Reflection Characteristics of Displacement Deposited Sn for LED Lead Frame

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In order to obtain a high reflecting coating for the LED lead frame, Sn displacement deposition was done and the reflection characteristics of displacement deposited Sn was investigated. The Sn coating on the lead frame is expected to result in fine solderability and reduction of the cost relative to Ag coating. Before Sn displacement deposition, Cu electro deposition was carried out to offer a fresh and bright Cu layer (Electroplated Cu, ED Cu) to Sn displacement deposition. With immersion time from 2–4 min, Sn layer was deposited on ED Cu in the bath of Sn displacement deposition. As a result, optical density of Sn layer was more than 0.8 and the reflectance of that was around 90% at the immersion time 2–3.5 min, indicating the Sn layer had excellent reflection characteristics compared with Ag. It is also confirmed that lower roughness, smaller grain size and fewer whiskers resulted in higher reflectance of Sn layer, indicating good reflection characteristics for LED lead frame. [doi:10.2320/matertrans.M2011322]

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1. Introduction

LED (light emitting diode) is eco-friendly electroluminescence component which converts electrical energy into luminous energy.1–3) Compared to other light sources, it has many advantages such as small size, long life, low voltage requirement and high energy saving capacity. However, low efficiency and high cost are big factors to be improved in LED industry. The packaging of LED plays a major role to reduce cost and improve efficiency.

Lead frame is one of key parts for LED packaging which is required to provide excellent electrical, thermal and mechanical properties. LED lead frame is generally made of high performance Cu alloy due to their high electrical conductivity and high thermal conductivity.4,5) A coating layer on the surface of LED lead frame can not only enhance heat dissipation and solderability, but also improves the reflection characteristics resulting in high luminous efficiency. There is a potential for greater improvement of LED luminous efficiency by using higher reflective metal plating on the lead frame. Ag layer is generally used as the high reflective layer which has the highest reflectivity of 86–99% in the given wavelength.6,7) However, because of increasing price of Ag nowadays, Sn as coating material on the lead frame is gaining much attention because of excellent solderability, low cost and environmental protection. In present work, the reflection characteristics of Sn are studied to assess its potential as coating material for LED lead frame to replace Ag.

Previous studies indicate that making flatter and brighter Sn coating layer surface increase the reflection characteristics.8,9) Fujiiwara9) used the contact immersion process (also called ‘the Alchemists Dream Process’) to deposit Sn on Cu substrate. However the deposition rate is very slow. On the other hand, displacement deposition process looks promising to get faster Sn deposition rate along with flatter and brighter deposit on lead frame. Displacement deposition involves the dissolution of the less noble metal substrate to provide electrons for the noble metal deposition without external current.9,10) The role of an additive is very important for displacement between Sn and Cu to occur. Because in normal solution without any additive, the standard electrode potential (Φ) of Cu²⁺/Cu (0.3419 V) and Cu⁺/Cu (0.512 V) is much higher than that of Sn²⁺/Sn (−0.1375 V), that means displacement reaction between Sn and Cu is impossible to occur. Use of additives can reduce the standard electrode potential of Cu²⁺/Cu and the displacement reaction between Cu and Sn (2Cu = 2Cu⁺ + 2e⁻, Sn²⁺ + 2e⁻ = Sn) occur.11)

2. Experimental Procedure

2.1 Cu electro deposition

Pure Cu (99.99%) sheets of size 15 mm × 15 mm × 0.3 mm were prepared as substrates. The copper sheet was polished mechanically with SiC papers (Grit 1000, Grit 2400), and then etched in 2% HCl acid solution for 10 s. The bright Copper electrolytic bath was prepared by 200 g/L CuSO₄·5H₂O, 60 g/L H₂SO₄, 60 mg/L HCL, and 0.5 g/L additive. The electrolyte was agitated using rotating magnetic bar and the stirring speed was 200 rpm. A Pt plate sized 15 mm × 15 mm × 0.3 mm was used as anode. The current density was kept at 60 mA/cm² for 3 min at room temperature (See Fig. 1(a)).

