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# Calculating the diffusivity of Cu and Sn in Cu<sub>3</sub>Sn intermetallic by molecular dynamics simulations

Feng Gao<sup>a</sup>, Jianmin Qu<sup>a,b,\*</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, Northwestern University, Evanston, IL 60208, USA

<sup>b</sup> Department of Mechanical Engineering, Northwestern University, Evanston, IL 60208, USA

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## ABSTRACT

In this paper, molecular dynamics (MD) simulations are performed to calculate the diffusivity of Cu and Sn atoms in the Cu<sub>3</sub>Sn intermetallic compound. Our MD results show that Cu atoms are the dominant diffusion species in Cu<sub>3</sub>Sn. The diffusion coefficient of Cu atoms in Cu<sub>3</sub>Sn is about 17 times higher at room temperature (300 K), and 7 times higher at the annealing temperature (423 K) than that of Sn. This large difference in diffusivity between Cu and Sn is believed to be the main cause of Kirkendall void formation within the Cu<sub>3</sub>Sn layer in lead-free solder joints.

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## 1. Introduction

In lead-free solder joints in microelectronic packaging, Kirkendall voids are often found in the Cu<sub>3</sub>Sn intermetallic compound (IMC) near the interface between the IMC layer and the Cu metallization after annealing [1,2]. Shown in Fig. 1 is a scanning electron microscopy (SEM) photograph of interfacial microstructure between a Sn–3.5Ag solder and a Cu substrate. The Sn–3.5Ag alloy was soldered onto the Cu substrate at 523 K, followed by a subsequent annealing at 423 K for 1008 h. Two distinct IMC layers can be clearly observed, namely, the Cu<sub>6</sub>Sn<sub>5</sub> layer next to the solder alloy, and the Cu<sub>3</sub>Sn layer next to the Cu substrate. More importantly, Kirkendall voids can be clearly observed within the Cu<sub>3</sub>Sn layer and at the Cu<sub>3</sub>Sn/Cu interface. These voids can weaken the interfacial strength dramatically, thus reduce the reliability of the solder joints significantly [3–5].

Therefore, to improve solder joint reliability, it is crucial to understand the formation of Kirkendall voids at the Cu<sub>3</sub>Sn IMC layer, and to develop means to control the void formation. It is well-known that Kirkendall voids are formed in binary IMC by interdiffusion caused by the large difference in diffusivity between the two different species [2,4]. However, the diffusivity of Cu and Sn in Cu<sub>3</sub>Sn has never been well established. The reported values of Cu and Sn diffusivities in Cu<sub>3</sub>Sn are sparse and fall in a wide range [6–10]. In fact, there is not even a consensus on whether Cu or Sn diffuses faster in Cu<sub>3</sub>Sn [2,4,11–14]. In other words, it is still an open question that whether

Cu or Sn is the dominant diffusion species in the Cu<sub>3</sub>Sn IMC, and by how much.

To answer the above question, molecular dynamics (MD) simulations are performed in this study to determine the diffusivity of Cu and Sn in Cu<sub>3</sub>Sn IMC. As a byproduct, the diffusion activity energy of both species is also extracted. Those parameters are essential for the quantitative analysis of Cu<sub>3</sub>Sn IMC growth and the understanding of Kirkendall void formation, which enables the optimal design of under bump metallization (UBM) and Pb-free solders.

## 2. Simulation results and discussion

The Cu<sub>3</sub>Sn compound is a hexagonal close-packed Cu<sub>3</sub>Ti-type transition-metal IMC belonging to the space group 63 with *Cmcm* symmetry. It has been reported that the ordered Cu<sub>3</sub>Sn is a long-period superlattice alloy with periodic antiphase domains similar to the ordered Cu<sub>3</sub>Au [15]. One unit cell of Cu<sub>3</sub>Sn contains 80 atoms. A supercell consisting of 2560 atoms is used in our MD simulations. Periodic boundary conditions (PBCs) are prescribed in all three orthogonal directions.

The MD simulations were performed by using LAMMPS [16]. The modified embedded atom method (MEAM) interatomic potential [17] was used to describe the interactions among the atoms in the Cu<sub>3</sub>Sn structure. The Cu–Cu MEAM and Cu–Sn MEAM interatomic potentials are adopted from Baskes' previous work [18], which had been used to study the wetting of Sn–Cu alloys on Cu surfaces. The Sn–Sn MEAM interatomic potential with diamond reference structure is taken from the database in LAMMPS [16], in that a much better stability of Cu<sub>3</sub>Sn phase is achieved at finite temperature (e.g., 300 K). The Cu<sub>3</sub>Sn supercell was then minimized based the aforementioned

\* Corresponding author at: Department of Civil and Environmental Engineering, Department of Mechanical Engineering, Northwestern University, Evanston, IL 60208, USA. Tel.: +1 847 467 4528.

