

First-principles investigation of the structural stability and electronic properties of Pd doped monoclinic Cu₆Sn₅ intermetallic compounds

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Tri-layer Au/Pd/Ni(P) films have been widely used as surface finish over the Cu pads in high-end packaging applications. It was found that a thin $(Cu,Pd)_6Sn_5$ IMC layer was beneficial in effective reducing inter-diffusion between a Cu substrate and a solder, and therefore the growth of the IMC layer and the EM (electromigration) processes. In this study, the structural properties and phase stability of monoclinic Cu₆Sn₅-based structures with Pd substitutions were studied by using the first-principles method. The (Cu,Pd)₆Sn₅ structure with the 4e site substituted by Pd has the lowest heat of formation and is the most stable among (Cu,Pd)₆Sn₅ structures. Hybridization of Pd-d and Sn-p states is a dominant factor for stability improvement. Moreover, Pd atoms concentration corresponding to the most stable structure of (Cu,Pd)₆Sn₅ was found to be 1.69 %, which is consistent with the experimental results.

Keywords: intermetallic compounds (IMC); thermal stability; site occupancy; ab-initio calculations

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1. Introduction

Recently, tri-layer Au/Pd/Ni(P) films have been widely used as surface finish over the Cu pads in high-end packaging applications [1–3]. In comparison with the Au/Ni(P) bi-layer, the additional Pd layer can protect Ni(P) metallization against Auinduced galvanic hyper-corrosion that gives rise to the concern of "black pads" [4]. In case, when SnAgCu solder joint is formed on an electroless Ni/electroless Pd/immersion Au substrate, Pd layer quickly dissolves into the solder matrix after reflow, which reduces the growth of intermetallic compounds [5].

It is known that material performance could be improved by doping [6]. There are many studies on the effect of Pd addition on the reliability and interfacial reactions [7]. It has been found that a thin $(Cu,Pd)_6Sn_5$ IMC layer is beneficial in effective reducing inter-diffusion between a Cu substrate and the solder, and, consequently, in the growth of the IMC layer and the EM (electromigration) processes [8]. Regarding the structure of the Cu–Pd–Sn IMC many researchers have found that the $(Cu,Pd)_6Sn_5$ has a similar crystal structure as Cu₆Sn₅ [7, 8], in which Pd atoms occupy the Cu atom sub-lattice. However, the role of Pd in $(Cu,Pd)_6Sn_5$ IMC has not been fully understood up to now. Works in this area include atomiclevel simulations based on density-functional theory (DFT) to study the effects of Zn or Co substitution on the properties of Cu₆Sn₅ [9–11]. Few works have been reported on the (Cu,Pd)₆Sn₅ phase.

Atomistic modeling based on the DFT and approximation conditions consider interactions between core and core, core and electron, and electron and electron, which are usually used to investigate the effects of dopants on the properties

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of IMCs [12] and can also be employed to assess the role of Pd in $(Cu,Pd)_6Sn_5$ IMC. In addition, a lower Pd concentration (around 1.68 at.%) in the $(Cu,Pd)_6Sn_5$ has been found in experimental works [7, 8], but it has not been studied theoretically. This paper is devoted to address these issues by exploring the thermodynamic and electronic structure properties of $(Cu,Pd)_6Sn_5$.

2. Model and methods

First-principles calculations were carried out by using CASTEP software [13]. The software used the plane-wave pseudopotential method and performed energy minimization by the BFGS (Broyden-Fletcher-Goldfarb-Shanno) method [14]. The generalized gradient approximation (GGA) functional, presented by Perdew and Wang [15], was employed to deal with the exchange correlation. The ultrasoft pseudopotential (USP) scheme devised by Vanderbilt [16] was used. The pseudoatomic calculation was conducted for the following electron configurations: 4d10 of Pd, 3d104s1 of Cu, and 5s25p2 of Sn.

