The Formation of Nano Compounds during Sn/Cu Wetting

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Abstract. When soldering copper-based chips in electronic industry, the growth of tin whisker on Sn/Cu interface under compressive stress was caused by nano-size intermetallic compounds (IMC), Cu_6Sn_5. Reactive wetting process of Cu substrate by pure Sn was observed in an experimental device, and its kinetic mechanism was investigated by performing molecular dynamics calculations. When Sn/Cu wetting was assisted with ultrasonic vibrations, the vertical growth of nano-size Cu_6Sn_5 particles won solid-liquid interface was inhibited, so the occurrence of a new compound Cu_3Sn in ultrasonic wetting which changed the morphology of interface, was beneficial to eliminate tin whisker on Sn/Cu interface.

1. Introduction

Wetting is a fundamental problem in many subjects, it also has some important scientific and technical applications like self-cleaning, bio-surfactant production and soldering. Metal solders substrates are used for soldering. Substrates like Cu plates can be joint together utilizing the wetting behaviors of molten solders like Sn, wets well on Cu. In this process, Sn and Cu have interfacial reactions, forming a compound layer between solid and liquid. Wetting with this kind of dynamic process is named as reactive wetting, and the kinetic is overally governed by the interfacial reaction [1].

Generally, the continuous layer of compound only has a nano-level thickness when wetting ends, but has a significant influence on the mechanical properties of soldering joint. Take a typical reactive wetting system, Sn/Cu, as an example. The electronics industry has relied on Sn to make connections in electronic components, but something problematic is, Sn solders are easy to form whiskers under high wetting temperature, so if temperature is not controlled well in soldering, the formation of tin whiskers between Cu substrates are inevitable. When soldering circuit boards, tin whiskers can electrically connect multiple Cu chips resulting in electrical shorts [2].

It is generally accepted that compressive stress is the driving force of tin whisker growth [3], in Sn/Cu reactive wetting system, the origin of stress may come from IMC growth [4]. This makes it important to investigate on the microstructure of Cu-Sn interface in a wetting process. The component of interfacial products can be analyzed by ED's spectrum, and structure of which can be captured in scanning electron microscope (SEM). However, the kinetic formation of IMC still need researching, Molecular dynamic (MD) method has been widely used to calculate the interaction and motion between nano-size particles. The motion behavior of atoms is described by the classical Newtonian equations of motion, so properties

of compound related with microscopic transport are easier to be tested by MD simulations than experimental methods [5].

2. Experimental Methods

2.1. Test Methods for Sn/Cu Wetting
The spreading of Sn solder on a Cu substrate was first performed in a testing experiment, in which wetting properties like contact angle, spreading area were recorded, test methods all followed the national standard [6], where sessile drop method was used, by placing a small drop on a flat and rigid solid surface, there spontaneously forms a solid-liquid interface if the temperature of solid surface surpass the melting point of the solder material.

2.2. Simulation Model and Method
The simulation model generated the initial configurations of a Sn droplet placed on the (110) miller surface of Cu substrate as follows. Sn hemisphere, containing 9,600 atoms. *Was* cut from a Sn FCC superlattice, with a radius of 5nm. When in relaxations, solder atoms were simulated as in free motion. While a 1nm thick Cu substrate was arranged in a finite slab, the lateral area of slab was 30nm × 30nm. The Cu slab model comprised 96600 atom, two directions (*x* and *y*) had periodic boundary conditions, and three layers in the bottom of Cu slab was kept rigid. Seeing the model in Figure 1.
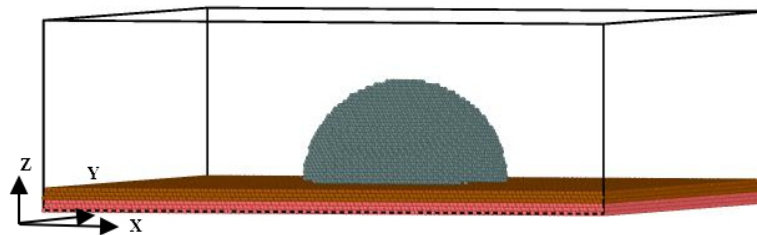

Figure 1. The initial simulation model of Sn/Cu wetting.

Interatomic interactions for Cu-Cu, Sn-Sn and Cu-Sn are represented by the modified embedded-atom method (MEAM), all parameters are listed in Table 1 [7].

Table 1. MEAM potential parameters for Cu and Sn.