E-mail address: [j-qu@northwestern.edu](mailto:j-qu@northwestern.edu) (J. Qu).

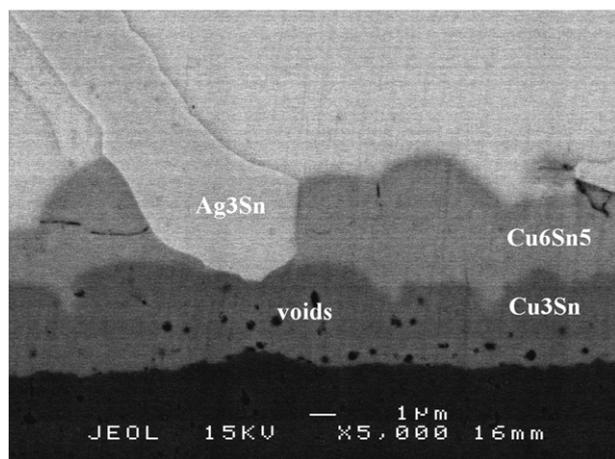


Fig. 1. The lead-free Sn-3.5Ag/Cu solder joint with Kirkendall voids formed within Cu<sub>3</sub>Sn layer and at Cu<sub>3</sub>Sn/Cu interface after annealing at 423 K for 1008 h.

MEAM interatomic potentials. The lattice constants after minimization are  $a = 5.345 \text{ \AA}$ ,  $b = 46.254 \text{ \AA}$ , and  $c = 4.470 \text{ \AA}$ . These values are very close to the experimental results ( $a = 5.529 \text{ \AA}$ ,  $b = 47.750 \text{ \AA}$ , and  $c = 4.323 \text{ \AA}$ ) [15], as well as the ones by ab initio calculations ( $a = 5.516 \text{ \AA}$ ,  $b = 48.790 \text{ \AA}$ , and  $c = 4.342 \text{ \AA}$ ) [13].

More material properties were extracted from MD simulations to validate the accuracy of the MEAM interatomic potentials used for the Cu<sub>3</sub>Sn structure. For instance, the orthorhombic elastic stiffness tensor was computed by applying a strain field to the simulation cell [19]. The results are listed in Table 1, together with the corresponding values from ab initio computations [13,20]. It is seen that our MD results are in excellent agreement with the ab initio calculations, except for the relatively large magnitude of  $C_{33}$ .

Once the orthorhombic elastic stiffness tensor is known, the isotropic elastic constants of the polycrystalline Cu<sub>3</sub>Sn IMC, such as the Young's modulus and Poisson's ratio etc., can be computed following the Voigt–Reuss–Hill (VRH) scheme [21]. Displayed in Table 2 are the so computed isotropic elastic constants based on the orthorhombic elastic stiffness tensor from our MD simulations and the existing ab initio results [13,20], respectively. For comparison purpose, some existing experimental values are also listed in Table 2. Clearly, our MD results fall within the range of the experimental data, and very close to the values determined by ab initio calculations. This is an indication that the MEAM interatomic potentials for Cu–Cu, Sn–Sn and Cu–Sn in this study are appropriate.

To compute the diffusivity of Cu (or Sn) atoms in Cu<sub>3</sub>Sn, the mean square displacement (MSD) of Cu (or Sn) was calculated by MD simulations. MSD has been extensively used to describe the movement of atoms in solids, liquids and gases. It has been shown that the MSD will increase linearly with time when diffusion occurs [25], and the slope of the MSD vs. time curve gives the diffusion constant  $D$  for Cu (or Sn) in Cu<sub>3</sub>Sn phase,

$$D = \lim_{t \rightarrow \infty} \frac{\text{MSD}(t)}{6t} = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{r}_i(t) - \mathbf{r}_0(0)|^2 \rangle}{6t}, \quad (1)$$

where  $\mathbf{r}_i(t)$  is the position of the Cu (Sn) atom  $i$  at the time  $t$ , and the symbol  $\langle \rangle$  denotes the average over all Cu (Sn) atoms in the

Table 1  
Computed elastic constants by our MD and existing ab initio approaches (unit: in GPa).

