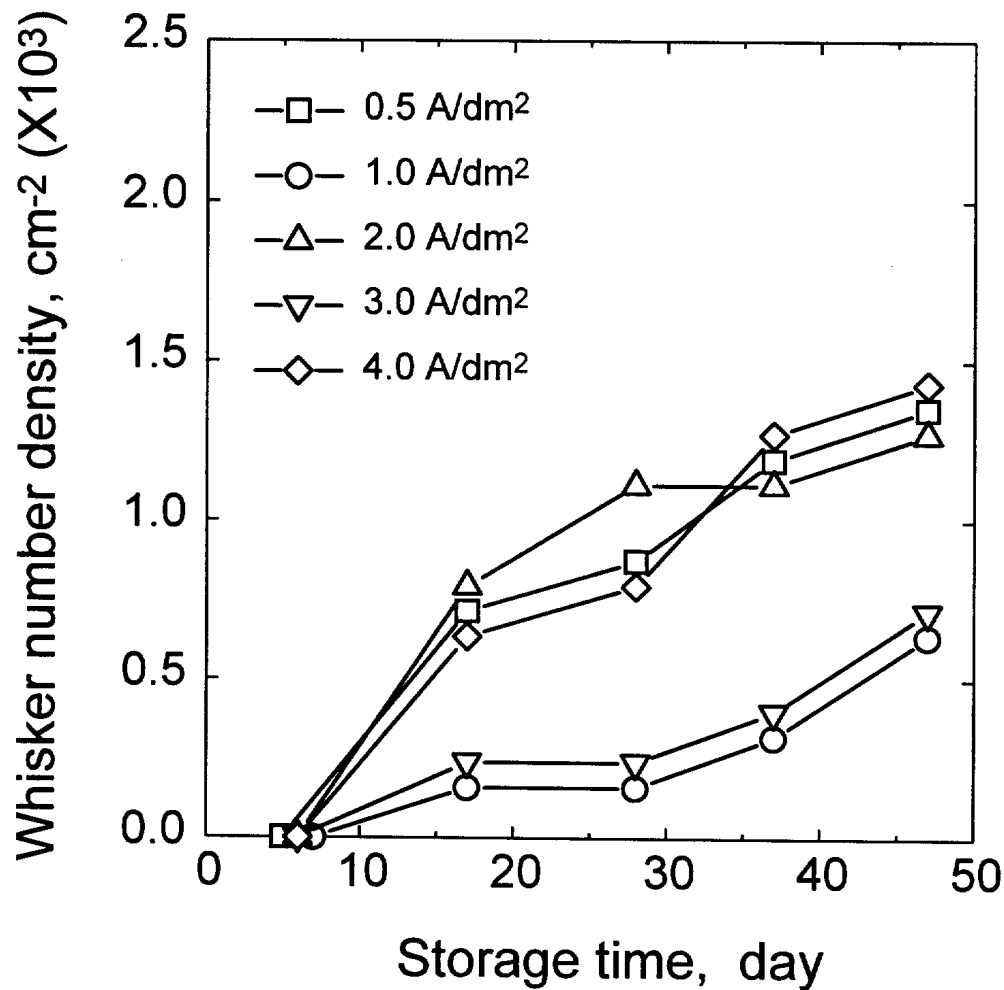


Bright field



Dark field

20 μ m or longer whisker on Sn electrodeposits



>Larger grain size

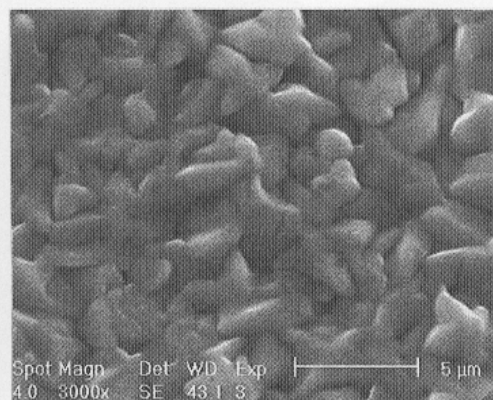
Surface morphologies of Sn electrodeposits