Ele-ment	E_C (eV)	$R_0 \times 10^{-10}$ m	$\alpha \times 10^{-5}$ MPa	Structural Parameters									
				A	β_0	β_1	β_2	β_3	t_1	t_2	t_3	C_{min}	C_{max}
Cu	3.54	2.50	5.106	1.077 191.243 240.073 257.682 376.138 367.183	3.62	2.2	6.0	2.2	3.14	2.49	2.95	2.0	2.8
Sn	3.08	3.44	6.20	1.00	6.20	6.0	6.0	6.0	4.50	6.50	-0.18	0.8	2.8
Cu-Sn	3.5	2.68	5.38	-	-	-	-	-	-	-	-	-	-

The diffusion coefficient *D* was essential for describing the trend of Cu, Sn atomic groups diffusing into interfacial layers, *D* was the first-derivative value of mean square displacement (MSD), being a function of time. MSD was listed in output data files when making MD simulations with LAMMPS. So calculation for *D* in each group of Cu/Sn atoms follows (1), where $r_i(0)$ is the initial displacement vector of atom *i*, similarly, $r_i(t)$ is that of simulation time *t*.

$$D = \lim_{t \to \infty} \frac{\text{MSD } (t)}{6t} = \lim_{t \to \infty} \frac{\langle |r_i(t) - r_i(0)|^2 \rangle}{6t} \qquad (1)$$

2.3. Experimental Procedures

The Cu substrate is 30mm × 50mm × 2mm. A well-equipped device was used for observing the spreading of Sn solders, shown in Figure 2, which includes a furnace, a vacuum system, a heating system and an additional ultrasonic-assisted system. Ultrasonic equipment was assembled by a generator, an amplitude and an ultrasonic horn made of titanium alloy. Pure Sn solder was accurately weighed 0.04 + 0.001g, then put on the middle of the substrate surface. When older was melted into a small hemisphere shape, started to time, and observed the wetting process.
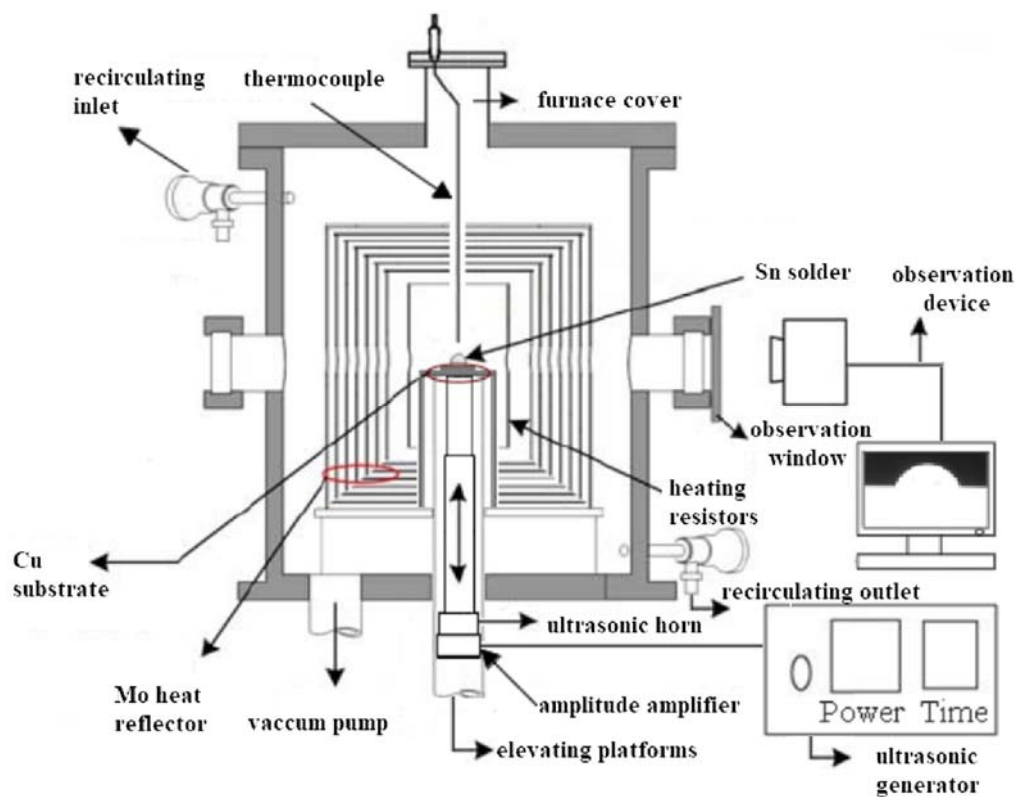

Figure 2. Wetting experimental device equipped with ultrasonic devices.

