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Effects of alloying elements on the dissolution and diffusion of Bi in Sn: A first-principles study

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Abstract. Interfacial Bi segregation in Sn-based solders is a critical issue that affects the reliability of solder joints. Doping alloying elements into Sn-Bi solders is considered as a potential way to improve the Bi precipitation. We provided insights into the mechanism of Bi segregation at the atomic scale, by calculating the dissolution and diffusion energies of Bi in the Sn bulk. Importantly, we investigated the effects of alloying elements on the Bi dissolution and diffusion, which varies much with element species. The addition of elements such as Pt, Pd, and Au could enhance the dissolution and weaken the diffusion of Bi in the Sn bulk, thus suppressing the interfacial Bi segregation to some extent. However, other elements such as In, Ag, Sb, and Ga have slight impacts on the dissolution and diffusion of Bi. The bonding characters between the third elements, Bi, and Sn atoms explain different influences of alloying elements on Bi segregation in Sn-based solders.

1. Introduction

Sn-Pb solders were widely employed as micro-nano interconnect materials in electronic packaging, due to low production cost, suitable operating temperature and good mechanical properties [1]. However, the long-term use of toxic lead elements will endanger human health and pollute the environment [2,3]. Hence, numerous research efforts have been devoted to achieve lead-free in solders by fabricating various types of Sn-X alloys [4]. Sn-Bi solders are one of the most promising candidates for replacing traditional Sn-Pb solders, because they have good wettability, high tensile strength, and low melting point particularly [5].

Since Bi is brittle in nature, the formation of Bi-rich phases at the interface will have an adverse effect on the mechanical properties of Sn-Bi solders [6,7], reducing the tensile strength and plasticity. In order to improve the interfacial Bi precipitation, alloying elements with minor amounts were added into Sn-Bi solders to refine the microstructure and the mechanical property [8]. It was reported that the addition of In [4], Ag [9], Sb [10], Ni [6], Al [6], Zn [11], and Cu [11] could increase the tensile strength of Sn-Bi solders. However, the impacts of alloying elements vary with element species and doping concentrations [5,12]. It is thus desirable to unravel the explicit effects of the third elements on Bi coarsening in Sn-based solders.

Atomic calculations based on density functional theory (DFT) are widely applied in predicting the properties of materials and revealing the underlying microscopic mechanism. In this paper, we employed first-principles methods in the framework of DFT to study the influence of alloying elements M (Pt, Pd,



Au, In, Ag, Sb, Ga, Al, Cu) on the dissolution and diffusion behavior of Bi in Sn, which is related with the interfacial Bi segregation at the atomic scale. We computed the dissolution energies and diffusion energy barriers of Bi with the presence of the third elements M. Then, we discussed the bonding interactions between M, Bi and Sn atoms to reveal the essential reason for different impacts of M on the Bi segregation. Based on the results, we screen out several alloying elements that show positive effects to suppress the Bi segregation from the Sn bulk towards the surface.

2. Computational details

We employed the projector-augmented wave (PAW) [13] method with spin-polarization as implemented in the Vienna ab initio simulation package (VASP) code [14,15]. The electron exchange and correlation was treated using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form [16]. The energy cutoff for the plane wave basis was set to 420 eV. β -Sn adopts a body-centered-tetragonal (b.c.t) structure (see Fig. 1a), and is experimentally stable at temperatures above 286 K [17]. The calculated lattice constants are $a = 5.93 \text{ \AA}$ and $c = 3.22 \text{ \AA}$, which are in agreement with experimental values [18] and previous first-principles calculations [19]. We constructed a $(2 \times 2 \times 4)$ supercell of β -Sn with 64 atoms to simulate the interactions between M atom and Bi. A $(3 \times 3 \times 3)$ k-point mesh generated by the Monkhorst-Pack method was used to sample the Brillouin zone. The atom positions were fully relaxed until the force on each atom was less than $0.01 \text{ eV/\AA}$.

The dissolution energy of the doped atom M in the Sn bulk is defined as

$$E^{\text{sol}}(\text{M}) = E_{\text{tot}}(\text{Sn}_{\text{bulk}} + \text{M}) - E_{\text{tot}}(\text{Sn}_{\text{bulk}}) - \sum_i n_i \mu_i \quad (1)$$

where $E_{\text{tot}}(\text{Sn}_{\text{bulk}} + \text{M})$ is the total energy of Sn supercell with a doped atom M, and $E_{\text{tot}}(\text{Sn}_{\text{bulk}})$ is the total energy of the same Sn supercell. μ_i is the chemical potential of the doped atom which is referenced to the energy of Mi bulk per atom. n_i is the number of Mi that have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell.