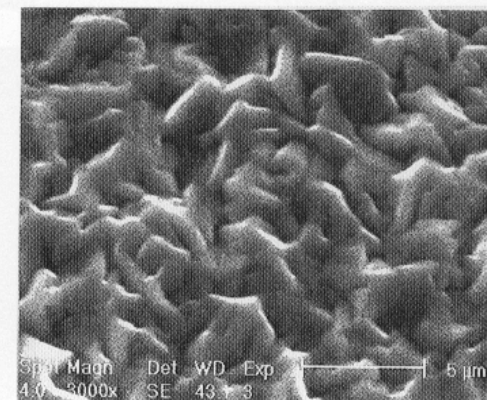
0.5 A/dm²



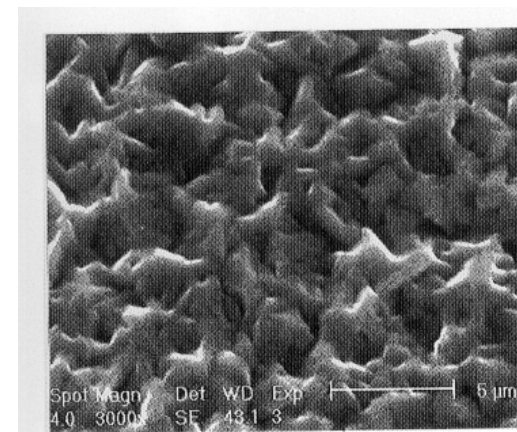
1 A/dm²



2 A/dm²

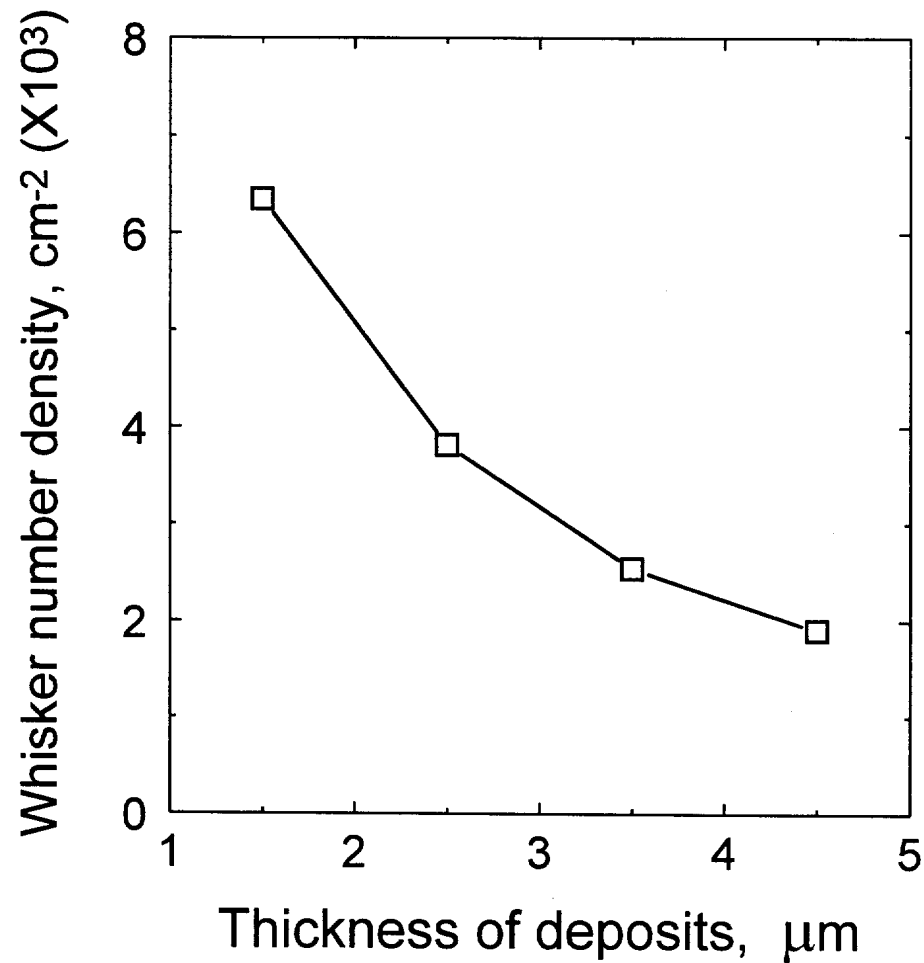


3 A/dm²

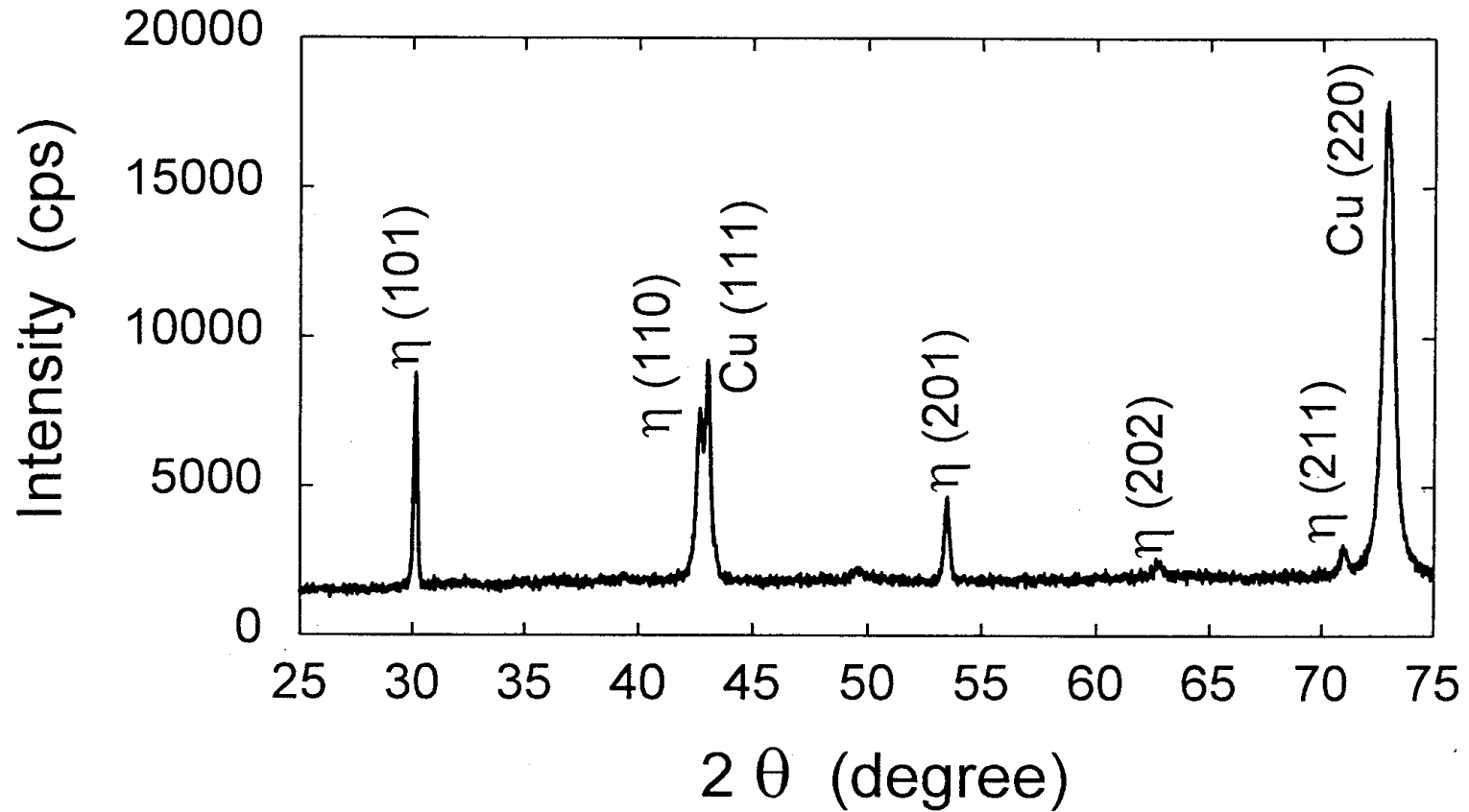


