# XPS Analysis and Solder Wettability of Sn-Cu and Sn-Pb Platings Accelerated by Various Methods

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The wettability of Sn-Cu and Sn-Pb solder platings accelerated by pressure cooker test and high temperature shelf test was evaluated through meniscograph and the platings were surface analyzed through XPS, SEM and EDX for the determination of main factors to reduce the wettability. The surface of Sn-Cu platings has a stable oxide layer, $SnO_2$, which is thicker for the samples kept in higher humidity atmosphere. Wettability of Sn-Cu platings does not decrease even in high temperature atmosphere, but that of thin (1μm) Sn-Pb platings reduced. Both of Sn-Cu and Sn-Pb platings do not show remarkable change in the wettability by the component of solder bath. It is suggested that the diffused Cu atoms from the brass substrate and Ni atoms from the plating under the solder plating does not effectively obstruct the wettability. Thus, the main factor for wettability reduction is concluded to be the surface oxide layer and its thickness.

## 1. Introduction

Solder plating is widely applied to the board packaging technology. However, one would rarely encounter a problem that opposite solder paste does not wet to the solder plating. Besides, an environmental pollution by dissolved lead from scraped electronic devices is also a serious problem, so that Pb-free soldering techniques have been vigorously researched and developed recently [1-4]. Hence, it is very important to clarify the factors that hinder the wettability of those solder platings.

In this report, the wettability of Sn-1.0mass%Cu (abbreviated as Sn-Cu) plating samples accelerated by various conditions was evaluated and the surface was analyzed through XPS, SEM and EDX. Moreover, results were compared with those for the conventional Sn-10mass%Pb (abbreviated as Sn-Pb) plating.

## 2. Experiment

### 2-1. Samples

After Ni plating with the thickness of 1 to 5 μm on the brass substrate (5 x 2 x 0.65 mm), Sn-Cu or Sn-Pb layer was formed on the surface by electroplating. Samples were then experienced to the accelerated environmental tests, Pressure Cooker Test (PCT, 105°C, 1.2atm and 100%RH), also called as Highly-Accelarated Temperature and Humidity Stress Test (HAST), and High Temperature Shelf Test (HTST, 155°C and 9-10%RH).

### 2-2. Evaluation of wettability

Solder wettability was measured with a meniscogragh tester and evaluated by the zero cross time. The schematic illustration of the test (dipping a sample plate into solder bath) is shown in Fig.1. X-axis is the time from the beginning of dipping and y-axis is the weight of a sample plate. After dipping a sample, there is a point showing zero weight (zero cross time, Δt). If Δt is less than 2 sec, the wettability of the sample is high enough. Solder baths used were Sn-37Pb, Sn-2.5Ag-0.5Cu-1.0Bi and Sn-3.0Ag-0.5Cu (numbers imply mass%).

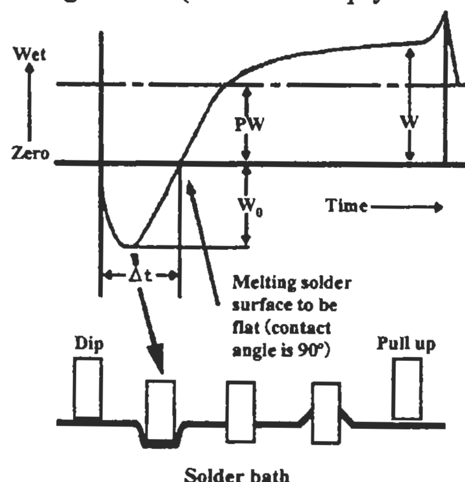



Fig. 1 Schematic illustration of meniscograph method.

### 2-3. Surface analysis

The surfaces of original and tested samples were analyzed by XPS (Physical Electronics ESCA 5600, Monochromatic Al*Kα* x-ray source at a power of 150W), SEM (Hitachi S-4500) and EDX (Horiba EMAX-5770). XPS spectra were obtained in profile mode (pass energy of 58.7 eV) with Ar ion sputtering (1 kV, raster size = 2 x 2 mm) for C1s, O1s, Sn3d, Cu2p, Pb4f and Ni2p regions. Binding energies for the spectra were calibrated to set the C1s peak at 284.8 eV. Atomic concentration was obtained from the peak areas divided by elemental sensitivity factors provided for the instrument used, after the Shirly type background was removed.

## 3. Results and Discussion

### 3-1. Evaluation of wettability by Menisco-gragh

The wettability of original and tested samples was evaluated by meniscograph method. As shown in Fig.2a, the wettability of the Sn-Cu samples accelerated by PCT for 2 and 4 h was good and was reduced by aging for 8 h or more for the Sn-Pb bath, and there was no considerable effects of the thickness of solder platings. These behaviors were the same for other baths (Fig.2c and 2d). On the other hand, almost all Sn-Pb plating samples do not show any wettability reduction for all baths used even after 16 h aging by PCT and 36h by HTST except for the samples with the solder thickenss of 1μm (Fig. 2b shows the results for only Sn-Pb bath). Thus the wettability of Sn-Cu plating is more sensitive to the humidity of acceleration test.

