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ARTICLE

Effect of Direct Current on Wetting of Cu Substrate in Liquid Sn Solder

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Abstract: The wetting behavior of liquid tin (Sn) solder on copper (Cu) substrate at 250 °C was investigated by the wetting balance method under the action of direct current (DC). The curves of wetting balance were measured and the morphology of the intermetallic compound (IMC) precipitated at the interface were observed. Results show that DC has a significant effect on the wettability and IMC. As the current increases, the balance wetting force and the thickness of the IMC layer increase. The direction of the DC also has a certain effect on the balance wetting force and IMC layer. When the current is negative, the final balance wetting force and the thickness of the Cu_6Sn_5 layer are significantly higher than those in the positive current case, which is attributed to electromigration. The IMC precipitation at the interface provides a chemical driving force for the movement of the triple junction. The interaction of the interface atoms and the chemical reaction are enhanced by DC, thereby improving wettability. Meanwhile, the Marangoni convection caused by DC inside liquid Sn solder changes the structure of triple junction, which provides a physical driving force for the spread of the liquid Sn solder on the Cu substrate.

Key words: wetting balance method; DC; interfacial reaction; IMC; Marangoni convection

1 Introduction

With the development of microelectronics technology towards nanometerization and precision, higher requirements have been put forward for the reliability and stability of solder joints of electronic components. The electronic packaging industry also faces great challenges, necessitating improvements in traditional soldering materials and methodologies to meet developing industry requirements. Sn-based solders are widely used in the electronics industry because of their good mechanical properties and excellent creep resistance[1–2]. However, compared with traditional solder, Sn-based solder has poor wettability on Cu surface. In order to improve the wettability of lead-free solders, researchers have many approaches to enhance solder wettability. On the one hand, the wettability of the system is improved by adding microelement to lead-free solder. Sui et al[3] studied the effect of Ti addition on the wettability of molten Sn on the Al_2O_3 matrix, and found that the wettability was improved due to the adsorption of Ti that reduces the molten-solid interfacial free energy. Wang et al[4] studied the effect of Zn addition on the wettability of SnCu solder on Cu matrix. The results showed that the surface tension increased monotonically with Zn content, while the wetting angle firstly increased and then decreased. This behavior was attributed to the phase transformation of interfacial intermetallic compound (IMC) from Cu_6Sn_5 to CuZn-γ when the content of Zn exceeded 0.88%. Therefore, the wettability of the system changed. Sabri et al[5] studied the effect of Al addition on the wettability of Sn-1Ag-0.5Cu solder on the Cu matrix. The results showed that the wettability was improved when 0.1wt% Al was added, but when 0.5wt% Al was added, the wettability was suppressed. Wang[6] and Bi[7] et al found that Ni and Co additions could improve the mechanical properties of solder joints and inhibit the growth of IMC layer at the interface. On the other hand, the wettability of solder on the

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substrate can be improved by introducing external stress fields, such as ultrasound, magnetic field, and electric field. Wu[8] and Sun[9] et al demonstrated that the ultrasonic waves improved the wettability through multiple mechanisms: accelerating interfacial atomic diffusion, promoting interfacial reactions, and removing surface oxidation film. Xiao et al[10] studied the wettability of molten metal on solid substrates under external high magnetic field. The results showed that the magnetic field mainly affected the distribution of interface elements to improve the wettability. In reaction system, the magnetic field mainly changed the physical properties of the molten metal to improve the wettability. Yang et al[11] studied the wetting behavior of CuFe alloy on W substrate under electric field. The results showed that the wettability of W substrate was improved by the applied electric field, and the wetting angle gradually decreased with increasing the electric field strength.

Direct current (DC) also has a significant effect on the wettability of the solder. Wang et al[12] studied the wettability of Sn(Sn-Pb)/Cu system under DC application, and explained the wettability enhancement through the Gouy-Chapman model and the Stern model. Xu et al[13] found that the wettability of molten Bi and Sn$_{57}$Bi solders on Cu substrate was improved under the action of applied current, attributing this effect to the electromagnetic pressure gradient inside the solder. Gu et al[14] argued that the primary mechanism for wettability improvement was current-induced oxide film breakdown rather than electromagnetic forces.

As described above, the mechanism of the effect of external DC on the wettability of metal systems was controversial, and there are relatively few studies in this field. Therefore, in this research, the wettability of molten Sn solder on Cu substrate under DC action was studied by the wetting balance method, and the influencing mechanism of the DC on the wettability of the reaction system was studied.