4 A/dm²

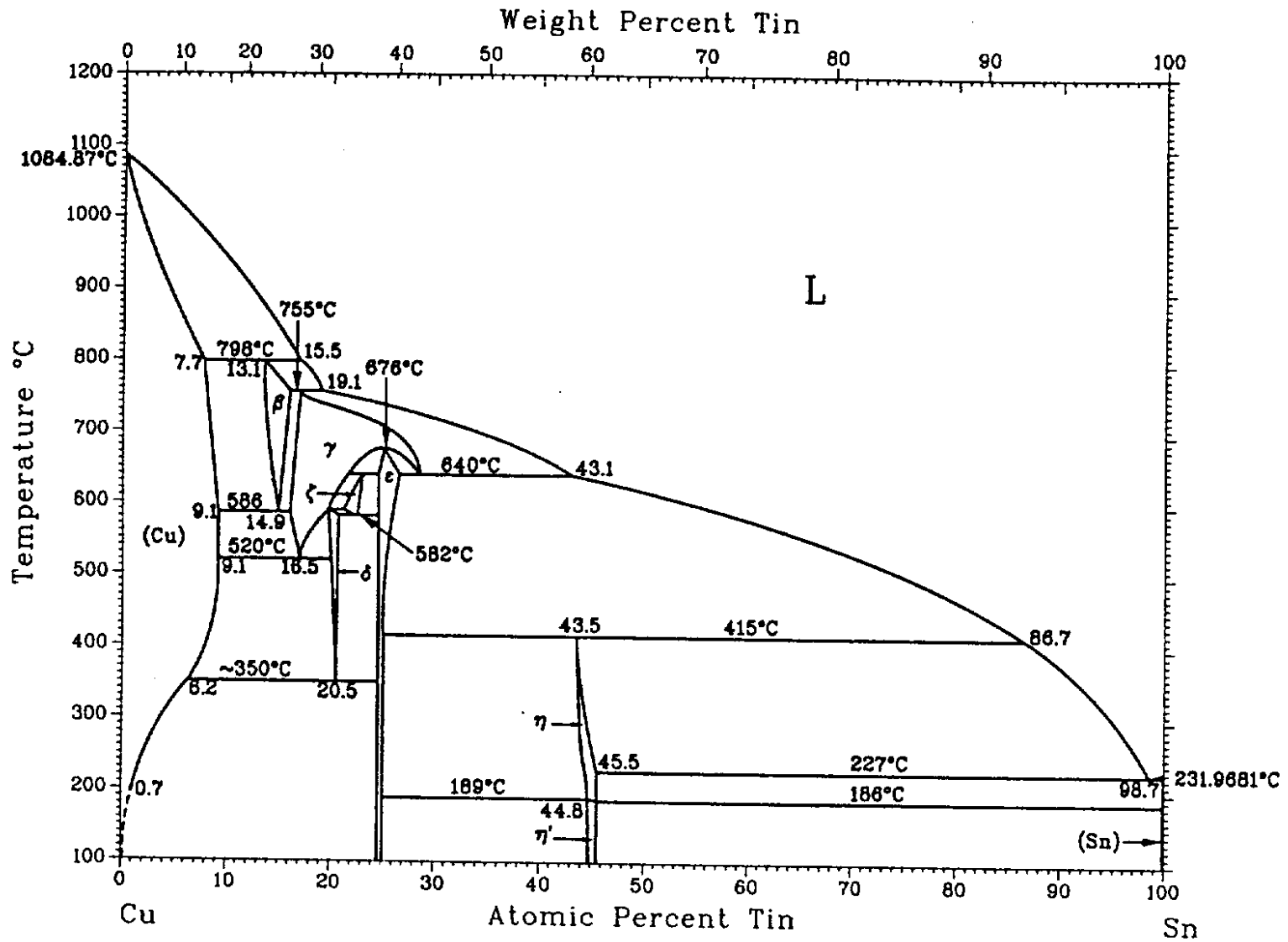
Number density of 20 μm or longer whisker vs. thickness of Sn electrodeposit obtained at 1.8 A/dm² after 30 days storage.



