Electronic Structure Mechanism for the Wettability of Sn-Based Solder Alloys

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The developments of quantum theory, solid-state physics, and computational methods make it feasible to understand properties of materials by means of calculation. In this work, five octahedron clusters were designed to study the wettability of Sn-based solder alloys, which are applied in modern electronic mounting and packaging. Then, relativistic DV-Xα calculation, which is a molecular orbital method based on Hartree-Fock-Dirac approximation, was carried out. Heavy atoms, such as Pb, Bi, Sn, and Sb, were included in our clusters, so relativistic effects were taken into account in the calculation. The electronic parameter, Bo, the orbital interaction between atoms, was obtained through a Mulliken analysis of electronic structure. The electronic structure mechanism for the wettability of Sn-based solder alloys on a Cu substrate was put forward based on the analysis of orbital interactions between atoms. We believe that the wettability of the Sn_xM_y alloy would be improved only if orbital interactions between Sn atoms and Cu atoms are enforced because of the existence of the M element. The spreading and wetting behavior of Sn-based solder alloys were predicted and then explained by this quantum method on the basis of electronic structure theory. Predictions from analysis on calculation results were validated by wettability experiments and energy-dispersive x-ray (EDX) analysis.

Key words: Sn-based solder, quantum theory, relativistic DV-Xα calculation, orbital interaction, wettability, electronic mounting, and packaging

INTRODUCTION

The spreading and wetting behavior of solder are the most foundational issues in soldering. Usually, the following famous Young's equation is extensively used to discuss the wettability of solders:

$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \quad (1)$$

where γ_{SG} is the solid-gas interface tension, γ_{LG} is the liquid-gas interface tension, γ_{SL} is the solid-liquid interface tension, and θ is the contact angle. Obviously, a smaller contact angle means good wettability. However, the spreading and wetting of solder on a substrate is a typical process not completed instantly. It is extremely difficult to accurately measure γ_{SG} and γ_{LG} in this equation. Furthermore, the current data on surface tension and solid-liquid tension may be inaccurate. So the contact angle is not easily calculated through the Young's equation. Sometimes the contact is measured through experimental approaches. But, it is also difficult to get the ideal contact angle, θ. Therefore, it is difficult to use the Young's equation to evaluate the wettability of solder exactly in practice. In view of microscopic interaction, the spreading and wetting behavior of solder should depend on the interaction of atoms in the solder and substrate. In other words, the states of electronic structure formed through the interaction of atoms will essentially result in the spreading and wetting behavior. Consequently, a promising and useful approach to predict spreading and wetting behavior at the atom or electron level is calculating the corresponding electronic states and finding the intrinsic relationships between electronic parameters and properties of solder.

(Received May 30, 2001; Accepted October 18, 2001)

The developments of quantum theory, solid-state physics, and computational methods make it feasible to understand the properties of material by means of calculation. The wettability of Sn-based solder alloys, prominently used material for the mounting and packaging of modern electronic devices over the past several decades, is explained with the electronic structure mechanism in this thesis. Some preliminary but related works, such as research on the spreading and wetting mechanism of solder under a vacuum/controlled atmosphere[1] and the analysis on establishing cluster in calculating the molecular orbital of solder alloys,[2] have been completed. In this work, five octahedron clusters were designed to study the wettability of Sn-based Sn_xM_y (M = Zn, Ag, Cd, In, Sn, Sb, Pb, and Bi) solder alloys on Cu. Then, relativistic DV-Xα calculation, which is a molecular orbital method based on quantum theory, was performed. Relationships between orbital interaction and wettability of Sn-based solder alloys were obtained. With the aid of this atomic approach by means of electronic structure calculation, we believe the wettability of solder alloys can be understood in a fundamental manner.