3. Results and discussions

3.1. Influence of M atom on Bi dissolution

When Bi dissolving in the Sn bulk, it prefers to substitute one Sn atom in the bulk. The dissolution energy of Bi is calculated using Eq. (1), which is 0.16 eV . The positive value suggests that the Bi dissolution in Sn is an endothermic process. The alloying elements M doped in the Sn bulk also favour the substitutional sites. The calculated dissolution energies of M atoms (Ag, Au, Pt, Pd, In, Sb, Al, Cu, Ga) are shown in Table 1. We find that the dissolution energies vary much with element species. For Pd, Pt, and Au, the dissolution energies are negative which are in the range of $-0.86 \sim -0.43 \text{ eV}$, indicating that they can very easily be added into Sn as solute atoms. Elements such as Ag, In, Sb, and Ga have dissolution energies around 0 eV . This suggests that these alloying elements can be doped in Sn without much energy gain or energy loss. While, the dissolution energies of Cu and Al are more positive compared with other elements.

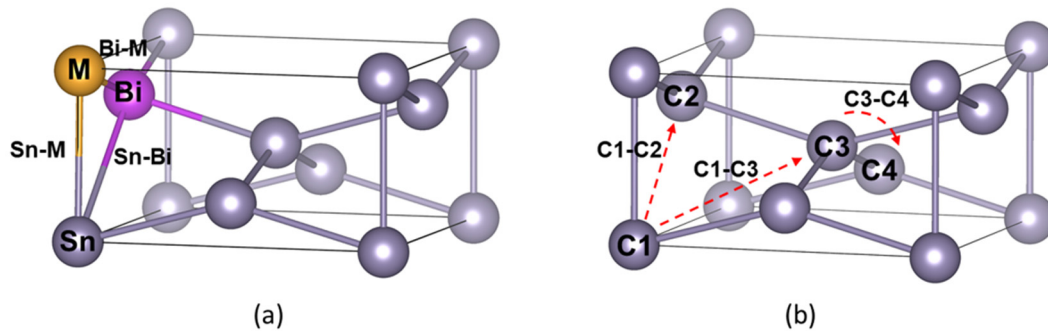


Figure 1. (a) Atomic structure of β -Sn with the addition of Bi and M atom. (b) Diffusion paths of Bi from one Sn lattice site to the neighbouring vacant site. The purple sphere represents the Bi atom, the yellow sphere shows the M atom, and the other spheres represent the bulk Sn atoms.

Table 1. Dissolution energies [$E^{\text{sol}}(\text{M})$] of M atoms in the Sn bulk.

Add element	Pt	Pd	Au	In	Sb	Ag	Ga	Al	Cu
$E^{\text{sol}}(\text{M})$ (eV)	-0.86	-0.72	-0.43	-0.05	0.07	0.02	0.01	0.19	0.48

We then place the alloying elements at the nearest-neighbouring site of Bi in the Sn bulk to explore their impacts on the Bi dissolution, as shown in Fig. 1(a). We computed the dissolution energies of Bi with the presence of M atom and displayed the results in Fig. 2. The changes in Bi dissolution energies are different with different elements. The addition of Pt, Pd, and Au leads to a great decrease of Bi dissolution energy which changes from 0.16 eV to -0.86 eV, -0.72 eV, -0.43 eV, respectively. The results show that the dissolution of Bi in the Sn bulk becomes more energetically favourable when Pt, Pd, and Au is doped. The enhanced dissolution of Bi in the Sn bulk may reduce the tendency of Bi segregation towards the surface. On the other hand, the Bi dissolution energies remain nearly unchanged with the addition of Ag, In, Sb, and Ga. When Cu and Al is doped in Sn, however, the dissolution of Bi becomes more unstable with a dissolution energy of 0.45 eV and 0.34 eV, respectively.

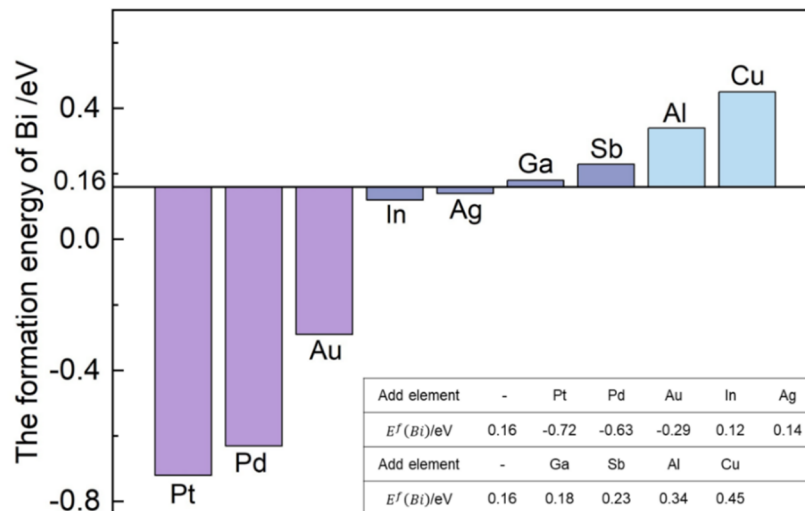


Figure 2. Formation energies of Bi in the Sn bulk with the presence of M atoms.