X-ray intensity profile of Cu_6Sn_5 formed between tin film and phosphor bronze substrate. [Lee and Lee]



Phase diagram of Cu-Sn





The density of Cu: 8.96 g/cm³

Sn: 7.28

Cu₆Sn₅: 8.27

copper atoms are the dominant diffusing species

Cu atoms are the dominant diffusing species in the room temperature growth of Cu_6Sn_5 between Cu and Sn films by using a flash of W film as the diffusion marker [Tu and Thompson 1982]

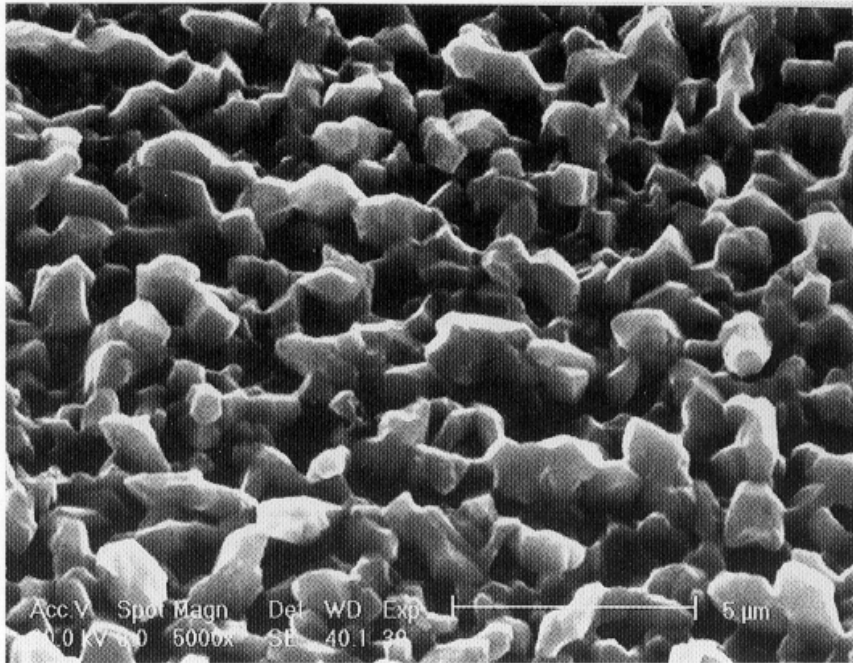
compressive stress in the Sn layer

If Cu_6Sn_5 forms flatly in the interface between **Cu** and **Sn** no residual stress will develop in Sn layer, regardless of diffusion coefficients of concerned species.

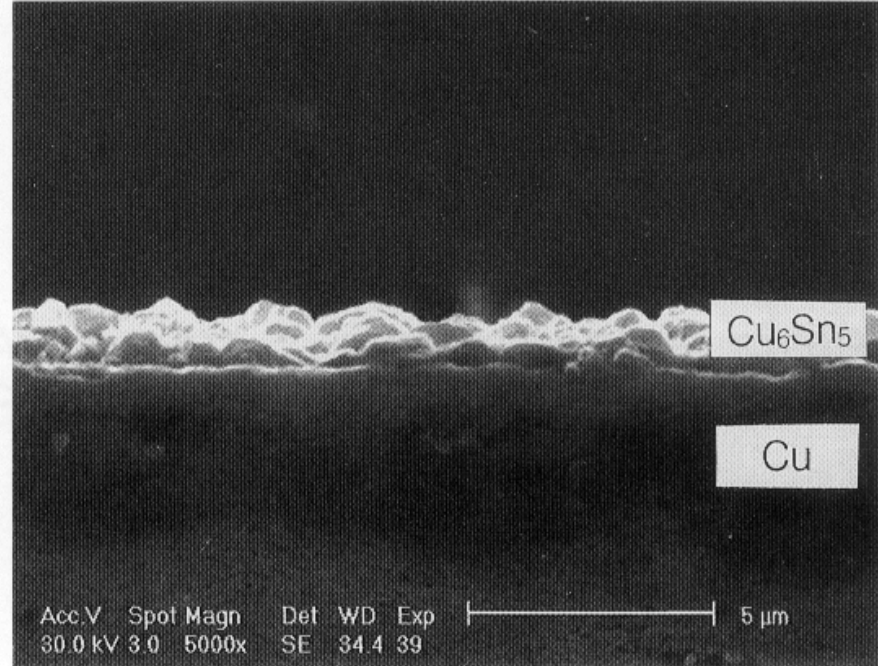
However, if the intermetallic compound layer forms in the Sn grain boundaries, it will give rise to **the compressive stress in the Sn layer**, because Cu atoms are dominant diffusing species.

CuSn formed between tin deposit and phosphor bronze substrate.

(a) Surface morphology, 30° tilted (b) cross-sectional morphology [Lee and Lee 1998]