2 Experiment

Pure tin (Sn) particles and the copper (Cu) sheet with dimensions of 25 mm×8 mm×0.3 mm (purity of 99.99wt%) were selected as the solder and the substrate, respectively. Wetting balance tests were performed by a solderability tester (SAT-5100, Rhesca, Japan) equipped with a data acquisition software. A DC power supply (ZHAOXIN, KXN-3010D, China) with a maximum output current of 10 A was used. The two poles of the power supply were connected to the Cu substrate and the graphite crucible, separately. The experiment temperature was 250 °C. For the convenience of description, it was specified that the current direction was positive from Cu to tin, and negative from tin to Cu. The current was set as 0, ±1, ±2, and ±3 A. The Sn particles were placed in a graphite crucible with dimensions of 50 mm×40 mm×20 mm, and heated on a heating platform. A K-type thermocouple was immobilized in molten Sn to monitor the real-time temperature, and the temperature-controlled error was ±2 °C. The schematic diagram of device is shown in Fig.1.

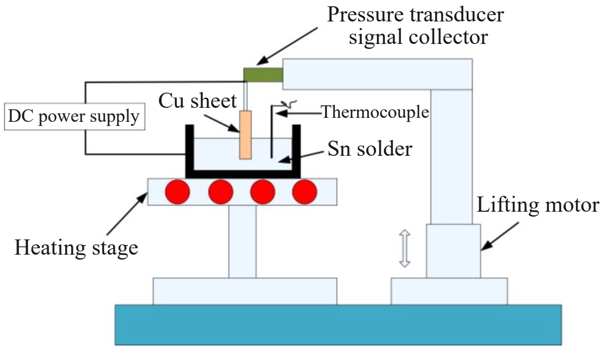

Fig.1 Schematic diagram of wetting balance device

Prior to experiments, the surfaces of the Cu sheets were mechanically polished to obtain surfaces with roughness (R_a) of 100 nm, which was measured by a stylus-type surface roughness measuring instrument (Laisida, TR200, China) to ensure that this aspect was identical in all samples. The samples were ultrasonically cleaned in acetone for 3 min, rinsed with distilled water, then blow-dried, and finally coated with rosin-based flux. At the beginning of the wetting experiment, the pre-prepared Cu sheet was fixed on the wetting balance tester. The temperature was kept constant once the solder temperature reached the experimental temperature. Upon activation of the DC power, the sample was lowered into the molten Sn bath at a speed of 3 mm/s. The descent was automatically terminated upon reaching the predetermined immersion depth of 5 mm. After the test for 40 s, the sample was elevated at the same speed of 3 mm/s until complete separation from the surface of molten Sn. The schematic diagram of the equilibrium wetting process and the corresponding standard curve are shown in Fig. 2. To ensure measurement reliability, each experimental condition was tested in triplicate, with the mean values being used for further observations.

After the experiments, the samples were prepared for microstructural analysis using two complementary approaches. First, part of samples was inlaid with conductive epoxy resin, and then mechanically polished along the cross section. Second, another part of the samples was corroded in

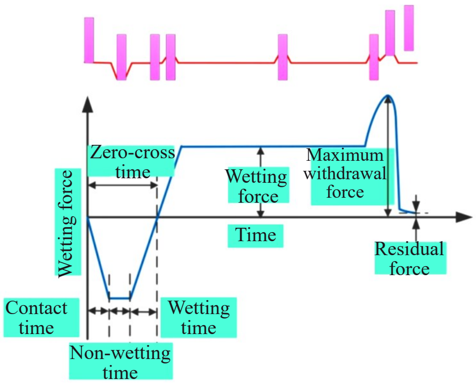

Fig.2 Schematic diagram of the wetting balance process and corresponding standard curve of the wetting balance

20% nitric acid to remove the residual Sn on the surface. The microstructures of the surface and the cross section were observed using scanning electron microscope (Quanta FEG450, FEI, USA) equipped with energy-dispersive spectrometer (EDS). Further, the interfacial reaction products were analyzed using micro-area X-ray diffractometer (XRD, D8 Advance, Bruker AXS, Karlsruhe, Germany).

3 Results

3.1 Effect of DC on wetting behavior

The curves of the wetting force of the molten Sn on Cu substrate are shown in Fig. 3. In the wetting process, the equilibrium wetting force gradually increases with the prolongation of wetting time. The values of zero cross-time (t_0), wetting force (F_{net}), maximum withdrawal force (F_{wd}), and residual force (F_d) can be determined, as listed in Table 1.