COMPUTATIONAL METHOD AND CLUSTER MODELS

DV-Xα Cluster Method

The DV-Xα cluster method is a molecular orbital method that can provide fairly accurate electronic structures even for a large size of atom clusters.[3] Usually, a nonrelativistic DV-Xα cluster method is applied in present material design. A nonrelativistic one-electron Hamiltonian is

$$H = p^2 + V(r) \tag{2}$$

where H represents the kinetic energy, V(r) is the potential energy, and $P = -i\hbar\nabla$ is the momentum operator. In the Slater's Xα approximation, the exchange part, V_x, in the potential is described with local electron density, ρ, as follows:

$$V(r) = V_{en}(r) + V_c(r) + V_x(r) \tag{3}$$

$$V_x(r) = -3\alpha\left[\frac{3}{8\pi}\rho(r)\right]^{1/3} \tag{4}$$

where V_x and V_c are the potential operators due to electron-nucleus interactions and Coulomb interactions among the electrons. The parameter, α, is fixed at 0.7.

However, electrons have high velocity near the nuclei of heavy atoms, such as Sb, Pb, and Bi, comparable to lighter elements. Electronic structures for the molecules and clusters containing those heavy atoms should be estimated with the relativistic wave equation. The relativistic effects, such as orbital splitting and energy level shifting, increase abruptly with atomic number. For heavy atoms, such as Sb, Pb, and Bi, relativistic effects are significant in the electronic structure. Therefore, the relativistic DV-Xα cluster method was applied to obtain exact results. In this computational method, the relativistic one-electron Hamiltonian (Dirac Hamiltonian) is[4]

(5)

where c is the velocity of light, and m is the rest mass of an electron. The operators $\hat{\alpha}$ and $\hat{\beta}$ are the Dirac matrices:

$$\hat{\alpha} = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \tag{6}$$

$$\hat{\beta} = \begin{pmatrix} I & o \\ 0 & I \end{pmatrix} \tag{7}$$

where σ is the 2 × 2 Pauli spin matrix, and I is the 2 × 2 unit matrix. The averaged density of up and down spins are used for V_x, which is expressed by the same equation as Eq. 3 in the present work. The molecular wave functions are expanded by symmetry-adapted orbitals.

The self-consistent charge method was used to approximate the self-consistent field for molecules. The present calculations were carried self-consistently until the difference in orbital populations between the initial and final states of the iterations was less than 0.01. The matrix elements of the Hamiltonian and overlap integrals were calculated by the weighted sum of integrant values at discrete sample points; instead of this discrete sampling method, no mathematical restriction is placed for the integration of these matrix elements. Also, in contrast to the SW-Xα method, a muffin-tin potential is not used in the DV-Xα cluster method. The molecular orbitals are constructed by a linear combination of numerically generated atomic orbitals. For an alloying element, M, Cu, or Zn, the atomic orbitals used were 1s-ns (n = 4 for Cu and Zn and n = 5 for Ag and Cd) or 1s-np (n = 5 for In, Sn, and Sb and n = 6 for Pb and Bi). The computational details of relativistic and nonrelativistic DV-Xα methods have been described elsewhere.[5,6]

Cluster Models

The spreading and wetting process of solder is not a simple adsorption but an energy falling process with complex chemical reactions. The solder can spread and wet well on a substrate only if the system energy falls more. Therefore, the wettability of solder can be predicted if the total energy of the system can be calculated with the quantum method. But, in fact, the current quantum computational ability is helpless to accurately complete a calculation with many atoms. However, in the case of Sn-based solder spreading and wetting on Cu, it could be supposed that the total energy of the system would fall if the interaction between Sn and Cu atoms is strengthened because of the presence of the alloying element M. Then, obviously, the wettability of the Sn_xM_y alloy would be improved.