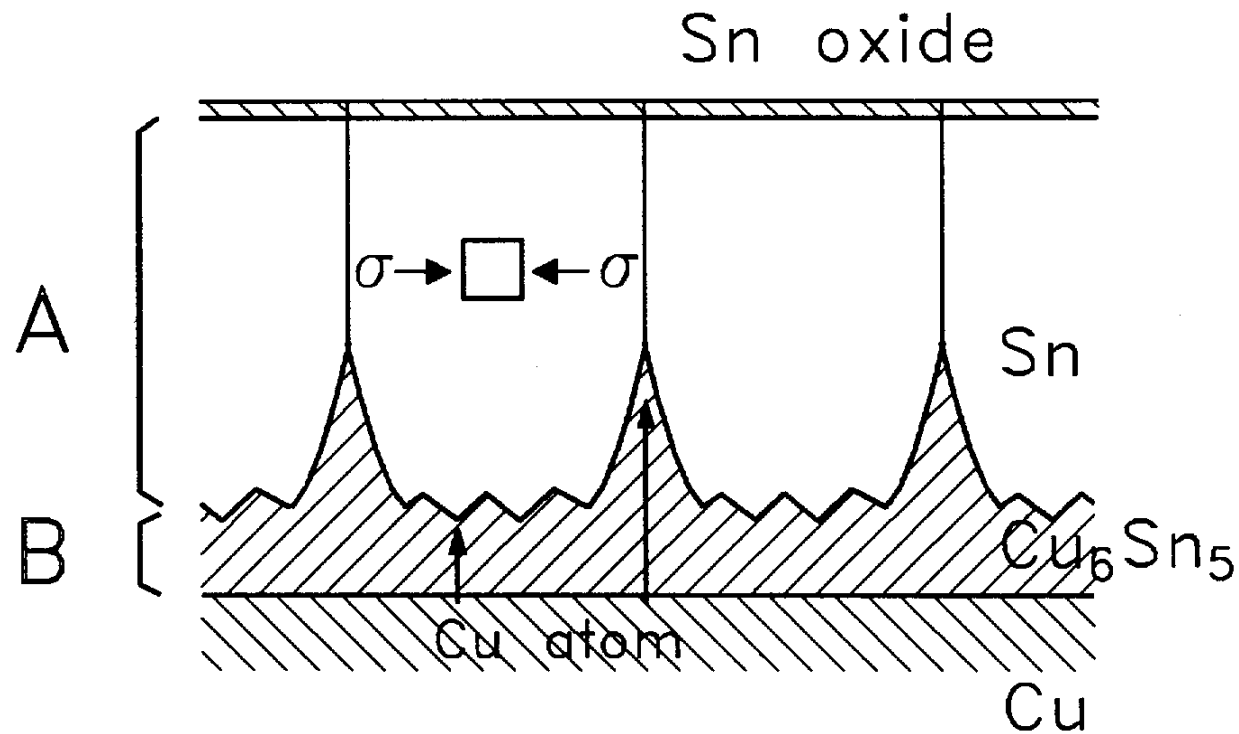


(a)



(b)

Sketch of Cu_6Sn_5 growth at interface of tin deposit [Lee, Lee 1998]



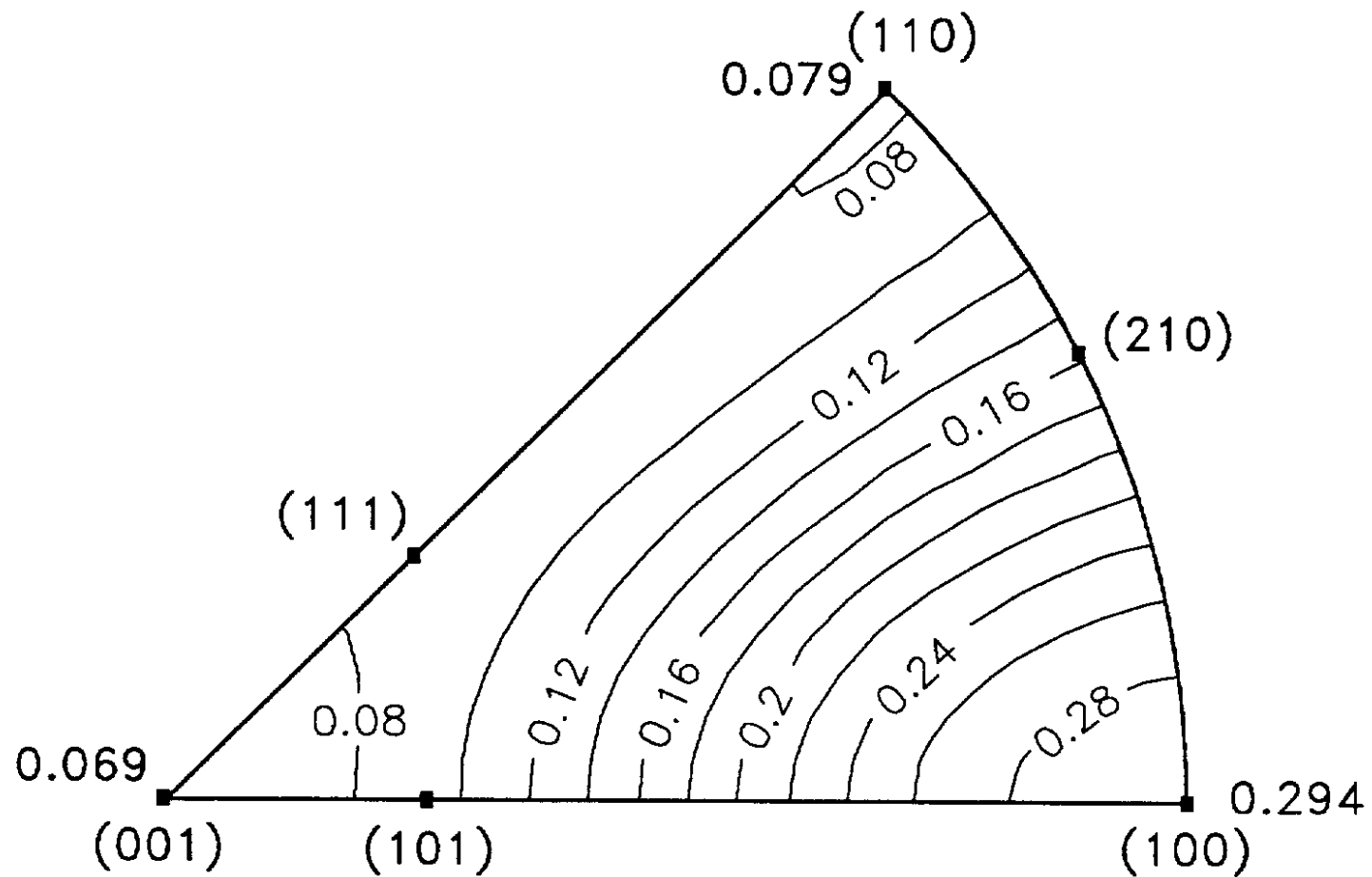
A region : compressive stress
B region : tensile stress

