Effect of the Formation of CuO Flowers and SnO2 on the Growth of Tin Whiskers on Immersion Tin Surface Finish

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Abstract. The effect of the formation of CuO flowers and SnO2 on tin whiskers formation and growth in 30°C/60%RH environmental condition for tin surface finish had been studied. Immersion plating method was used to coat a layer of tin onto a copper, Cu substrates. The coated surface was subjected to external stress by micro hardness indenter with 2N load in order to simulate an external stress in coating layer and to promote the formation of tin whiskers. FESEM and EDX was used to study the type and chemical composition of whiskers and oxides formed. Image analyser was used to measure the whiskers length using JEDEC Standard No 22-A121A. After 1 week of the exposure under 30°C/60%RH environmental condition, kinked-type whiskers were formed and the whiskers growth were discontinued at week 4 due to the distortion at the end-tip of kinked-type tin whisker to grow further when it touched the coating surface. An observation until 52 weeks of exposure time found that the formation and growth of CuO flowers and the oxidation of non-kinked-type of tin whiskers to form SnO2 promoted by external stress also contributed to the discontinuity of whiskers growth.

Introduction

Tin whiskers study on tin surface finish has been reported by many researchers [1-4] since it became major concern towards optimizing the use of lead-free tin alloys in electronic industry. Pure tin became the right choice after the banning of using lead, a toxic material in electronic components because it has good conductive [5], good wettability [2], and low cost [6] materials.

Tin whiskers can be described as monocrystalline metal protruding from tin surface finish which grow spontaneously and may cause short circuit when it touch each other [7]. Tin whiskers formed as early after 24 hours of deposition completed and exposed at room temperature as reported by Jo et al. in his research [8]. The conductivity of tin whiskers may cause serious failure towards components.

Even though the studied of tin whiskers was done by many researchers for more than six decades, the exact mechanism of tin whisker growth is still not completely understood. To date, researchers agreed that the main factor of tin whiskers growth is due to compressive stresses generates by intermetallics compounds (IMCs) types Cu6Sn5 which located between Cu substrate and tin layer [9-12]. In order to relieve the stress in tin layer, whiskers form and grow spontaneously. Chen et al. in his research stated that intermetallics phase (Cu6Sn5) forms as the immersion plating process starts thus growth over the time until all of the tin has been diffused into copper to form Cu-Sn alloys [9]. So it is clearly understood that the tin whiskers formation originates from the tin layer itself and further growth to relieve the stress. On top of that, researchers tried to relate the types of whiskers formed on the tin surface to the behavior of tin whiskers. They found that, kinked-type of tin whisker tend to form when external stress was generated on the surface finish and the kinked-type tin whiskers has limited length when it grow over exposure time [13,14].
Most of the previous studies focused on whisker growth on electroplated tin and almost none used immersion tin plating. The main purpose of this research is to investigate and understand the effects of oxidation of copper and tin with externally applied stress under controlled environmental storage conditions of temperature and humidity on tin whisker formation and growth. Externally applied stress will be induced by indentation from micro-hardness test to simulate the effect of stress on the formation and growth of whiskers. Further investigation was conducted in order to relate the formation of CuO flower and SnO$_2$ on the growth of tin whiskers.

**Experiment Method**

Materials used in this research is Cu substrate with dimension of 40 x 20 x 1 mm. Plating bath equipped with stainless steel heating coil was set up for plating process in order to maintain the temperature of plating. The plating bath was prepared by dissolving the 20 g/L of stannous chloride as a tin precursor, 16 g/L of sodium hypophosphite as a reducing agent, 37 ml/L of hydrochloric acid (37% ml), 50 ml/L of Sulfuric acid (50% ml), 200 g/L of thiourea, and 5 ml/L of henolsulfonic acid in 1L distilled water. The immersion tin process was conducted at temperature of 75 °C and the deposition time was 8 minutes in order to obtain 1.2 µm of tin thickness.

The tin deposited substrate was indented by using HMV SHIMADZU micro-hardness tester to generate an external stress on the tin surface finish. The samples (indented and non-indented samples) were stored in humidity chamber (Memmert HCP 108) with temperature and humidity of 30°C/60% RH which comply the JEDEC standard No. 22-A121A for temperature/humidity testing of whiskers. The surface morphology of exposed samples was observed by field emission scanning electron microscopy, FESEM (Supra-35VP, Carl Zeiss) equipped with energy dispersive x-ray, EDX to analyze the whiskers behavior and chemical composition respectively. Whiskers length was measured by using software (i-SOLUTION/LITE).

**Results and Discussion**

Figure 1 shows the graph of tin whiskers length of indented and non-indented samples over exposure time under 30°C/60%RH environmental condition at certain time interval (1 week, 4 weeks, 8 weeks, and 12 weeks). The graph shows that for the non-indented samples, whiskers length has increased directly proportional to the exposure time under 30°C/60%RH environmental condition. The results are consistent to most researches reported for samples with 1-2µm tin coating thickness [13,15-17].