3. Results and Discussion

The dynamic process of Sn solder spreading on Cu substrate was continuously observed on the display of external equipment. When the temperature inside the furnace reached 250°C, the solder melted and began to spread. After holding the wetting temperature for no more than one minute, the contact angle where the liquid surface intersected the solid surface saturated, which also indicated that spreading area had stopped expanding. When wetting at a higher temperature, the moving rate of solid/liquid contact line was promoted, the time wetting process only lasted for 10 to 20 seconds.

   Figure.3 shows microstructures of the Sn/Cu wetting system at temperature 270°C, with an IMC layer is on solid-liquid interface. EDS spectrum analysis shows that elements Cu and Sn are roughly equivalent in atom percentage, this result demonstrates the component of interfacial region in Figure 3 (a) is Cu_6Sn_5, The morphology of Cu_6Sn_5 particles are different in size and shape, while most of them are in the scallop shape, the size varies from hundred nanometers to several micrometers. Since the

Sn/Cu wetting sample suffered a cooling stage after spreading ended, during that period the IMC phases were growing further, so the average thickness of IMC in nanoscale during wetting processes.
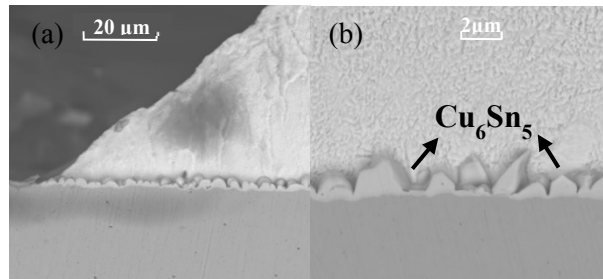

Figure 3. Microstructure of interfaces in Sn/Cu wetting.
(a) Microstructure of Sn/Cu wetting system at solid-liquid interfaces,
(b) The morphology of interfacial products magnifying 5000 times.

As aforementioned, the existence of Cu_6Sn_5 acts as a driven force for the propagation of tin whisker, Cu_6Sn_5 is a brittle compound phase, which generates great compressive force. Sn atoms are forced out the interfacial region, thus whisker grows along the crystal boundary of Cu_6Sn_5, forming a continuous layer of IMC will accelerate the growth rate of tin whisker, so inhibiting the production of nanoscale Cu_6Sn_5 particles during wetting or soldering processes is taken into consideration.

In order to identify which period nanoscale Cu_6Sn_5 phases take place in, whether the chemical reaction between Cu and Sn happened when Sn droplet was initially in contact with Cu substrate, or spreading of molten Sn on Cu was ahead of the interfacial compound formation process, we consider referring to a kinetic explanation of Sn/Cu reactive wetting, which can be drawn from MD simulations.

Figure 4 are snapshots of Sn/Cu wetting simulations at 270°C. The whole spreading process stabilized in 200ps. Sn drop was in shape of hemisphere and the contact angle between drop and the slab below was 90°, an energy state which wetting won't be spontaneous, while the temperature incensement in Sn/Cu system supplied internal energy for Sn atoms in the molten drop, contact angle soon decreased, approximately 60° at 50ps, partial wetting state occurred and Cu atoms also diffused into Sn drop. The contact line kept moving until 200ps, the angle value measured was 47.5° at that timestep. At the intersection area of triple phases, a new layer with mixed Cu-Sn atoms was being generated.
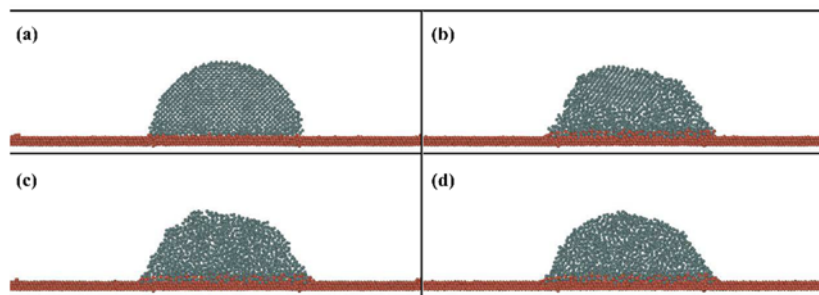

Figure 4. Snapshots of Sn/Cu wetting simulation at timestep: (a) 0ps, (b) 50ps, (c) 150ps, (d) 200ps.