The compressive stress in Sn film squeezes its grains in the direction normal to the film plane by σ_{33}'

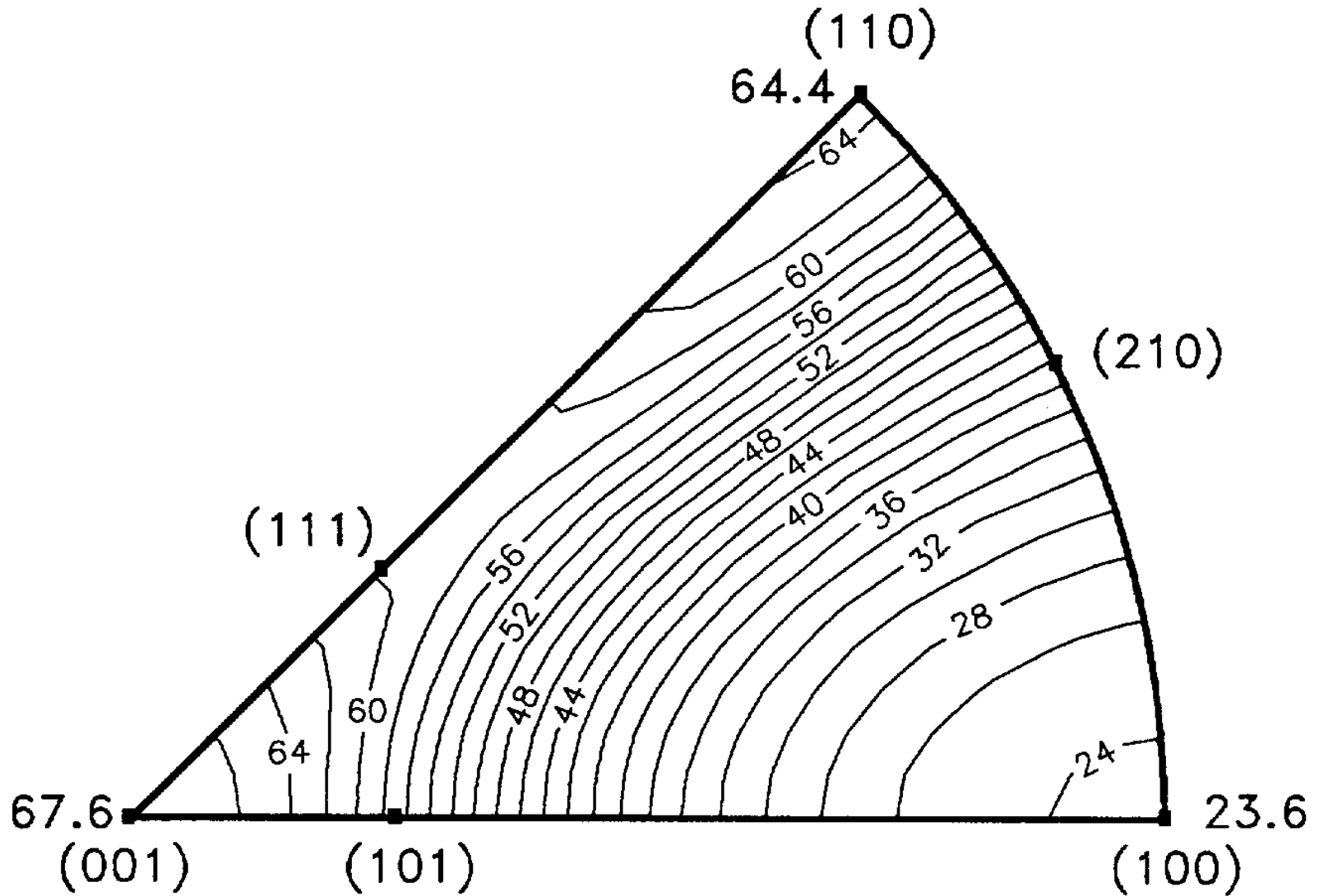
Elastic strain ϵ'_{33} (%) for biaxially stressed

$$\epsilon'_{33} = (S'_{3311} + S'_{3322}) \sigma$$

$$\sigma = -8 \text{ MPa}$$



Elastic modulus of tin (GPa)