The effect of current on wetting time is not obvious. This observation can be attributed to the initial wetting stage, where the rosin-based flux effectively removes the oxide layer from the Cu substrate surface, enabling rapid spreading of molten Sn on the surface of Cu substrate to achieve wetting. Therefore, the effect of current is relatively small. However, the DC has a significant effect on the final wetting force. With the increase in the current, the maximum equilibrium wetting force also increases. The maximum equilibrium wetting force under negative current is higher than that under positive current. With the increase in the current, the polarity of the current has a significant effect on the wettability of the molten Sn solder on the Cu substrate, as shown in Fig.4.

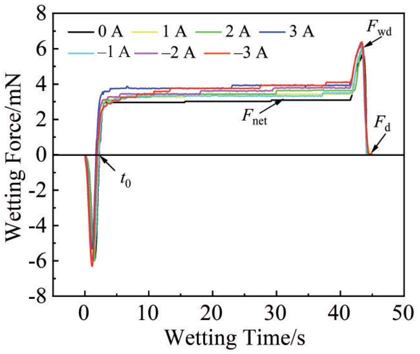

Fig.3 Wetting force in the wetting process under different currents

Table 1 Wetting properties of Sn solder on Cu substrate under different currents

Current/A	t_0/s	F_{net}/mN	F_{wd}/mN	F_d/mN
0	2.23	3.09	5.68	0.02
1	2.10	3.44	6.1	0.05
2	2.20	3.63	6.01	0.02
3	1.73	3.94	6.25	0.03
–1	2.18	3.49	6.11	0.04
–2	1.84	3.79	6.36	0.04
–3	1.85	4.10	6.39	0.05

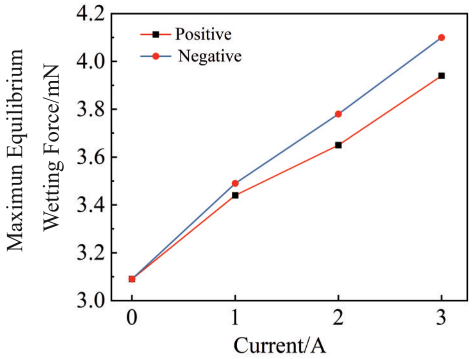

Fig.4 Relationship between maximum equilibrium wetting force and applied current

3.2 Effect of DC on interfacial microstructures

Fig. 5 shows the backscattered electron (BSE) micrographs at the triple junction regions under DC. The scallop-shaped IMCs are precipitated at the Sn/Cu interface, which are determined as Cu_6Sn_5 by EDS, as shown Fig.6.

The thickness of the Cu_6Sn_5 layer was calculated by Image-J software. As shown in Fig. 7, the thickness of the Cu_6Sn_5 layer increases with increasing the current. The current polarity also has a certain influence on the thickness of the Cu_6Sn_5 layer. When the current is negative, the thickness of Cu_6Sn_5 layer is greater than that in the positive current conditions, indicating that the mass transfer at the interface is affected by the DC applied on the molten Sn solder during the spreading process on the surface of Cu substrate. This result is consistent with the findings of Zhao et al[15–16].

4 Discussion

For the metal reaction system, the IMCs precipitated at the molten-solid interface during the wetting process have an important influence on the wetting. Studies have shown that the wettability of liquid Sn solder on Cu_6Sn_5 and Cu_3Sn substrates is better than that on pure Cu substrate[17]. Protsenko et al[18] found that the main reason for the improved wettability is the replacement of original oxidized surface by the IMC generated by the reaction. During the spreading process of liquid Sn solder on the surface of Cu substrate, the interfacial reaction and the imbalance of surface energy can drive the movement of the triple junction. The schematic diagram of the driving mechanism for the triple junction is shown in Fig.8.

Introducing a quasi-static balance force, the modified Young equation can be express by Eq.(1)[19]:

$$\sigma_{lv}\cos\theta + \sigma_{sl} - \sigma_{sv} = F \tag{1}$$

where σ_{lv}, σ_{sl}, and σ_{sv} are the surface tension at liquid Sn/air, liquid Sn/IMC, and Cu/air interfaces, respectively, and F is additional tension at the triple junction, which is balanced by the existing surface forces and changes the equilibrium wetting angle θ from its initial contact angle θ_0. The additional tension is composed of two components: the driving force stemming from interface reaction and the physical driving