Five octahedron clusters, as shown in Fig. 1, were designed to evaluate the effects of alloying element

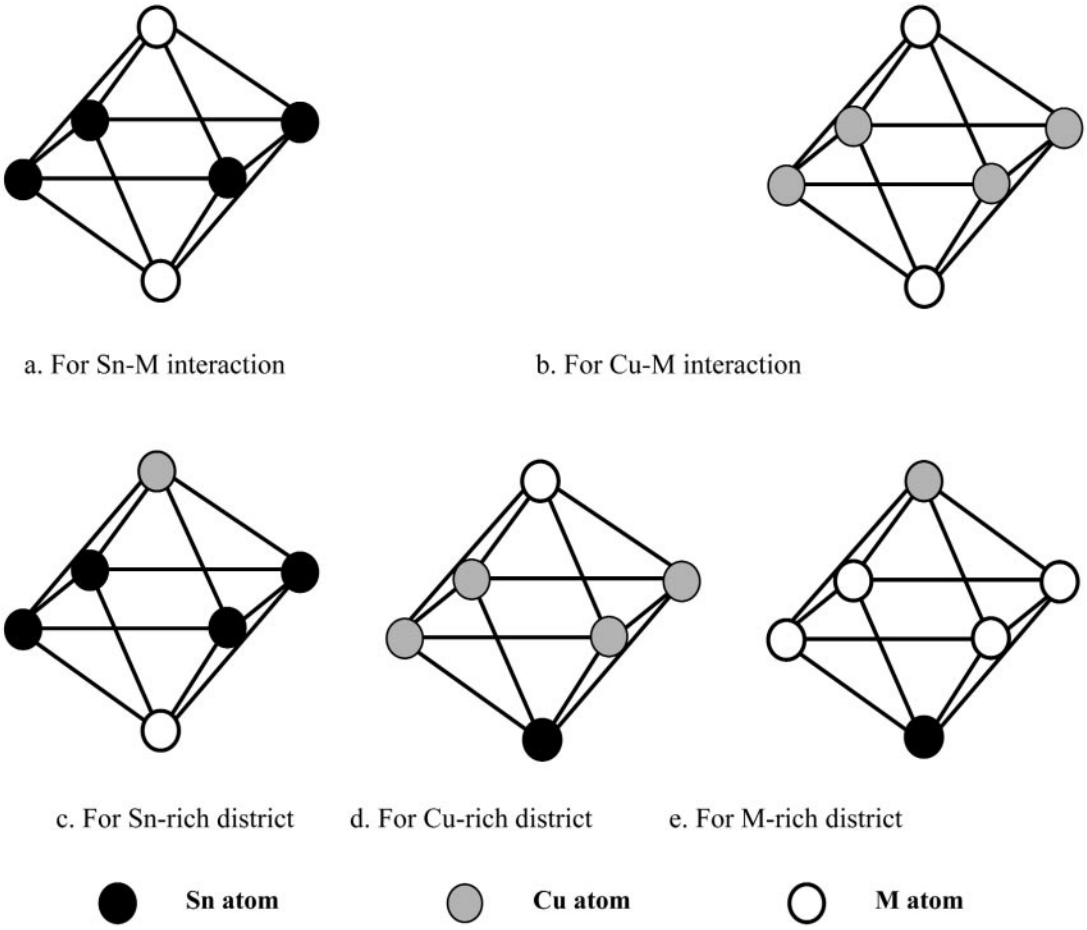

Fig. 1. Octahedron clusters for wettabilities of Sn-based solders: (a) Sn-M interaction, (b) Cu-M interaction, (c) Sn-rich district, (d) Cu-rich district, and (e) M-rich district.

M on the interaction between Sn and Cu atoms and then to understand the wettability of Sn-based solder alloys, which are applied in modern electronic mounting and packaging. They were made up of Sn, Cu (substrate metal atom), and M (M = Zn, Ag, Cd, In, Sn, Sb, Pb, and Bi) elements. In order to meet the need of Mulliken analysis after calculation, the C2V group was applied in all input files for electronic structure calculation.