Calculation of elastic modulus

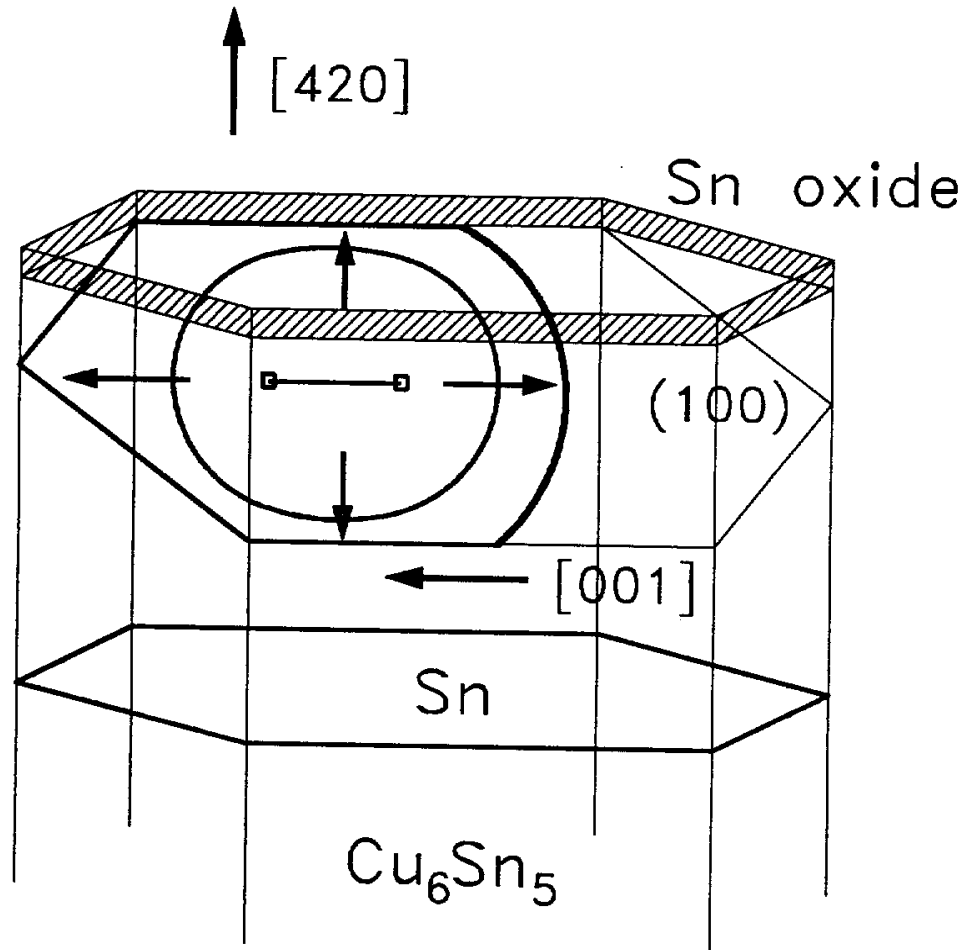
$$\frac{1}{E_f} = S_{11} (a_{11}^4 + a_{12}^4) + 2S_{12} a_{11}^2 a_{12}^2 + 2S_{13} (a_{11}^2 a_{13}^2 + a_{12}^2 a_{13}^2) \\ + S_{33} a_{13}^4 + S_{44} (a_{11}^2 a_{13}^2 + a_{12}^2 a_{13}^2) + S_{66} a_{11}^2 a_{12}^2$$

a_{ij} is the directional cosine of an arbitrary direction x_i with j referring to the crystal coordinate directions

Elastic strains ϵ_{33}' (%) for a biaxially stressed tin film

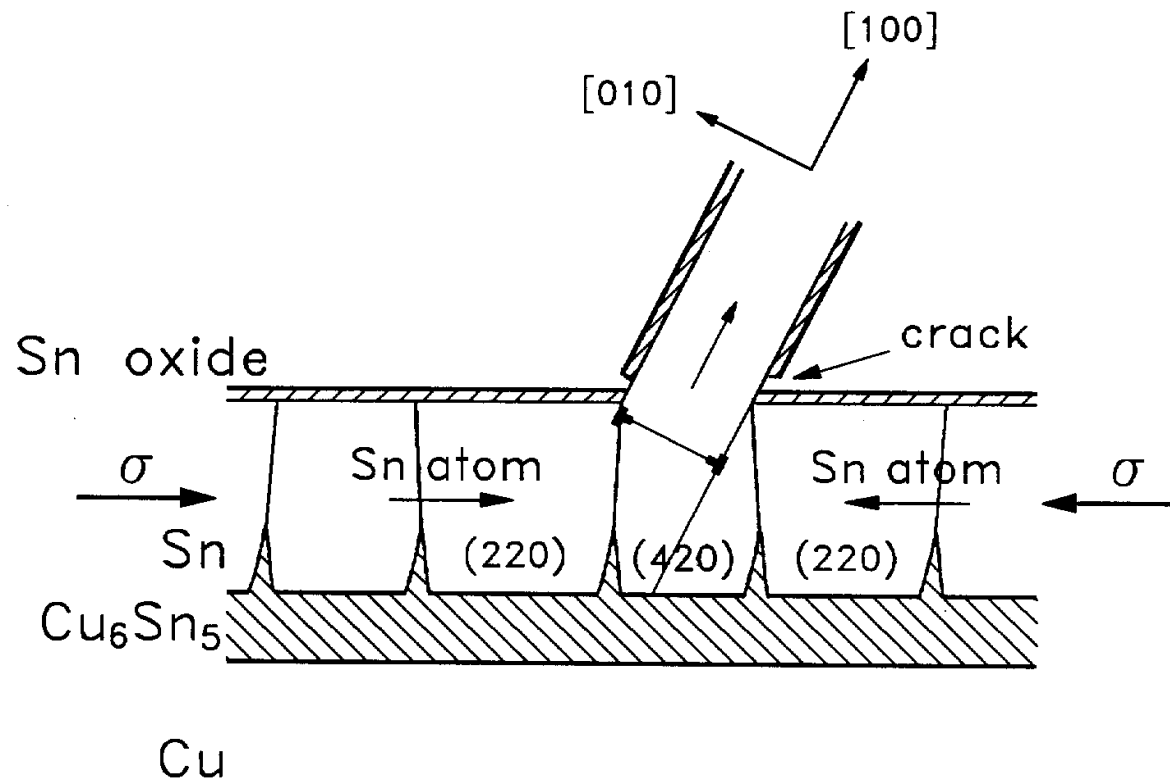
Grain Orientation	ϵ_{33}' (%)	$\epsilon_{33}'_{(hkl)} - \epsilon_{33}'_{(200)}$ (%)	$\epsilon_{33}'_{(hkl)} - \epsilon_{33}'_{(220)}$ (%)
[200]	0.294	0	.
[220]	0.079	- 0.215	0
[321]	0.115	.	0.036
[420]	0.153	- 0.141	0.074
[501]	0.251	.	0.172
[620]	0.219	- 0.075	.