The statistical law of atoms in motion supplies an evidence, MSD of the Sn atom group in three directions is separately calculated according to Einstein diffusion equation. The diffusion coefficient D_x, D_y are 3.125m^2/s and 2.792m^2/s, the difference between D_x and D_y dependents on the atom arrangement of Cu atoms in slab surface, which is cut in the (110) plane of a supercell. In z direction, the vertical diffusion of Sn atom was significantly different, the change of vertical displacement with timestep is nonlinear, after suffering a sharp increasing trend, the diffusion rate of Sn towards Cu slows down,

which indicates that most of atom dissolution between liquid and solid happens in initially spreading process, and nanoscale IMC production continually controls further steps of wetting.
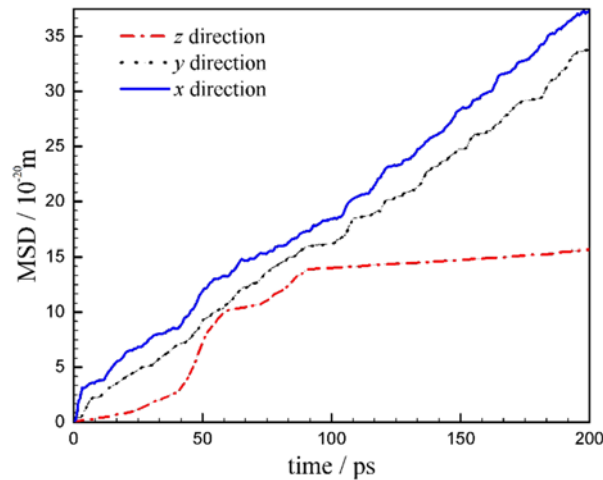

Figure 5. MSD curves of solder atoms changing with timestep.

With extra energy involved into the interfacial region during the wetting process, nanoscale Cu_6Sn_5 compound were transferred into another chemical reaction, see (2). After wetting, the morphology of interface was changed, thus scallop particles was inhibited from vertical growth.

$$Cu + Cu_6Sn_5 \rightarrow Cu_3Sn \tag{2}$$

Switched on the ultrasonic generator when temperature of furnace reached 270℃, With 1400W power, ultrasonic wave was spreading through ultrasonic horn, dispersing into the substrate, finally reached the interface, We found that contact angle suffered sharply decreasing, the wettability of Sn/Cu system got an enhancement. Compare with no ultrasonic wetting, the microstructure of wetting sample under the ultrasonic field also had differences. Cu_3Sn reaction products with an average thickness of about 2μm was found on solid-liquid interface, vertical growth of Cu_6Sn_5 met obstruction, some Cu_6Sn_5 particles were thrust by the Cu_3Sn compound covering overhead. The average size of IMC compounds were even smaller than before. Nucleating got promoted but the growth of continuous Cu_6Sn_5 layer was inhibited in the direction perpendicular to the substrate surface.
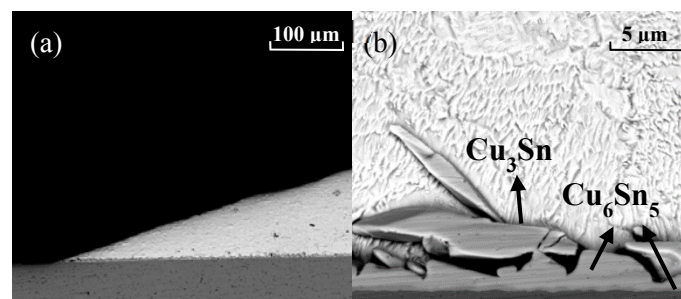

Figure 6. Microstructure of interfaces in Sn/Cu wetting under ultrasonic field.
(a) The solid-liquid interfacial microstructure (wetting involves extra ultrasonic energy),
(b) The new nanoscale interfacial products produced with ultrasonic energy.

The cavitation effect of the ultrasonic wave in the melt took account for the reaction transformation of interfacial reactions in reactive wetting systems. Due to the change in morphology and particle size by ultrasonic, the distribution of nanoscale Cu_6Sn_5 will be propitious to diminishing tin whiskers.

4. Conclusion

For a Sn/Cu reactive wetting system, Cu_6Sn_5 particles together form an IMC layer on Sn/Cu interface, size of these compounds us in nanoscale. Molecular dynamic simulation proves that the formation of Sn-Cu compounds originate from atom diffusion in vertical direction, which is ahead of spreading process in kinetics, Adding an ultrasonic field to Sn/Cu wetting brings change to the morphology of IMC layer. Extra ultrasonic energy leads to the formation of a new Cu_3Sn compound layer, which obstructs the perpendicular growth of Cu_6Sn_5 nano compound.

Acknowledgments

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