RESULTS

In the Mulliken analysis of electronic structure, the overlap population of electrons between two atoms V and U is defined as follows:

$$BO = \sum_{l} \sum_{i,j} C_{il}^{V} C_{jl}^{U} \int \psi_i^V \psi_j^U dv \quad (8)$$

Here, Ψ_i^V and Ψ_j^U are the wave functions of the i and j orbitals of atoms V and U, respectively. C_{il}^V and C_{jl}^U are the coefficients that show the magnitude of the linear combination of atomic orbitals in the lth molecular orbital. The sum over l runs only over the occupied orbitals. The term Bo is the orbital interaction between atoms. For alloy, $\overline{Bo}$ (the average value of Bo) is defined as

$$\overline{Bo} = \sum_i x_i Bo_i \quad (9)$$

where Bo_i is the Bo value for component I, and x_i is the mole fraction of component i in the alloy. The calculated results are listed in Table I.

ORBITAL INTERACTION AND WETTABILITY

The presence of alloying atom M will change the orbital interaction between atoms. As discussed previously, the wettability depends on the change of orbital interaction between atoms. That is, the wetting on Cu of Sn-based solder occurs only if the orbital interaction between the Sn atom and the Cu (substrate) atom is increased because of alloying atom M. The data used to analyze the orbital interaction between atoms are shown in Table I.

Sn/Pb, Sn/Bi, Sn/Ag, and Sn/In Solder Alloys

The orbital interaction between Pb and Cu atoms is quite weak. In contrast, the interaction between Pb and Sn atoms is strong. So, in the interface district for solder spreading on the Cu substrate, there will be only intensive interaction between Sn and Cu. No atom but Sn and Cu exists in the narrow district of the interface. However, the orbital interac-

Table I. Orbital Interactions between Atoms in Octahedron Clusters

Model	β_o	M							
		Sn	Pb	Bi	Ag	In	Sb	Cd	Zn
Sn-M cluster	M-Sn	0.522	0.574	0.460	0.542	0.532	0.507	0.521	0.701
	Sn-Sn	0.522	0.646	0.495	0.561	0.538	0.441	0.447	0.453
Cu-M cluster	M-Cu	0.617	0.452	0.540	0.480	0.636	0.738	0.672	0.657
	Cu-Cu	0.572	0.721	0.648	0.693	0.411	0.471	0.565	0.568
Sn-rich district	M-Sn	0.558	0.518	0.550	0.508	0.402	0.567	0.680	—
	Sn-Cu	0.578	0.615	0.607	0.601	0.584	0.563	0.546	—
	Sn-Sn	0.554	0.600	0.518	0.528	0.524	0.501	0.686	—
Cu-rich district	M-Cu	0.617	—	—	—	0.441	0.646	0.384	—
	Sn-Cu	0.617	—	—	—	0.622	0.610	0.602	—
	Cu-Cu	0.572	—	—	—	0.648	0.530	0.643	—
M-rich district	Cu-M	0.617	—	—	—	0.564	0.518	0.587	0.580
	Sn-M	0.617	—	—	—	0.484	0.505	0.457	0.467
	M-M	0.572	—	—	—	0.279	0.344	0.229	0.794

tion between Sn and Cu atoms could be increased by 3.02% due to the role of Pb atoms. Consequently, the wettability of the Sn/Pb solder on Cu substrate is better than Sn alone.

In the same way, the orbital interactions of Bi-Cu and Ag-Cu were all weak. Comparatively, those of Bi-Sn and Ag-Sn were much stronger. In the narrow district of the interface, only Sn and Cu coexist for both Sn/Bi and Sn/Ag solder alloys to spread and wet on Cu. Neither Bi nor Ag will appear in the interaction district between solder and substrate. Being similar to Pb, both Bi and Ag increased the orbital interaction between Sn and Cu by 1.68% and 0.67%, respectively. Therefore, it is possible for Sn/Bi and Sn/Ag solder alloys to spread and wet well on Cu.