The Brillouin-zone integrations were performed using a Monkhorst-Pack grid of special k-point meshes [17], and electronic occupancies were determined according to the Methfessel Paxton scheme with a 0.1 eV energy smearing. The energy cutoff was set as 330 eV, and the k-points set was $7 \times 7 \times 5$. The energy of the Cu₆Sn₅-based crystal structure was minimized with respect to the lattice constants and the interior degree of freedom. Convergence was considered to be achieved when the following conditions were met simultaneously: energy change below 5×10^{-6} eV/atom, force less than 0.01 eV/Å, stress less than 0.02 GPa, and displacement change less than 5×10^{-4} Å.

The experimental crystal structure of η '-Cu₆Sn₅ [18] was used as an initial model. The Cu₆Sn₅ intermetallic compound crystallizes in the monoclinic structure (space group C2/c, no. 15) with the cell parameters of a = 11.022, b = 7.282, c = 9.827 Å and β = 98.84°. Cu atoms occupy different sites in the Cu₆Sn₅ compound, that is four atoms occupy two different 8f sites, and the other two occupy 4a and 4e sites, respectively. For $(Cu,Pd)_6Sn_5$ phases, the additions can be either interstitial or substitutional in nature. There is no data about the specific structure of $(Cu,Pd)_6Sn_5$. It is known that the IMC has a similar crystal structure to that of Cu_6Sn_5 . It was assumed that Pd atoms substitute for Cu at different sites. It could be compared to the heats of formation of four kinds of structures, in which Pd atoms replace 8f1, 8f2, 4a, or 4e sites of Cu, respectively. To increase the calculation rate, a primitive cell-based supercell structure containing 22, 44, 88 and 176 atoms was established.

3. Results and discussions

3.1. Heats of formation

As presented in Table 1, all the CuPdSn ternary IMCs showed a more negative heat of formation than Cu₆Sn₅ did in this work. It indicated that the doped Pd would thermodynamically stabilize monoclinic Cu₆Sn₅. As aforementioned, in case, where SnAgCu solder joint was formed on electroless Ni/electroless Pd/immersion Au substrate, Pd layer quickly dissolved into the solder matrix after reflow, and $(Cu,Pd)_6Sn_5$ IMC appeared [7, 8], which indicated that (Cu, Pd)₆Sn₅ was more stable than pure Cu₆Sn₅ at the same condition. Moreover, it could be found that Pd with different occupancy sites in the Cu₆Sn₅ showed different effects on the phase stability. According to the heats of formation, it could be concluded that the Pd atom preferentially occupied the 4e site.

3.2. Electronic structures

To further understand the mechanisms, the electronic properties of Cu_6Sn_5 and $(Cu_{0.98},Pd_{0.02})_6Sn_5$ were analyzed based on partial density of states (PDOS). The density of states (DOS) for a system describes the number of states at each energy level, which are available to be occupied in the condensed matter physics. A high DOS at a specific energy level means that there are many states available for occupation. As shown in the Fig. 1a and 1b, the main difference is the bonding peaks between -5.95 eV and -2.84 eV. For Cu_6Sn_5 , the



Fig. 1. Partial density of states (PDOS) of pure (a) and Pd doped (b) monoclinic Cu₆Sn₅.

PDOS peak is mainly contributed to Cu-d, Sn-p and Sn-s states, i.e. Cu-d, Sn-p, Sn-s and Pd-d states for $(Cu_{0.98},Pd_{0.02})_6Sn_5$ with the 4e substitution. Besides the hybridization of Cu-d and Sn-p states, the new hybridization of Cu-d and Pd-d, Sn-p and Pd-d states appears. The hybridization reduces the energy of exclusion among different atoms, which leads to formation of more stable bonds. This result was consistent with the conclusion obtained from the heats of formation energy.

Table 1. Calculated total energies and the heats of for-
mation for pristine and Pd doped samples.

