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Application of the Critical Gradient Concept to First Phase Formation in Cu/Sn Nano-Multilayered Systems

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INTRODUCTION

Cu-Sn is one of the important systems for interconnects in microelectronics. Mechanical, electric and other properties of interconnect contact are determined mainly by the intermetallic phases appearing during reactions at the interface. For example, appearance of Cu3Sn1 phase at the joint interface leads to Kirkendall voiding and to degradation of interconnects contacts. And a question, how to escape or at least postpone the Cu3Sn1 phase formation remains extremely important especially for power electronics. Yet, many problems concerning kinetics of reaction, morphology of contact zone, mechanical properties of the reaction zone, remain unsolved.

- In this work the formation of metastable Cu41Sn11 as the first phase to form in Cu/Sn nanosized multilayer system could be explained in the frame of *Nucleation in the concentration gradient concept*.

EXPERIMENTAL BACKGROUND

Experimental investigations of Cu/Sn multilayers with the aim to determine the size effect on the phase formation sequence have been done by the EMPA team. The results appeared to be completely different from those for macroscopic Cu-Sn materials.

- *In the case of Cu(60nm)/Sn(50nm) layers the first phase was Cu6Sn5 as in case of bulk materials.*
- *But in the case of Cu(9nm)/Sn(6nm) multilayers the phase Cu41Sn11 was observed as a first phase to growth at the room temperature.*

TABLE 1. Phase formation sequence in Cu/Sn multilayers system at the initial stages of reactive diffusion

Cu/Sn multilayers thicknesses	Initial temperature	First intermediate phase	Temperature of second phase formation	Intermediate phases
Cu(6nm)/ Sn(5nm)	30°C	**Cu41Sn11**	110°C	Cu41Sn11 Cu3Sn
Cu(9nm)/ Sn(6nm)	30°C	**Cu41Sn11**	120°C	Cu41Sn11 Cu3Sn
Cu(30nm)/ Sn(10nm)	30°C	CuSn	150°C	CuSn Cu3Sn
Cu(30nm)/ Sn(20nm)	30°C	CuSn	150°C	CuSn Cu3Sn
Cu(60nm)/ Sn(50nm)	30°C	Cu6Sn5	150°C	Cu6Sn5 Cu3Sn

METASTABLE PHASE DIAGRAM

The interdiffusion process in this system starts from formation of solid solutions with the concentration gap at the interface between copper and tin. Intermediate phases appear later, at the base of this interface or at the base one of two solutions.

- **Critical gradient concept**: *The nucleation of any phase becomes possible after decreasing of the concentration gradient below certain critical magnitude.*

The metastable phase diagram for the equilibrium between Cu and Sn based solutions was calculated using Termo-Calc software (Fig. 1).

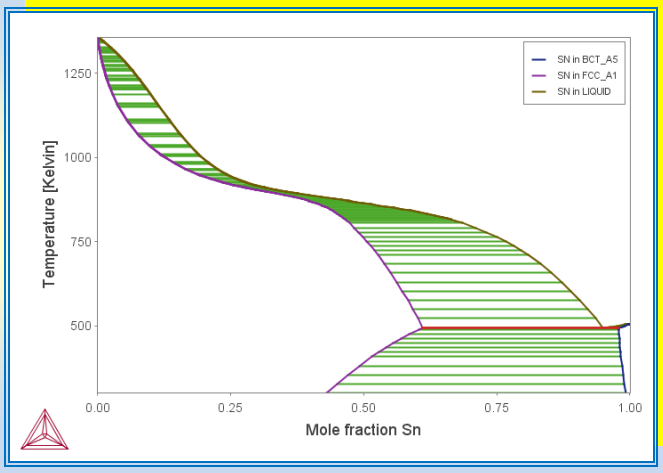

Fig. 1. Metastable Cu-Sn phase diagram for the equilibrium between solution Sn in Cu (FCC_A1), solution Cu in Sn (BCT_A5) and liquid Cu-Sn.

The phase diagram (Fig. 1) is valid only for the metastable equilibrium of two solid solutions before nucleation any intermediate phase.

The solubility of Sn in Cu-based solution is significant before the nucleation of first intermediate phase. On the other hand solubility of Cu in Sn-based solution can be neglected.

- *Accordingly to phase equilibria rule, only Cu-based solution is formed during diffusion process at the initial Cu-Sn interface.*

Diffusion process proceeds mainly via dissolution of Sn atoms in Cu-layer. Dissolution of Cu in Sn is practically negligible.

- *The first phase formation in Cu/Sn nanosized multilayer system does not depend on Sn layer thickness.*

DIFFUSION PROBLEM

It is important that the parent phase is sharply inhomogeneous, that is sharp concentration gradient exists.

- *Nucleation of each phase becomes possible if the concentration gradient in the place of nucleation becomes less than some **critical value**, specific for this phase.*
- According to the **Critical gradient concept**, *at the very initial stage of reactive diffusion, nucleation can be suppressed even without diffusive competition, due to a too narrow space region, favorable for transformation.*

Diffusion equation in Cu-based solid solution is

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2},\ (0 \le x \le l)$$

where $c(t,x)$ – concentration of Sn in solution, D – diffusivity, t – time, x – distance from center of Cu layer in direction perpendicular to Cu/Sn interface, $l(t)$ – position of moving Cu/Sn interphase boundary. Initial and boundary conditions are

$$c(t=0, x<l)=0,\ c(t, x=l)=c_{eq},\ \left.\frac{\partial c}{\partial t}\right|_{x=0}=0,$$

$$(c_{eq}-0)\frac{dl}{dt} = -D\left.\frac{\partial c}{\partial x}\right|_{l-0},\ l(t=0)=l_0.$$

Here c_{eq} – equilibrium concentration of Sn in Cu-based solution at the contact with Sn, l_0 – initial position of Cu/Sn interface.