3.2. Influence of M on Bi diffusion

Kinetically, the segregation of Bi would be affected by the diffusion of Bi. We thus computed the diffusion barriers of Bi in the Sn bulk for the diffusion paths shown in Fig. 1(b), using the climbing-image nudge elastic band (CI-NEB) method [20]. Since Bi prefers the substitutional site in Sn, the diffusion of Bi follows the vacancy mechanism. Bi would jump from one Sn lattice site (e.g., C1 site in

Fig. 1b) to another neighbouring vacant site (e.g., C2 site), leaving C1 site as a vacancy. The diffusion energies as a function of reaction coordinate of Bi along the diffusion paths of C1–C2, C1–C3, and C3–C4 are shown in Fig. 3. We find that the diffusion energy barrier of Bi is related with the distance between initial and final states and the motion trajectory. The Bi diffusion along the C1–C3 path has the highest energy barrier of 0.44 eV with a maximum distance of 4.50 Å. For diffusion paths of C1–C2 and C3–C4, the energy barriers of Bi diffusion are 0.10 eV and 0.17 eV, respectively. It is noted that the C1–C2 diffusion path with a distance of 3.83 Å has a lower energy barrier than that of the C3–C4 path, of which the distance is 3.07 Å. This should be ascribed to different jumping trajectory of Bi along the diffusion path. Namely, the Bi diffusion along the C1–C2 path is a linear way, while the C3–C4 diffusion path is zigzag, as shown in the left insets in Fig. 3(a) and (c).

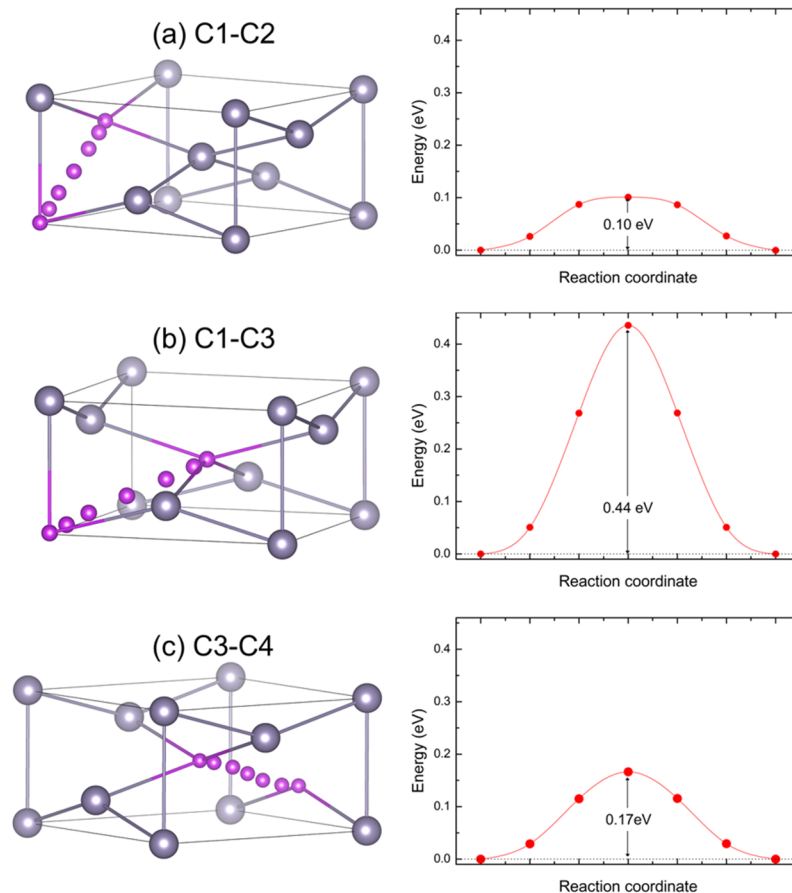


Figure 3. Migration profiles and energy barriers for Bi diffusion along routes C1–C2, C1–C3, and C3–C4 in the Sn bulk. The atomic configurations of Sn bulk are shown in the insets on the left, and the small purple spheres represent each positions of Bi atom along the diffusion path.