### 3-2. Surface observation by SEM

Figure 3 shows SEM images of Sn-Cu platings before and after acceleration by PCT. No abnormal depositions and whiskers are found on the sample surfaces accelerated by PCT and HTST. Thus, the surface morphology will not be the main factor for the reduction of wettability of solder platings.

### 3-3. Depth profile analysis by XPS

Figure 4 shows the atomic concentration change by Ar ion etching for the original

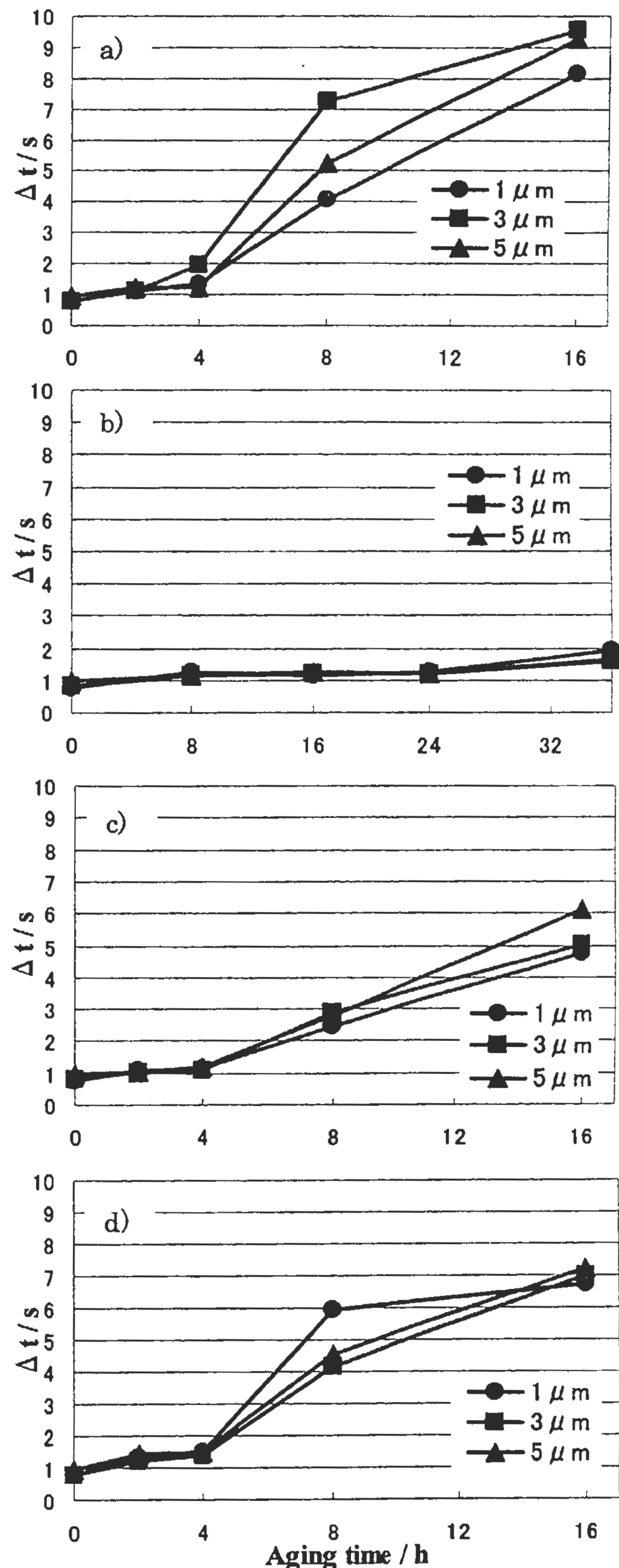



Fig. 2 Zero cross time (Δt) v.s. aging time of PCT. The thickness of solder plating is shown in legend and the thickness of Ni underplating is 3μm.
a) Sn-Cu plating into Sn-Pb bath
b) Sn-Pb plating into Sn-Pb bath
c) Sn-Cu plating into Sn-2.5Ag-0.5Cu-1.0Bi bath
d) Sn-Cu plating into Sn-3.0Ag-0.5Cu bath