	$C_{11}$	$C_{22}$	$C_{33}$	$C_{12}$	$C_{13}$	$C_{23}$	$C_{44}$	$C_{55}$	$C_{66}$
Our MD	208	230	265	103	90	77	47	57	65
Ab initio[13]	203	165	219	94	106	106	61	64	39
Ab initio[20]	207	226	194	93	94	94	58	47	57

Table 2

The isotropic elastic constants of Cu<sub>3</sub>Sn polycrystalline IMC by our MD simulations, ab initio calculations, and experimental measurements (unit: in GPa).

	$B$	$E$	$G$	$\nu$
MD	138	132	49	0.34
Ab initio	132.22 [20]	134.16 [13], 147.54 [20]	56.14 [20]	0.314 [20]
Experiment		143 [22], 134 [23], 122 [24]		

simulation cell. Ideally, the MSD( $t$ ) is a linear function of  $t$  so that the  $D$  calculated from MSD( $t$ ) is independent of  $t$ . In reality, there are always fluctuations in the MSD( $t$ ) when calculated by MD simulations. Thus, linear regression, instead of numerical derivative, is used to calculate the diffusivity  $D$  from the MSD( $t$ ) curve.

Fig. 2a–b shows the calculated MSD of Cu and Sn atoms, respectively, in Cu<sub>3</sub>Sn at various temperatures. The diffusion constant  $D$  at different temperatures can then be calculated from the slope of these curves. We note that the thermally activated diffusivity at different temperatures is related through the following Arrhenius equation,

$$D = A \exp\left(-\frac{Q}{RT}\right), \quad (2)$$

where  $T$  is the absolute temperature in Kelvin,  $D$  is the diffusion constant at temperature  $T$ ,  $A$  is a material constant,  $Q$  is the thermal activation energy, and  $R$  is the standard gas constant. It thus follows that,

$$\ln D = \left(-\frac{Q}{R}\right) \cdot \frac{1}{T} + \ln A. \quad (3)$$

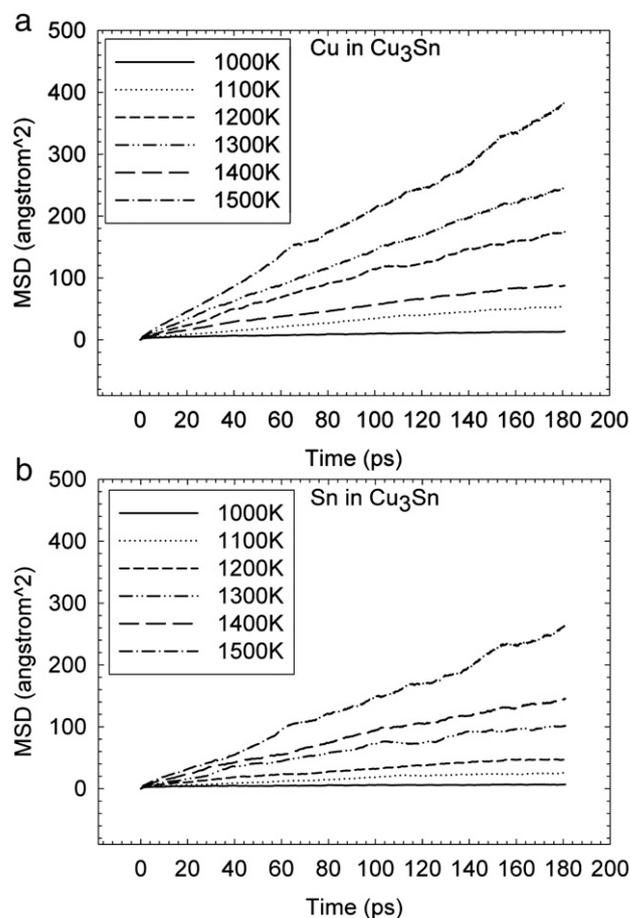


Fig. 2. Mean square displacement (MSD) of (a) Cu and (b) Sn in Cu<sub>3</sub>Sn versus time at different temperatures.

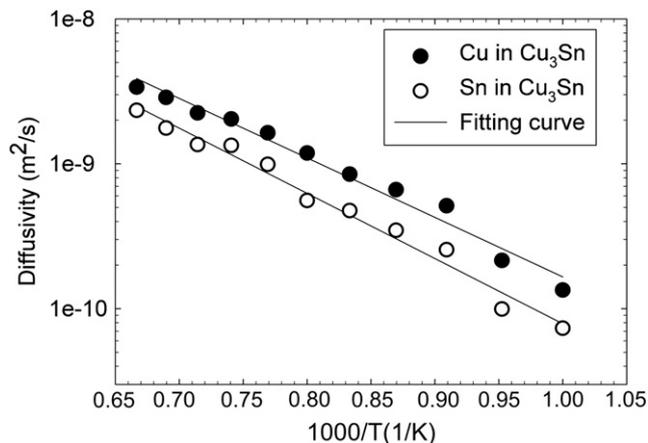


Fig. 3. The  $\ln(D)$  vs.  $(1/T)$  curves for Cu and Sn in  $\text{Cu}_3\text{Sn}$ .