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2.2 Sn displacement deposition

The bath for Sn displacement deposition was composed of 42.8 g/L SnSO₄, 26.8 g/L H₂SO₄, 22.84 g/L thiourea and 1 g/L additive. The stirring speed of rotating magnetic bar was 200 rpm. The ED Cu (Electro deposited Cu) obtained in bath of Cu electro deposition was immersed into the bath of Sn displacement deposition followed by distilled water cleaning. The immersion time was 2–4 min and the temperature was kept at room temperature (See Fig. 1(b)).

2.3 Analysis

In this study, optical density was recorded by a densitometer called ND-11 (Nippon Denshoku Industries, Japan). The micro area roughness and topography of the surface was determined by AFM (Atomic Force Microscopy). EDS (Energy-dispersive X-ray spectroscopy) analysis was performed to testify whether Sn was successfully deposited on ED Cu. FE-SEM (Field Emission Scanning Electron Microscope, S-4300 by HITACHI) analysis was carried out to investigate the grain size and the morphology of whisker.

3. Results and Discussion

In Cu electro deposition, a smooth and bright ED Cu layer of 4–7 μm thickness was deposited on the Cu sheet. The ED Cu provides Sn displacement deposition with a flat, smooth and fresh Cu surface without any oxidation film. In Sn displacement deposition, the appearance of ED Cu was changed to silver-bright as shown in Fig. 2(a). By EDS analysis, the silver-bright layer was confirmed as the Sn layer as shown in Fig. 2(b). The displacement deposited Sn layer displays a silver-bright appearance indicating a high reflecting power. The Sn⁺² ion in the solution replaces the Cu surface atom and deposits at the original site of Cu surface atom, thus the surface topography of the thin, bright Sn layer is similar to the ED Cu. It can be inferred that the high reflective appearance of Sn is inherited from ED Cu.

Figure 3 shows the XRD patterns of the displacement deposited Sn layer on ED Cu. It can be seen that the crystalline quality and texture of all the samples are very similar. ßSn[12] is observed with a small amount. The Sn layer mostly exists as a Cu–Sn intermetallic phase, Cu₆Sn₅[13], instead of elemental Sn. According to Budevski, et al.,[14] alloys are formed consisting of deposited metal and substrate metal when they can form solid solution. On the other hand, due to solid-state diffusion process, Cu diffuse into Sn layer and even to the surface, as Sn layer is extremely thin.

Figure 4 shows the optical density and reflectance of Sn layer surface as a function of immersion time. According to Parmigiani,[15] optical density can be expressed by eq. (1).

\[ D = \log_{10}(1/T) \]  

(1)
Where $D$ is optical density, and $T$ is transmittance. Besides transmission, when a light beam is incident on a surface, light is reflected and absorbed by the surface.\(^{16}\) Thus $T$ is also can be written as a simple equation.

$$T = \frac{1}{C_0} \frac{R}{C_0} \frac{A}{D} \quad (2)$$

where $R$ is reflectance, and $A$ is absorbance. As the thickness of Sn layer is extremely small, the absorption of light by Sn layer can be neglected. Thus, when eq. (1) is combined with eq. (2), the reflectance can be computed approximately as eq. (3).

$$R = 1 - 10^{-D} \quad (3)$$

The reflection characteristics of samples are excellent from 2–3.5 min and best value of reflectance is obtained at immersion time 3.5 min as shown in Fig. 4. The displacement deposited Sn obtained in 4 min displays a lower optical density and reflectance than others. The possible reason is that the Sn displacement deposition stops after 3.5 min due to the disappearance of thermodynamic interaction between Cu atom and Sn\(^{2+}\) and the acid solution starts to destroy the Sn surface topography. The effect of topography on the reflection characteristics is discussed below.

### 3.1 Surface roughness

Figure 5 shows the atomic force microscopy (AFM) profiles of the surface morphology of the displacement deposited Sn for different immersion time. Roughness is the index indicating the micro surface topography, where fewer and lower peaks mean higher surface roughness. The relationship between surface roughness and reflection characteristics is plotted in Fig. 6. It can be seen that the reflectance value is highest when the roughness is lowest. Figure 6 also confirms the result of U. Beck et al.\(^{17}\) that an increase of surface roughness leads to a decrease of reflectance over the whole spectral range. A rougher surface has not only larger micro area to reflect light but also there is more loss of light by absorption, thus decreasing the reflectance which eventually lead to drop in luminous efficiency.