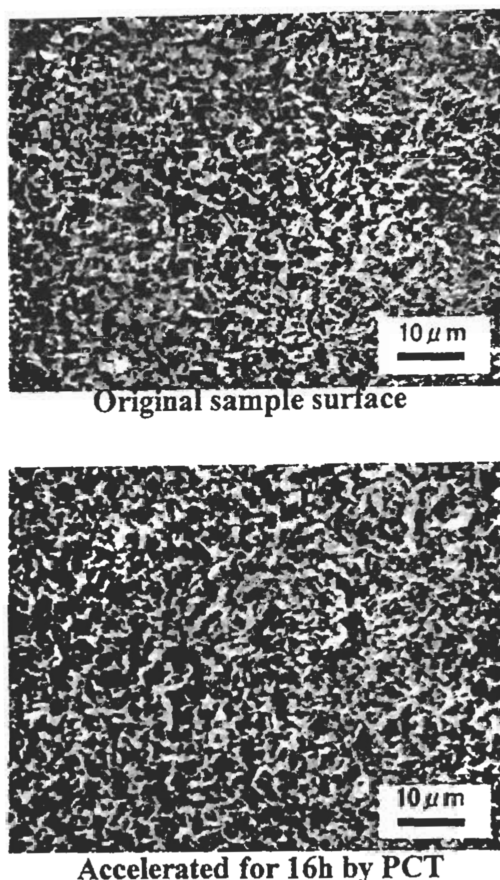



Fig.3 SEM images of Sn-Cu platings before and after acceleration test.

sample and that accelerated by PCT and HTST. The topmost surface of all samples was covered by $SnO_2$ thin layer as the ratio of O/Sn is about 2. And the surface of the sample accelerated by PCT was covered by thicker tin oxides ($SnO_2$ and SnO) layer than that of original and the sample accelerated by HTST. Figure 5 shows the depth profile of Sn3d region for Sn-Cu sample accelerated by PCT for 16h which showed poor wettability. As the Ar ion etching proceeds, the oxide surface is removed and metallic peak appears. Furthermore, the wide scan spectra of initial surfaces of the samples accelerated by PCT and HTST have no Ni peaks, indicating no Ni containing compounds such as $Ni_5Sn_3$ and NiO are formed on the topmost surface. Therefore, the reduction of wettability is considered to be caused by the formation of thicker oxide layer mainly composed of stable $SnO_2$ in highly humidified atmosphere.

### 3-4. Cross-sectional analysis by SEM and EDX

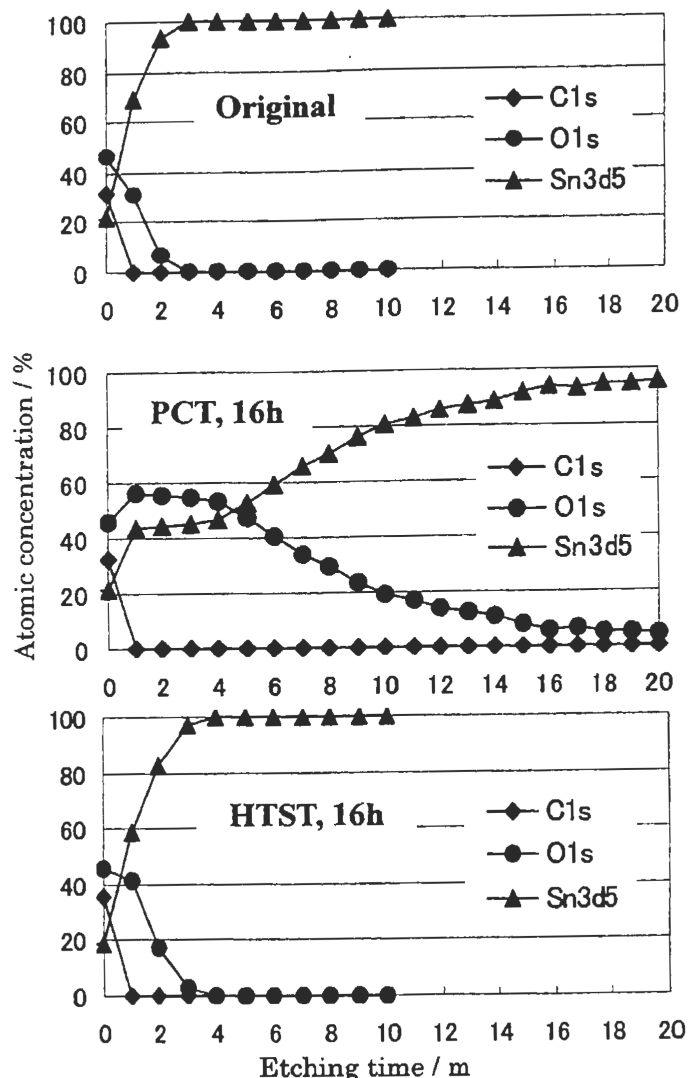



Fig.4 The depth profile of atomic concentration for original and tested samples.