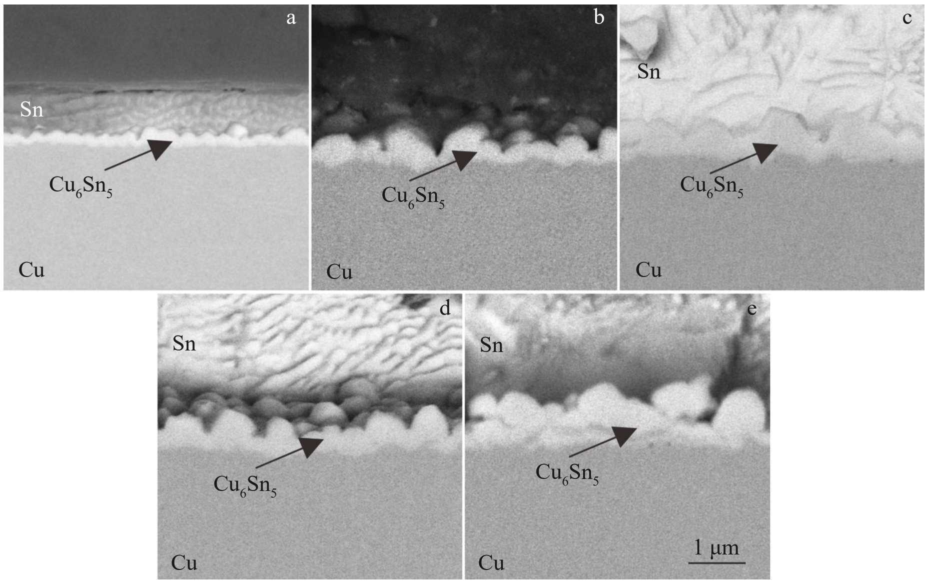

Fig.5 Microstructures of interface at the triple junction after wetting test under different currents: (a) 0 A; (b) 1 A; (c) 3 A; (d) −1 A; (e) −3 A

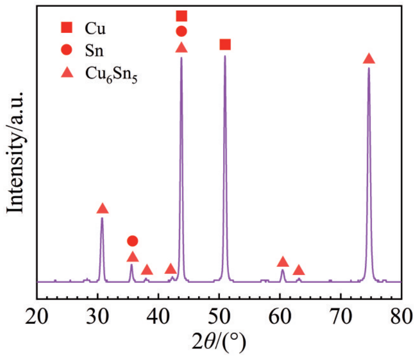

Fig.6 XRD pattern of interface

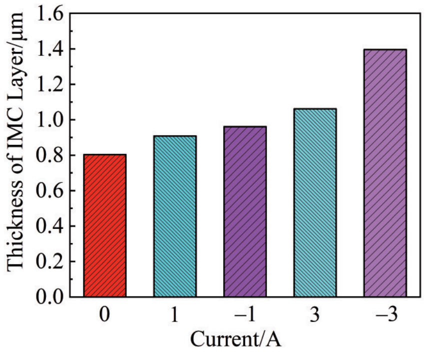

Fig.7 Thickness of IMC layer (Cu_6Sn_5) at the triple junction line under different currents

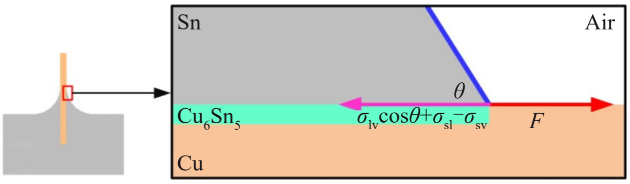

Fig.8 Schematic illustration of the force at the triple junction

force caused by convection inside the solder, as discussed below.

The following reaction will occur at the Sn/Cu interface.

$$6Cu + 5Sn = Cu_6Sn_5 \tag{2}$$

According to Yost's finding[20], the energy transformation (E) of a system per unit spreading length of liquid Sn can be expressed by Eq.(3):

$$\frac{dE}{dr} = 2\pi r\left[\xi + \gamma_{lv}^{Sn}\left(cos\theta_i - cos\theta\right)\right] \tag{3}$$

where r is the instantaneous radius of spreading; ξ is the driving force caused by the formation of Cu_6Sn_5 through interface reaction; γ_{lv}^{Sn} is the surface energy of the liquid Sn (0.56 J/m^2); θ_i and θ are dynamic wetting angle and equilibrium wetting angle, respectively. The second item in brackets is the driving force caused by the imbalance of surface tension. In the spreading process of Sn-based solder on Cu matrix, the driving force of interface reaction plays a leading role. The driving force of Cu_6Sn_5 generated by interface reaction can be expressed by Eq.(4):

$$\xi = \frac{\rho_{Cu} l_{Cu}}{6M_{Cu}}\Delta G \tag{4}$$

where ρ_{Cu}, M_{Cu}, and l_{Cu} are density, molar mass, and reaction thickness of the Cu substrate, respectively; ΔG is the Gibbs free energy change of the Cu_6Sn_5 formation at the interface, and its value is $7747.65 - 0.371T$ J/mol[21]. Through the calculation of the above equation, it can be obtained that when the currents are 0, 1, 3, −1, and −3 A, the values of ξ are 149.49, 169.06, 197.53, 178.853, and 259.90 J/m^2, respectively. Thus, the driving force for interface reaction increases with increase of DC; when the current is negative, the driving force of interface reaction is higher than that in the case when the current is positive.