The diffusion problem with moving interphase boundary was solved using dimensionless variables.

APPLICATION OF CONCENTRATION GRADIENT CONCEPT

- According to the ***Theory of nucleation in the concentration gradient***, *each intermediate phase is characterized by the critical gradient in the parent solid solution, below which the phase formation becomes inevitable.*

This condition is fulfilled only after some period of profile smoothening during interdiffusion in the metastable parent solid solution.

- *The phase, for which such condition is first reached, will appear as the **first phase to form**.*

In general, time of reaching the mentioned condition, is a phase nucleation suppression time. As the result we could explain the influence of period of Cu/Sn multilayers on first product phase in Cu/Sn interaction.

RESULTS AND DISCUSSION

According to results of experimental investigations (Table 1) only Cu41Sn11 and Cu6Sn5 intermediate phases were considered as possible phases for nucleation during reactive diffusion between Cu and Sn solutions.

The principal influence is interrelation between critical gradients. In our consideration they are

$$\nabla^*_{Cu6Sn5} > \nabla^*_{Cu41Sn11},\ \nabla^*_{Cu3Sn1} > \nabla^*_{Cu6Sn5}.$$

In particular the dependences of real time of nucleation suppression on the thickness of copper film for three intermediate phase where calculated (fig. 2). Points of intersection here mean change of the first phase to form.

- *At small thicknesses of Cu layer the first phase to form is Cu41Sn11, at large thicknesses the first phase is Cu6Sn5.*

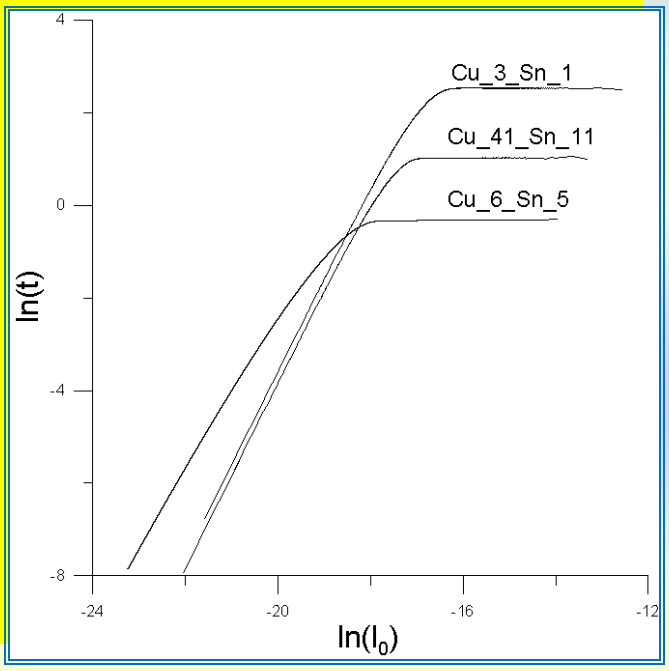

Fig. 2. Dependences of nucleation time suppression on the thickness of copper film for three intermediate compounds, calculated for $\nabla^*_{Cu41Sn11} = 10^7 m^{-1}$ and $D = 10^{-16} m^2/s$.

Note the real values of $\nabla^*_{Cu41Sn11}$ and D only moves dependencies of $t_i^*(l_0)$ in $\ln(t^*)$ and $\ln(l_0)$ axis without changing relative position between them.

CONCLUSIONS

- Accordingly to phase equilibrium rule, only Cu-based solution is formed during diffusion process at the Cu-Sn interface before the first intermediate phase formation.
- Interdiffusion process goes through dissolution of Sn and formation of Sn-rich Cu-based solution layer.
- The strong dependence of first phase formation on Cu/Sn multilayers thicknesses established experimentally could be explained in the frame of *concentration gradient concept*.
- Kinetics of the first phase formation in Cu/Sn nanosized multilayer system depends mainly on Cu layer thickness.
- *Theory of nucleation in sharp concentration gradient* could be applied to the explanation of Cu41Sn11 phase formation in Cu/Sn nanosized multilayer system.

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[1] J.Janczak-Rusch, Final report of the SNF grant 200020_134565, 2012.

[2] K.K. Sobol-Sosnowska, PhD Thesis, ETHZ, 2014.

[3] M.O.Pasichnyy, G.Schmitz, A.M.Gusak, V.Vovk, Physical Review B, 2005, vol.72, p.014118.

[4]: A.M.Gusak, T.V.Zaporozhets, Yu.O.Lyashenko, S.V.Kornienko, M.O.Pasichnyy, A.S.Shirinyan, Diffusion-controlled Solid State Reactions: in Alloys, Thin-Films, and Nanosystems, Wiley-VCH, Berlin, 2010.