In this analysis, Sn/Pb solder alloys are predicted to have the best wetting potential, followed by Sn/Bi solder alloys and then Sn/Ag solder alloys.

Differently, In atoms have strong orbital interaction with Sn as well as with Cu. The atoms In, Sn, and Cu will coexist in the interface. But, the orbital interaction between Sn and Cu atoms could also be increased (by 1.01%) due to the presence of In. Accordingly, the wettability of Sn/In solder on the Cu substrate could be ideal even though In atoms have a relatively strong orbital interaction with Cu atoms.

Sn/Sb, Sn/Cd, and Sn/Zn Solder Alloys

The orbital interactions of Sb-Sn and Cd-Sn were all stronger than that of Sn-Sn. Furthermore, the orbital interactions of Sb-Cu and Cd-Cu were also stronger than that of Cu-Cu. Therefore, both Sb and Cd will appear with Sn and Cu in the interaction district between the solder and substrate. Results from calculations of a Sb-rich cluster model and a Cd-rich cluster model showed that the orbital interaction of Sb-Cu was stronger than that of Sb-Sn, and the orbital interaction of Cd-Cu was also stronger than that of Cd-Sn. Therefore, more Sb and Cd will exist in the interfacial district. In addition, the orbital interactions of Sb-Sb and Cd-Cd were the weakest couple in their M-rich clusters, which means there will be neither a real Sb-rich band nor a Cd-rich band in the interfacial district.

Unfortunately, both Sb and Cd could decrease the orbital interaction between Sn and Cu by 1.68% and 3.85%, respectively. Therefore, Sn/Sb and Sn/Cd solder alloys do not spread and wet well on Cu. Moreover, the wetting potential of Sn/Cd solder alloys should be worse than that of Sn/Sb solder alloys.

As shown in Table I, the orbital interaction between the Zn atom and the Cu atom is much stronger than that between Cu atoms. The orbital interaction between the Zn atom and the Sn atom was much stronger than that between Sn atoms as well. Therefore, there must be a Zn element in the interaction district between Sn/Zn solder alloys and the substrate. Results from calculations of the Zn-rich cluster model showed that the orbital interaction between Zn atoms (0.794) was the strongest, the interaction between Zn-Cu (0.580) was next, and the interaction between the Zn atom and the Sn atom (0.467) was the weakest. Therefore, Zn forms a Zn-rich band near the Cu substrate in the solder due to the intensive interaction between Zn atoms, and the strong interaction between Zn and Cu could force Sn far away from the interfacial district so that only Cu and Zn coexist in the interface. Due to the role of Zn, the orbital interaction between the Sn atom and the Cu atom will be seriously weakened; even Sn will not interact with Cu because it is forced to be far away from the interface. The wettability of Sn/Zn solder alloys, inevitably, is very poor. Therefore, it is difficult for this solder to spread and wet well even when the soldering process is carried out with special soldering technology. Other researchers[7] also indicated that the wettability of Sn/Zn solders was quite poor even when the soldering was carried out in a vacuum to avoid oxidation effects.

SPREADING AND WETTING BEHAVIOR OF Sn-BASED SOLDER ALLOYS

Test Method and Material Preparation

The spreading and wetting area of a same mass Sn-based solder is defined as a standard to evaluate wettability. A solder preform of 10 mg forms each solder joint. The Sn-based solder alloys are shown in

Table II. The preparation flow of Cu substrate is as follows:

1. polishing with sand paper to get rid of oxidation film on the Cu surface
2. ultrasonic cleaning in acetone and then ultrasonic cleaning in absolute ethyl alcohol
3. drying and then soldering in an infrared reflow stove

The normal rosin flux was used in the experiment. We tried to perform the wettability experiment without flux but under vacuum surroundings so as to avoid the effect of flux on the wettability. But, some solders, such as Sn/Zn and Sn/Cd, could hardly spread and wet on Cu because they were impeded by the rapid oxidation. The wettability difference among those solders can hardly be distinguished evidently. So, finally, the normal rosin flux was used in the experiments for all Sn-based solder alloys.