	Additive	Heat of formation
	occupancy	(eV)
Cu ₆ Sn ₅	_	-28.57
$(Cu_{0.98}, Pd_{0.02})_6Sn_5$	8f1	-29.65
$(Cu_{0.98}, Pd_{0.02})_6Sn$	8f2	-29.68
$(Cu_{0.98}, Pd_{0.02})_6Sn$	4a	-29.33
$(Cu_{0.98}, Pd_{0.02})_6Sn$	4e	-30.10

As aforementioned, the Pd shows different effects on the phase stability depending on its occupancy sites. According to Fig. 1b and Fig. 2a, hybridization of Cu-d and Pd-d, Sn-p and Pd-d states leads to stability improvement for the 4a and 4e substitutions. The amplitude of Pd-d state (indicated by the arrow) at -3.98 eV for the 4e

occupancy is higher than that of the 4a occupancy. Therefore, the hybridization of the Sn-p and the Pdd states for the 4e substitution is stronger than that of the 4a occupancy. Moreover, as shown in Fig. 2b, the bonding electron number of Cu-d state is 279.3 per atom for 4e substitution at -2.89 eV, and 275.1 for 4a substitution. Larger bonding electron numbers correspond to stronger charge interaction [19], causing that the structural stability of an alloy is improved. Hence, (Cu_{0.98},Pd_{0.02})₆Sn₅ with the 4e substitution is more stable than that with the 4a occupancy. The Pd atoms prefer to occupy the 4e position at the same concentration.

3.3. Pd atoms concentration in the monoclinic Cu₆Sn₅

As shown in Fig. 3, the 4e substitution, $(Cu,Pd)_6Sn_5$ with different Pd concentrations corresponds to different heats of formation. The heat of formation decreases at first and then increases with increasing Pd concentration. The decreasing formation energy is the driving force for Pd diffusion into $(Cu,Pd)_6Sn_5$ in the Sn–Cu–Pd alloy. The lowest formation energy corresponds to the maximum Pd solubility in the Sn–Cu–Pd phase diagram. In order to find the proper concentration corresponding to the most stable structure, the plot of formation energy versus Pd concentration was constructed based on the polynomial function in Fig. 3.



Fig. 2. (a) PDOS of Pd doped Cu_6Sn_5 ; (b) Cu-d states of $(Cu_{0.98}, Pd_{0.02})_6Sn_5$ with 4e or 4a substitution.



Fig. 3. Calculated formation energy of $(Cu,Pd)_6Sn_5$ as a function of Pd atoms concentration.

According to the fitting equation, it was stated that the concentration corresponding to the minimum formation energy is 1.69 %, which is close to the concentration of 1.68 % obtained from the experimental work [8].

4. Discussion

The transition from one compound to another is determined by thermodynamics and the possible mechanism is provided in the literature [20]. To gain a better understanding of the transformation of the reaction product in the Cu–Sn–Pd system, one may start from the equilibrium system of all of the relevant elements, i.e. Sn, Cu, and Pd. Unfortunately, the literature review has revealed that there are no available data on this quaternary system. More thermodynamic information on the Cu– Sn–Pd metallurgical system is necessary to verify the above calculated results.

Although there are no well established data related to Pd diffusion in molten solders, a high diffusivity of Pd can be expected because most noble metals (e.g. Ag, Au, Pd) are so-called fast diffusers in solders. When a solder is in a molten state, the diffusivity of such metals can even reach a very high level of approximately 10^{-5} cm²/s [21]. thus, extremely fast resettlement of (Cu,Pd)₆Sn₅ to the interface is obtained. This (Cu, Pd)₆Sn₅ growth mechanism is quite similar to the resettlement of AuSn₄ to the interface [22]. Kinetically, the formation of (Cu,Pd)₆Sn₅ at the interface relies on the diffusion of Pd atoms/ions from solder to the interface, where the Pd reacts with Cu and Sn to form (Cu,Pd)₆Sn₅. The Pd inside the molten solder might exist in the form of Pd atom or (Cu,Pd)₆Sn₅ intermetallic compound, depending on the Pd content.

5. Conclusions

In summary, the influence of Pd doping on the stability of monoclinic Cu₆Sn₅ was investigated

using the first-principles approach. It was found that the phase stability of $(Cu,Pd)_6Sn_5$ could be improved by the Pd doping and the Pd preferentially occupied the 4e site. The hybridization of Pd-d and Sn-p state was the dominant factor for the stability improvement. These results are helpful to explain the mechanism of structure stability improvement of Pd on Cu₆Sn₅. They are also useful for further calculations of the properties of $(Cu,Pd)_6Sn_5$, including the mechanical properties.

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