Next, we evaluate the influence of alloying elements on the diffusion behavior of Bi. We choose the C1–C2 diffusion path with the lowest energy barrier as the research object, and place the M atom at the neighboring site of C1 and C2 (see Fig. 1a). Since the Bi diffusion follows the vacancy mechanism, the activation energy for Bi diffusion is the sum of the energy barrier and the vacancy formation energy. Considering the vacancy formation energy as 0.62 eV in Sn, the activation energy for Bi diffusion along the C1–C2 path is 0.72 eV. With the presence of Pt, Pd, Au, In, Sb, Ag, and Cu, the activation energies of Bi are changed to 1.02 eV, 0.93 eV, 0.80 eV, 0.78 eV, 0.75 eV, 0.73 eV, and 0.90 eV, respectively. The increase of energy barrier suggests that the Bi diffusion would be limited with the presence of M atoms. Therefore, according to our calculations, the addition of Au, Pd, Pt, and Cu could restrict the Bi diffusion process in the Sn bulk.

3.3. Interactions between M and Bi

We have revealed the influences of alloying elements on the dissolution and diffusion behaviors of Bi in the Sn bulk in above discussions. Different M atoms play different roles in changing the solution energy and diffusion energy barrier of Bi. In this section, we analyzed the bonding characters between M, Bi, and Sn atoms to reveal the essential reasons for different impacts of alloying elements on the Bi segregation. We employed the density derived electrostatic and chemical (DDEC6) method implemented in the CHARGEMOL program [21,22] to calculate the bonding strengths between Bi-M, Sn-M, and Sn-Bi bonds, as marked in Fig. 1(a). The results of calculated bond orders are listed in Table 2. Compared with the Sn-Bi bond order of 0.09 without the M atom, the bond strength is obviously increased with the addition of Pt, Pd, and Au. Moreover, the bond orders of Bi-M and Sn-M bonds are increased for the cases of Pt, Pd, and Au. This indicates that the bonding interaction between Bi, Sn, and M atoms in the system is enhanced when doping elements such as Pt, Pd, and Au. This should also explain the decrease of dissolution energy and the increase of diffusion energy barrier of Bi in Sn with the presence of Pt, Pd, Au in the above sections. Therefore, we could conclude that the interfacial Bi segregation in Sn solders would be suppressed to some extent when doping with Pt, Pd, Au. For elements such as In, Ag, Sb, etc., which shows tiny effects on the Bi dissolution and diffusion in Sn, the bond orders of Sn-Bi, Bi-M, and Sn-M bonds are also slightly been changed. According to our calculations, the addition of Cu makes the Bi dissolution in Sn more difficult with an increased dissolution energy, but shows a positive effect in holding back the diffusion of Bi. The bond order analysis shows that the Sn-Bi bond is apparently increased with the presence of Cu. However, the bond orders of Sn-Cu and Bi-Cu are decreased compared with the corresponding Sn-Bi bonds, leading to the unchanged sum of bond orders. Hence, the exact impact of Cu on the Bi segregation needs further exploration.

Table 2. Bond orders of different bonds between Sn-Bi, Bi-M, and Sn-M.

Element		Sn	Pt	Pd	Au	In	Sb	Ag	Ga	Al	Cu
Bond order	Sn-Bi	0.09	0.17	0.17	0.15	0.11	0.10	0.14	0.12	0.12	0.19
	Bi-M	0.46	0.61	0.49	0.45	0.42	0.44	0.39	0.43	0.49	0.42
	Sn-M	0.35	0.56	0.43	0.39	0.29	0.33	0.32	0.26	0.28	0.32

4. Conclusions

We have performed first-principles calculations on the effects of alloying elements M (Pt, Pd, Au, In, Sb, Ag, Ga, Al, and Cu) on the dissolution and diffusion of Bi in the Sn bulk. By calculating the dissolution energy and diffusion energy barrier of Bi in Sn with the presence of M atoms, we find that different M atoms play different roles in changing the energetics. When adding Pt, Pd, and Au into the Sn bulk, both the dissolution energy and diffusion energy barrier of Bi were increased. This indicates that these elements would have positive effects in suppressing the interfacial Bi segregation in Sn. Our bond order analysis shows that the enhanced bond strength between M, Bi, and Sn atoms is the essential reason for this result. While, the dissolution and diffusion behavior of Bi in Sn has been only slightly changed in the presence of In, Sb, Ag, Ga, and Al. Our studies would provide a theoretical reference for the design of Sn-Bi solders with minor addition of alloying elements to improve the Bi-rich phase coarsening.

Acknowledgments

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