Energy-Dispersive X-ray Analysis and Wettability Experiment

Element distribution was examined by energy-dispersive x-ray (EDX) analysis. For Sn/Pb solder, Sn/Bi solder, and Sn/Ag solder, there were only Sn and Cu in the narrow district of interface; alloying elements Pb, Bi, and Ag did not appear at all. For Sn/In solder, Sn/Sb solder, and Sn/Cd solder, alloying elements In, Sb, and Cd coexisted with Sn and Cu in the interfacial district. However, for Sn/Zn solder, Zn gathered in the solder near the Cu substrate; only Cu and Zn were found in the interfacial district. The experimental results were consistent with predictions from electronic structure calculations. The details of the EDX analysis are shown elsewhere.[8]

Results of wettability experiments are shown in Table II. The wettability of Sn/Pb solder alloys was obviously better than that of pure Sn. The Pb enforced the orbital interaction between the Sn atom and the Cu atom and extremely improved the spreading and wetting on the Cu substrate. The wettability of eutectic Sn/Pb solder is the most excellent among all Sn/Pb solder alloys.

The wettability of Sn/Ag solder was better than that of pure Sn as well, which confirms the predicted results.

The wettability of Sn/Bi solder alloys was better than that of pure Sn. The Bi can improve the spreading and wetting on the Cu substrate. Moreover, the wettability of Sn/Bi solder depends on the quantity of Bi in the alloy. The solder could spread and wet best if there were 10at.%Bi in the solder. Above 10%, the wettability decreased with the increase of Bi quantity. When the quantity of Bi reached 30 at.%, the wettability was nearly the same as that of pure Sn. Finally, the wettability of eutectic solder (Sn-43at.%Bi) was worse than that of pure Sn, similar to that predicted. If there is a high level of Bi in the Sn/Bi alloy, Sn will no longer play the important role of base metal. Regarding Bi, the orbital interaction between the Bi atom and the Cu atom is not strong. Therefore, the wettability is worse with increasing levels of Bi.

The wettability of Sn/In solder alloys was also better than that of pure Sn. The result agrees well with what has been predicted through calculation.

The wettability of Sn/Sb solder alloys, Sn/Cd solder alloys, and Sn/Zn solder alloys are all poor. The wettability of the Sn/Zn solder alloy is so bad that it could not spread and wet well on Cu at all, even though the soldering process was performed in vacuum or inert atmosphere to reduce the effect of rapid oxidation on spreading and wetting.

As shown in Figs. 2 and 3, if the Sn-Cu orbital interaction is increased due to the presence of the M element in the alloy, the spreading area of the Sn-based solder could be larger. For Sn/M solder, the increased percentage of Sn-Cu orbital interaction, Bo_{In}, is defined as

$$Bo_{In} = \frac{Bo_{Sn/M} - Bo_{Sn}}{Bo_{Sn}} \times 100\% \qquad (10)$$

There is a good linear relationship between the increased percentage of the Sn-Cu orbital interaction and the spreading area of the Sn-based solder.

Table II. Wetting and Spreading of Sn-Based Binary Solder Alloys on the Cu Substrate

Solder System	Composition (at.%)	Wetting Area (mm^2)	Liquid Temperature (°C)	Solder System	Composition (at.%)	Wetting Area (mm^2)	Liquid Temperature (°C)
Sn/Pb	Sn-8Pb	7.403	214	Sn/Bi	Sn-10Bi	8.388	212.5
	Sn-16Pb	8.986	195		Sn-20Bi	8.360	195
	Sn-26.1Pb	10.617	183		Sn-30Bi	6.286	168
Sn/Ag	Sn-3.8Ag	6.345	221		Sn-43Bi	5.004	139
	Sn-10In	6.413	213	Sn/Cd	Sn-10Cd	3.904	212.5
	Sn-20In	6.450	194		Sn-20Cd	4.090	187.5
	Sn-30In	6.795	172		Sn-33.45Cd	3.939	176
	Sn-40In	6.707	146	Sn/Zn	Sn-14.9Zn	2.709	198.5
	Sn-50In	6.703	120		Sn-8Zn	2.979	207
Pure Sn	Sn	6.057	232	Sn/Sb	Sn-6.5Sb	5.859	250