In other words, the activation energy  $Q$  and the material constant  $A$  can be obtained directly from the linear relationship between  $\ln D$  and  $(1/T)$ . Based on the data in Fig. 2,  $\ln D$  is plotted as a function of  $(1/T)$  in Fig. 3, where the solid (open) circles denote the diffusivities of Cu (Sn) in  $\text{Cu}_3\text{Sn}$ . The fitting line for each curve is also presented. By extrapolating these straight lines, one can obtain the diffusivity of Cu and Sn in  $\text{Cu}_3\text{Sn}$  beyond the temperature range shown.

Based on the results shown in Fig. 3, one can extract the activation energies for thermally activated diffusion of Cu and Sn in  $\text{Cu}_3\text{Sn}$ . They are  $Q_{\text{Cu}} = 78.63$  kJ/mol,  $Q_{\text{Sn}} = 86.14$  kJ/mol,  $A_{\text{Cu}} = 2.12 \times 10^{-6}$  m<sup>2</sup>/s, and  $A_{\text{Sn}} = 2.49 \times 10^{-6}$  m<sup>2</sup>/s. The interdiffusion coefficient in  $\text{Cu}_3\text{Sn}$  can then be calculated from the following equation [26],

$$D_{\text{inter}} = X_{\text{Cu}}D_{\text{Sn}} + X_{\text{Sn}}D_{\text{Cu}}, \quad (4)$$

where  $X_{\text{Cu}} = 0.75$  and  $X_{\text{Sn}} = 0.25$  are the mole fractions of Cu and Sn in  $\text{Cu}_3\text{Sn}$ , respectively. Table 3 shows the comparison between our MD results and those from the open literature. It is seen that our MD results of interdiffusion fall in the range of the very limited set of experimental data available in the literature. However, it is also noteworthy that Chao et al. suggest Sn diffuses faster than Cu at annealing temperature (423 K) [26], while our results show that Cu should be the dominant diffusion species.

### 3. Conclusions

In summary, our MD results show that the diffusion activation energy for Cu in  $\text{Cu}_3\text{Sn}$  is about 10% lower than that for Sn. As a result, Cu in  $\text{Cu}_3\text{Sn}$  diffuses 17 times faster at 300 K and 7 times faster at 423 K than Sn does at the same temperatures. Consequently, one may conclude that Cu is the dominant diffusion species in forming the  $\text{Cu}_3\text{Sn}$  IMC layer in the solder joint during annealing (423 K).

Table 3  
Diffusivity of Cu and Sn in  $\text{Cu}_3\text{Sn}$  at room and annealing temperatures.

		$A$ (m <sup>2</sup> /s)	$Q$ (kJ/mol)	$D$ (300 K) (m <sup>2</sup> /s)	$D$ (423 K) (m <sup>2</sup> /s)
Cu in $\text{Cu}_3\text{Sn}$	This work	$2.12 \times 10^{-6}$	78.63	$4.32 \times 10^{-20}$	$4.13 \times 10^{-16}$
	Ref. [26]	–	–	–	$3.67 \times 10^{-17}$
Sn in $\text{Cu}_3\text{Sn}$	This work	$2.49 \times 10^{-6}$	86.14	$2.49 \times 10^{-21}$	$5.73 \times 10^{-17}$
	Ref. [26]	–	–	–	$2.35 \times 10^{-16}$
Interdiffusion	This work	$2.27 \times 10^{-6}$	83.33	$1.27 \times 10^{-20}$	$1.46 \times 10^{-16}$
	Ref. [27]	$1.43 \times 10^{-8}$	70.60	$6.63 \times 10^{-21}$	$2.87 \times 10^{-17}$
	Ref. [7]	$3.20 \times 10^{-6}$	83.91	$7.01 \times 10^{-21}$	$1.47 \times 10^{-16}$
	Ref. [8]	$8.08 \times 10^{-7}$	81.60	$4.48 \times 10^{-21}$	$7.15 \times 10^{-17}$
	Ref. [6]	$5.49 \times 10^{-9}$	61.86	$8.54 \times 10^{-20}$	$1.31 \times 10^{-16}$
	Ref. [26]	–	–	–	$1.87 \times 10^{-16}$

The new data presented in this paper is anticipated to provide insightful information for the growth of  $\text{Cu}_3\text{Sn}$  IMC and the formation of Kirkendall voids.

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