Without DC, the mass transfer at the liquid-solid interface is mainly driven by the atomic concentration gradient. With the progress of wetting, Cu atoms are enriched at the interface. When the local solubility of Cu reaches the saturation solubility, Cu_6Sn_5 precipitates at the interface and grows in a scallop-like morphology on the Cu substrate. With the continuous growth of Cu_6Sn_5 grain, the diffusion channel of Cu atom is blocked, causing the reaction rate to decelerate.

Under DC, the effects produced in the liquid-solid reaction couple include electromigration, the Peltier effect, and convection flow in the solder. For the metal reaction system, the Peltier coefficient is negligible, so its influence can be ignored. The increased growth of IMC layer at the interface is primarily attributed to the Joule heat and electromigration. During the spreading of liquid Sn solder on the surface of Cu substrate, the diffusion of Cu atoms into the solder and the precipitation of Cu_6Sn_5 layer lead to internal resistivity differences of the solder, resulting in temperature gradient in the solder. The coupling of concentration gradient and temperature gradient enhances interfacial atomic interaction, further increasing IMC layer formation by interfacial reaction. Notably, under identical current intensity but reversed polarity, the same thermal effect is produced in the liquid-solid reaction couple. However, the maximum equilibrium wetting force (Fig. 4) and the thickness of the Cu_6Sn_5 layer at the interface (Fig. 5) are different, which may be due to the effect of electromigration. It is reported that when the current density exceeds the electromigration threshold (10^2 A/cm^2), metal atoms will move in the direction of electrons[22]. In this experiment, the current density is $12-36$ A/cm^2, which is smaller than the electromigration threshold. However, the resistivity of Cu_6Sn_5 is 17.5 cm[23], which is higher than that of Sn and Cu. Therefore, the charge will accumulate in the scallop-like Cu_6Sn_5 groove at the interface, resulting in local current density exceeding the electromigration threshold and triggering electromigration. Considering the high resistivity of Cu_6Sn_5 under DC, the heat generated at the interface exceeds that generated inside solder. This temperature gradient causes Marangoni convection inside solder. On the one hand, it accelerates the diffusion of Cu atom and promotes the growth of Cu_6Sn_5 at the interface. On the other hand, the convection can change the structure of the triple junction and improve the wettability of the liquid Sn solder on the surface of the Cu substrate.

5 Conclusions

1) The DC has a significant effect on the spreading of the liquid Sn solder on the surface of the Cu substrate. As the DC increases, the equilibrium wetting force exhibits a corresponding rise. Notably, under negative current conditions, the equilibrium wetting force is greater than that observed under positive current conditions.

2) The interfacial precipitation of the Cu_6Sn_5 layer intensifies with increasing the current. The thickness of the Cu_6Sn_5 layer is notably greater under negative current than under positive current.

3) The improvement of wetting behavior of liquid Sn solder on Cu substrate under DC can be attributed to two main factors. Firstly, DC accelerates the atomic transfer at the interface, thereby enhancing the driving force for interfacial reactions. Secondly, the convective effect alters the structure of the triple junction, further enhancing the wetting performance.

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直流电对液态Sn钎料在Cu基体上润湿性的影响

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摘　要：采用润湿平衡测试方法，通过施加直流电，研究了温度为250 ℃时，液态Sn钎料在Cu基体上的润湿行为，并分析了平衡润湿曲线和界面析出金属间化合物（IMC）形貌。结果表明，施加直流电作用对润湿性和IMC有显著的影响。随着电流的增大，平衡润湿力和IMC层的厚度增加。电流的极性对平衡润湿力和IMC层的厚度也有一定的影响，当电流为负时，最终的平衡润湿力和IMC层的厚度明显高于电流为正。液态Sn钎料在Cu基体上铺展过程中，界面反应析出的IMC为三相线的移动提供了化学驱动力，而施加直电流作用，增加了界面原子的相互作用，加速了化学反应，促进了润湿性；同时，电流作用引起液态Sn钎料内部产生Marangoni对流，从而改变了三相线的结构，为液态Sn钎料在Cu基体上的铺展提供了物理驱动力。

关键词：润湿平衡法；直流电；界面反应；IMC；Marangoni对流

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