Dislocation motion forming excess atomic plane in grain of tin deposit (Bardeen-Herring dislocation source)

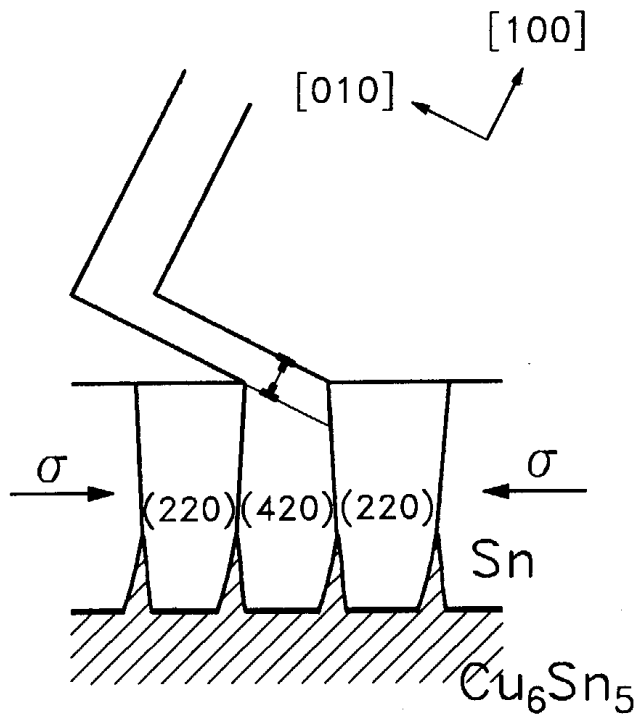


slip systems of tin crystal are $\{100\}\langle 001\rangle$ and $\{100\}\langle 010\rangle$

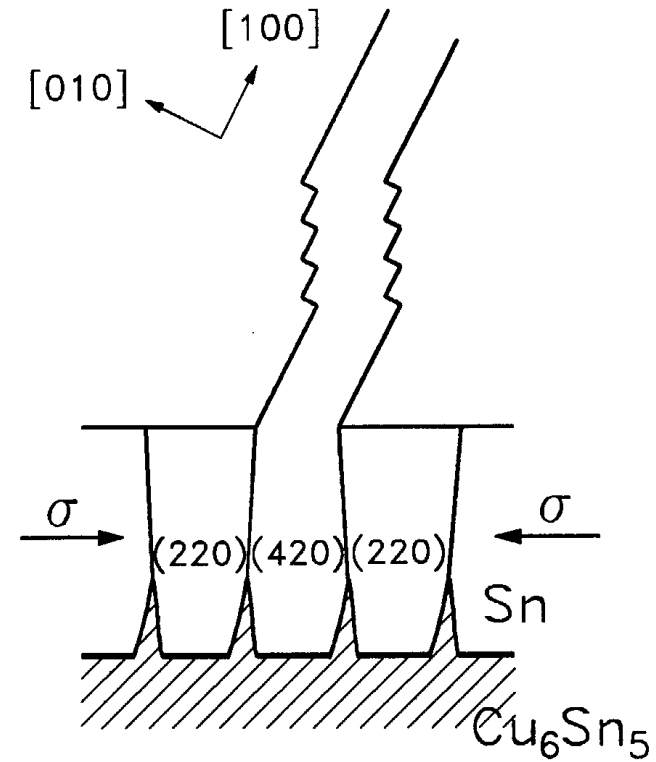
Whisker growth mechanism from tin deposit



Kinking mechanism of tin whisker. Kink angles of tin whiskers are (a) 90° and (b) 63 (or 27°). [Lee, Lee 1998]



90°



63 (or 27°)

Summary

The spontaneous generation of compressive stress in tin film is caused by the diffusion of copper atoms of phosphor bronze substrate into the tin film along its grain boundaries and their subsequent formation of Cu_6Sn_5 .

Tin whiskers grow from the grains whose orientation differs from the major orientation of the tin film. In this condition, the tin surface oxide film can be sheared along the boundaries of the grains. The shear force results from different strains generated in different grains in the direction normal to the substrate plane due to the biaxial compressive stress developed in the tin film. The different strains originate from the elastic anisotropy of tin.

Summary

To release the compressive stress in the tin film, tin whiskers grow from the grain whose surface oxide is sheared. The whisker growth is controlled by the expansion of the prismatic dislocation loop on the slip plane by climb, that is, by means of the operation of the Bardeen-Herring dislocation source. The dislocation loop expansion is restricted by the grain boundary. The loop now glides along its Burgers vector direction. As a result, tin whisker grows by one atomic step. The continuous operation of the Bardeen-Herring dislocation source gives rise to whisker growth until the stress is relieved.