Solder mass: 10 mg per point.
Soldering temperature: 40°C above liquid temperature of solder.

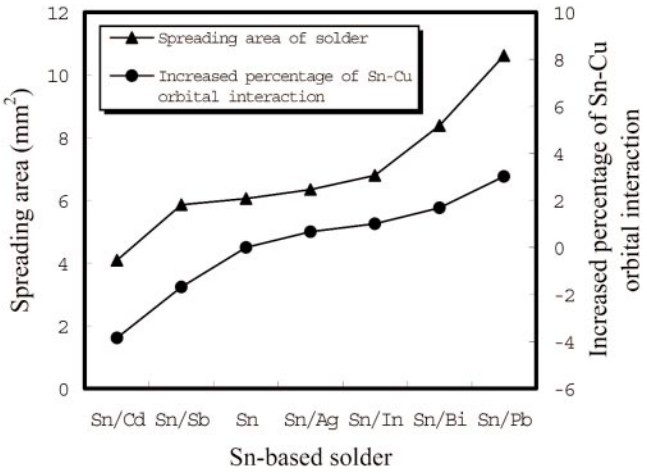

Fig. 2. Spreading area of Sn-based solders and Sn-Cu orbital interaction.

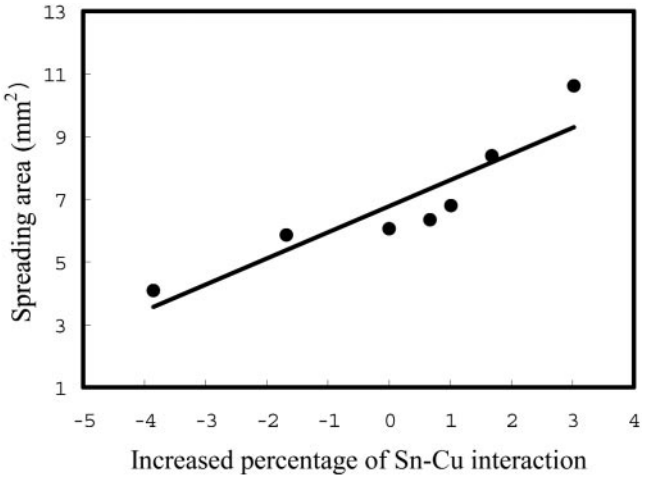

Fig. 3. Relationship between spreading area of Sn-based solders and Sn-Cu interaction.

CONCLUSIONS

Five octahedron clusters were designed to understand the wettability of Sn-based solder alloys, which are applied in modern electronic mounting and packaging. Heavy atoms, such as Pb, Bi, Sn, and Sb, were included in the clusters so relativistic effects must be taken into account in the calculation in order to obtain exact results.

The parameter Bo was obtained through relativistic DV-Xα calculation and Mulliken analysis. Then, the electronic structure mechanism for the wettability of Sn-based solder alloys on Cu substrate was put forward based on the analysis of orbital interactions between atoms. It is believed that the wettability of Sn_xM_y alloy would be improved only if orbital interactions between Sn atoms and Cu atoms were enforced because of the presence of the M element. Predictions from analysis on calculation results were validated by both spreading and wetting behavior experiments and EDX analysis.

ACKNOWLEDGEMENTS

The authors express their appreciation to Drs. H. Yukawa and Yi Liu, Nagoya University of Japan, for their useful help and advice.

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