For the indented samples, the whiskers length slightly increased after 1 week up until 4 weeks and then keeps constant up to 12 weeks exposed under 30°C/60% RH of environmental condition. From the results, it was clearly showed that the whiskers growth have discontinued even after 4 weeks exposed under controlled condition. This can be depicted by the whisker length for samples exposed for 4, 8 and 12 weeks has similar length. This trend is not consistent to the non-indented samples.
The whiskers growth has discontinued due to the relation of the indentation and kinked-type whisker. Fig. 2 shows the field emission scanning electron microscopy (FESEM) images of whiskers for the non indented samples after 12 weeks of exposure under 30°C/60% RH of environmental condition. Most of the whiskers formed in the straight, bent, twist, and striation shape (Fig. 2. a-d). However, for the indented samples, whiskers form in the kinked-type shape as shown in Fig. 3. High stress from external stress applied by indentation has promoted the formation of kinked-type whisker. The kinked-type whiskers have grown until at certain limit because they tend to stop growing due to the destruction occurred when the whisker end touched the surface of the substrate. Unlike the other types of whiskers, the whisker ends were free from the destruction. The phenomena has been presented by many researchers [13, 14] yet an exact mechanism to relate the external stress with the discontinuity of whiskers growth has not discussed in their research.

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Fig. 1. Graph of whiskers length versus exposure time for non-indented and indented surface after 12 weeks exposed under 30°C/60%RH environmental condition.

Fig. 2. FESEM images of the whiskers formed on the non-indented surfaces in the (a) straight, (b) twist, (c) bent, and (d) striation shapes after 12 weeks exposure under 30°C/60% RH of environmental condition.

Therefore, we have prolonged the exposure time up to 52 weeks under 30°C/60% RH of environmental condition to investigate whether tin whiskers growth as well as whiskers formation have completely discontinued. An observation by FESEM was conducted to monitor a selective whisker on indented surface from week 1 to week 12 of environmental exposure. Fig. 3 (a-d) show FERSEM images of a tin whisker in kinked-type shape formed on the tin surface exposed at time interval of 1 week, 4 weeks, 12 weeks, and 52 weeks respectively.
From the observation, we found that only tin whisker has formed after 1 week (Fig. 3.a) and 4 weeks (Fig. 3.b) of exposure time with significant increase in whisker length. However, after being exposed for 12 weeks (Fig. 3.c), the whisker length has not increased completely but fine CuO flowers formed around the particular tin whisker. In addition, we found that there was no new tin whiskers formed at that specific indentation area. Dispite the discontinuity of tin whiskers formation and growth, the high stress concentration from indentation has promoted the formation of CuO flower as examined by EDX to confirm its chemical composition (Fig 4.a). This is because external stress applied by indentation caused the formation of cracks and peel-off of tin coating thus exposed the surface of Cu substrate to the reaction with environment which is an oxidation process. When the exposure time was increased to 52 weeks, we found that CuO flowers were increased in size indicates that external stress has resulting in CuO flowers growth constantly. Meanwhile, tin whisker length remained unchanged even after 1 year. Nevertheless, the growth of CuO flowers was not as rapid as tin whiskers growth where after 52 weeks, the length of the rod-shape CuO flowers generally has doubled in size while tin whiskers for non-indented surface have grown into five times longer even after 12 weeks of exposure under 30°C/60%RH environmental condition (Fig. 1).

Besides the discontinuity of kinked-type whiskers and active oxidation activity by exposed copper substrate to form CuO flowers, other whiskers type behavior also was monitored. A short uncategorised-type of tin whisker was observed after 4 weeks of exposure under 30°C/60%RH environmental condition (Fig. 4.b-left hand side image). Clearly, it is not kinked-type tin whiskers and it tends to form any shape of tin whiskers whether a straight, twist, bent, or striation shapes. The EDX spectra of tin whiskers is shown in Fig. 4.b-right hand side image. After 52 weeks of exposure under 30°C/60%RH environmental condition, similar tin whisker was monitor under FESEM and the chemical composition was examined by EDX as shown in Fig. 4.c. The results showed that whisker length has not increased as aspected for a straight, twist, bent, or striation -type whiskers as shown by all types tin whisker for non indented tin surface finish in Fig. 2. Instead, the whisker was oxidized to
form SnO$_2$ as shown in Fig. 4.c. The oxidation of tin whiskers in non-kinked-type also contributed to the discontinuity of tin whiskers growth.

Conclusions

In conclusion, the whiskers have formed and grown on the immersion tin surface finish. The externally applied stress influenced the shape of whiskers form on the immersion tin surface. The whiskers formed in the straight, twist, bent, and striation shapes have grown continuously over the exposure time and they were found on the non-indented surfaces. For the indented surface, kinked-type whiskers were found and the whiskers growth were discontinued due to the distruction at the end-tip of kinked-type tin whisker, the formation and growth of CuO flowers, and the oxidation of non-kinked-type of tin whiskers to form SnO$_2$.

Fig. 4. FESEM images (left) and EDX spectras (right) for (a) CuO flowers after 52 weeks, (b) tin whiskers after 4 weeks, and (c) SnO$_2$ after 52 weeks of exposure under $30^\circ$C/60%RH environmental condition.
References