After cutting and polishing of samples, the cross-section was analyzed by SEM and EDX. Figure 6 shows the line analysis results by EDX. The line profile of the sample accelerated by PCT is almost same as that of original. On the other hand, it seems that the width of the Ni/Sn interface for the sample after HTST is wider than that of others. However, the PCT sample has low wettability and the HTST one has high wettability. Accordingly, we suggest that the diffusion of those atoms can not affect the wettability, although this should be confirmed by more detailed analysis.

## 4. Conclusion

The wettability and the surface of Sn-Cu solder platings after acceleration tests of PCT and HTST were evaluated through

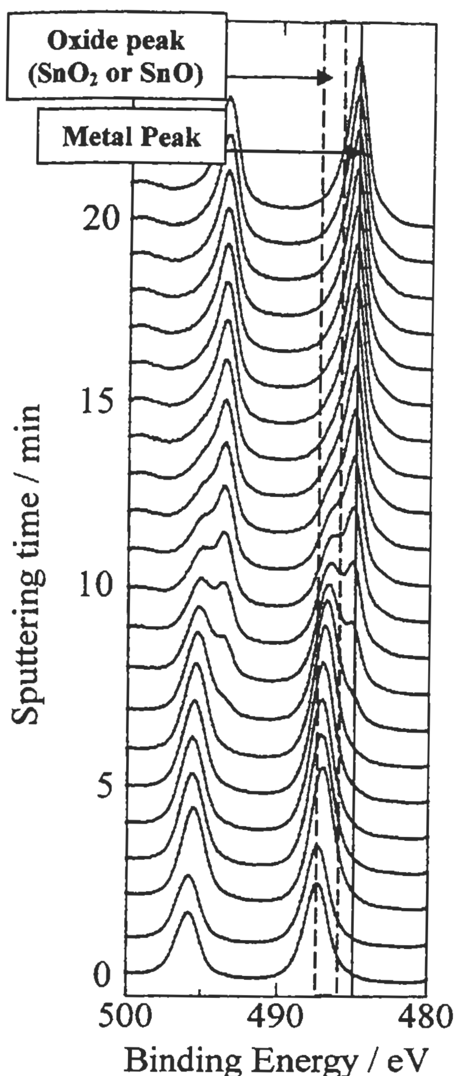



Fig.5 Changes of Sn3d5/2 spectra by Ar ion etching for the sample accelerated by PCT for 16h.

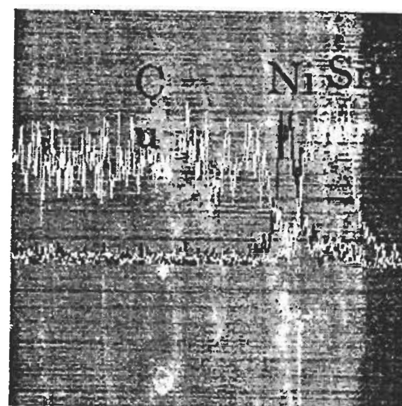
meniscograph method, XPS, SEM and EDX. From these results, followings are concluded:

(1) The surface of Sn-Cu solder platings has a stable oxide layer, $SnO_2$, which is thicker for the samples accelerated in highly humidified atmosphere.

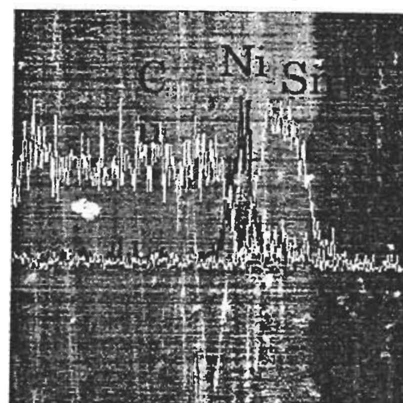
(2) Wettability of Sn-Cu solder platings does not reduce even in high temperature atmosphere, but that of thin (1 $\mu$ m) Sn-Pb solder platings reduced.

(3) Wettability of Sn-Cu and Sn-Pb platings does not change remarkably by the component of solder bath.

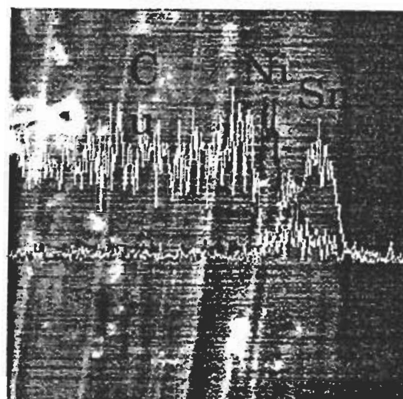
(4) The surface of platings does not show considerable change in morphology after the accelerating tests used.



Original sample



Accelerated by PCT for 16h



Accelerated by HTST for 16h

Fig.6 Analysis of sample cross section

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