![AFM profiles of displacement deposited Sn layer on ED Cu](image)

**Fig. 5** AFM profiles of displacement deposited Sn layer on ED Cu. The immersion time in the bath of Sn displacement deposition was (a) 2 min; (b) 2.5 min; (c) 3 min; (d) 3.5 min; (e) 4 min.

![Reflectance vs. RMS Roughness](image)

**Fig. 6** Reflectance of deposited Sn layer on ED Cu with root mean squared (RMS) roughness of Sn layer surface. The immersion time in the bath of Sn displacement deposition was (a) 2 min; (b) 2.5 min; (c) 3 min; (d) 3.5 min; (e) 4 min.

### 3.2 Grain size

Figure 7 shows series of FE-SEM microstructure of the surface obtained in the bath of Sn displacement deposition at different immersion time. As shown in Fig. 7, the micro surfaces of displacement deposited Sn obtained at different immersion time are flat, compact and fine grained except for Fig. 7(e). Referring to Fig. 6, it can be seen that the samples that display smaller grain size have a lower roughness and higher reflectance. The sample from Fig. 7(d) which has the highest reflectance displays the most compact micro surface and finest grain size i.e. less than 100 nm.

Theory about the structure of high reflective metal surfaces tells that metal surfaces are high reflective if their microstructure consists of crystallites smaller than the wavelength of visible light, i.e. smaller than 0.4 µm.\(^{9,18,19}\) The grain size of sample (a)–(d) are less than 0.4 µm and their appearances are bright and are high reflective. But the sample (e) whose grain size is bigger than 2 µm show dull-bright in appearance.

### 3.3 Sn whisker

Sn whiskers look like prills or needles and can be seen on
the micro surface in Fig. 8. Sn whiskers increase the roughness of micro surface, leading to a lower reflectance. Factors affecting whisker growth are thought to be stress, temperature, substrate, plating thickness and atmosphere. It is said that thin plating thickness (less than 3 µm) facilitates the whisker growth during plating and storage but hardly observed when the tin plating layer is thick.20) Figure 8(d) shows least and smallest whiskers on its surface because of thick Sn layer deposited in a long time, as compared to other samples. The internal stress of thick Sn layer, created during plating and during the metallic migration of the base metals through the film, do not affect the surface significantly, hence less whisker growth in sample (d) whereas in the case of Fig. 8(a), the stress is exerted on the surface and it accelerates whisker formation. Figure 8(e) should have displayed the smallest and least whiskers, but actually it has the biggest grain and compact structure, resulting in the greatest internal stress and longest whisker among these samples.

In order to estimate the effect of aging on the surface and reflection characteristics, the (a) sample from Fig. 8 was aged for 224 days at room temperature. The aged surface of Sn deposit is given in Fig. 8(f). By comparing Fig. 8(a) with Fig. 8(f), the 224 day-aged surfaces had larger whiskers. However, the whisker growth was not so obvious since the aged sample was stored at room temperature. The reflection characteristic of the 224 day-aged Sn surface is compared with that of not-aged (i.e. just after plating) one in Fig. 9.

The reflection characteristics of the aged sample decreased compared to that of not-aged one due to the larger whiskers. The amount of decreasing in optical density and reflectance are approximately 8% and 1.8%, respectively, after aging for 224 days.

4. Conclusion

To obtain an excellent reflection characteristic of lead frame for LED, the optical density and reflectance of Sn layer are studied in this study. The results are summarized as follows.

(1) The high reflective Sn layer was successfully deposited on the electroplated Cu in the bath of Sn displacement deposition.

(2) The optical density of Sn layer was more than 0.8 and the reflectance of Sn layer was around 90% at the immersion time 2–3.5 min.

(3) The reflectance of Sn layer decreased as roughness increased. The lowest roughness value of Sn layer was obtained as 30.19 nm.

(4) The finest grain size of Sn reached less than 100 nm which indicates excellent reflection characteristics. Sn layer with higher reflectance has a smaller grain size than that with lower reflectance.

(5) The Sn whisker formed due to various factors makes the micro surface coarser, leading to a higher roughness
and lower reflectance. Whisker growth by aging for 224 days enlarged whiskers and caused the drop of reflection characteristic.

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