Thermal Stability and Sulfidizing Resistance of High Reflective Multilayered Sn/Ag₃Sn and Sn/Ag Films Electrodeposited on Cu Alloy Sheets

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ABSTRACT

We reported multilayered Sn/Ag₃Sn and Sn/Ag films with Ag thickness of 20–300 nm that electroplated on a reflowed Sn layer on Cu alloy sheets as promising coating materials for LED lead-frames. The morphology, surface roughness, crystalline structure, and reflectance of multilayered Sn/Ag-based films are more dependent on plating baths than on Ag thickness. The Sn/Ag₃Sn film obtained from a cyanide Ag bath exhibited high specular reflectivity of 65–70% (480 nm), whereas the Sn/Ag films from a cyanide-free bath showed a high total reflectivity of 94% similar to commercial Ag films. The reflectance of both the multilayered Sn/Ag₃Sn and Sn/Ag films almost unchanged even after heating at 373 K for 120 h, in comparison with the apparent drop for a commercial Ag film. Moreover, the multilayered Sn/Ag₃Sn films, both the as-deposited and the annealed specimens, remained the reflectivity even after immersing in a

0.2% $(\text{NH}_4)_2\text{S}_x$ solution for 60 min. The excellent sulfidizing resistance of the Sn/Ag₃Sn films can be attributed to the chemically stable Ag₃Sn alloy layer with improved corrosion resistance and the protective SnO/SnO₂ thin film on the surface, thus inhibiting the chemical reaction of Ag and S²⁻ ions.

1. Introduction

Light emitting diode (LED) lamps are a fast emerging light source which is considered as the true alternative to the conventional lighting sources like fluorescent lamps and incandescent lamps. The LED lamps have high energy-saving capacity, low voltage requirement, small size, high efficient and long life, compared to the traditional lighting [1, 2]. One of the barriers for the commercial applications of energy-saving LED lamps, however, is that LED lamps are much more expensive than ordinary lamps. The reason for the high prices of LED lamps lies in the complicate LED package assembling components, which is composed of a housing, encapsulant, die, bond wires, die attach, lead frames, metal heat slug, and solder joints [3]. Of the package materials mentioned above, lead frames play an important role in the determination of the reliability for LED lamps, because they provide excellent electrical conductivity, low thermal resistivity, and necessary light reflective performance. Silver thin films that coated on Cu alloy plates are utilized as LED lead frames, because Ag films can achieve the maximum reflectivity other metallic coatings, and Cu alloys provide good electrical/thermal conductivity and satisfied mechanical strength [4].

However, Ag films are known as a thermally active material under high temperature circumstance due to the agglomeration process, during which Ag grains restructure and reshape the surface in order to reduce the overall energy of the system [5]. The agglomeration usually

causes a light scattering phenomenon and decreased conductivity with respect to the initial smooth layer, thus decreasing the specular reflection and conductivity [6–10]. In the past decade, thermal stability or thermal degradation (i.e., agglomeration) of Ag films on GaN-related semiconductors for LEDs have been extensively investigated in many studies [11–20]. One solution for improving the thermal stability of Ag films was proposed by adopting capping layers like NiZn alloy [11], SnO₂ [12], Zn [13], and IZO [15] on Ag films, or using interlayers like Ni [14] and Ir [15] layers beneath the Ag films, to retard the Ag agglomeration process at high temperature. Another solution was forming Ag alloy films by adding several percent of Al [16], La [17], Ni [18], Zn or Sn [19, 20] into Ag films to hinder the migration of Ag grains at high temperature. Moreover, Ag reacts readily with sulfur around and forms a silver sulfide film on the surface during assembling process and application circumstance, thus lowering their reflective performance and luminous efficiency of LED packages. Forming a protective capping layer or alloying Ag with metallic additives as mentioned above can also improve the sulfidizing resistance in addition to thermal stability of Ag films, but it had to sacrifice the reflectivity of Ag films to some extent. Furthermore, most of the studies focused the thermal stability of Ag films on GaN-related semiconductors while ignoring the effects of Ag films coated on lead frames.

Recently, several studies proposed electroless deposited Sn [21] and Sn-3.5Ag alloy [22] films to substitute costive Ag films for LED lead frame. In our previous studies, we had also reported a multilayered Sn/Ag film on Cu alloys with high reliability as a promising coating material for automotive connectors and electrical contacts. It was found that the multilayered Sn/Ag₃Sn films on Cu alloys exhibited excellent thermal stability of electric contact resistance, satisfied fretting corrosion resistance, Sn whisker-free, and good solderability [23–27]. Recently, we have also reported a multilayered Sn/Ag₃Sn film on Cu alloys toward high durability LED

lead frames [28], and found that the Sn/Ag₃Sn films possessed excellent sulfidizing resistance. The present study is aimed at investigating the thermal stability of various multilayered Sn/Ag films on Cu alloy sheets toward LED reflective materials and lead frames, which achieved by electroplating process with cyanide and cyanide-free plating baths. The effects of plating baths on the morphology, crystalline structure, and reflective characteristics of the multilayered Sn/Ag films were investigated. Moreover, the thermal stability and sulfidizing resistance on reflectivity of the Sn/Ag films in different plating baths were evaluated, in comparison with a commercial Ag film with 2- μ m thickness and a conventional reflowed Sn film with 1- μ m thickness.

2. Experimental

2.1 Fabrication of multilayered Sn/Ag-based films on Cu alloy sheets

Various multilayered Sn/Ag specimens were produced by consecutively electroplating Sn and Ag films on Cu alloy sheets. Briefly, a Sn film with 1.2 μ m thickness was first electrodeposited on Cu alloy sheets (CDA No. C19400: Cu 97.6–Fe 2.3–Zn 0.12–P 0.03, 50 $\times$ 50 $\times$ 0.15 mm) using an industrial sulfuric bath, followed by a heat treatment at 505–593 K and resolidification to get a reflowed Sn film (denoted as Sn-RF later). Here, the Sn-RF film were adopted to achieve a bright and smooth Sn film with high specific reflectivity, better soldering ability, and more importantly, to inhibit the growth of Sn whiskers. Then, silver electroplating was performed on the Sn-RF films at 4–10 mA cm⁻² and 293–323 K for 5–50 sec with a programmable power supply (YAMAMOTO-MS: YPP-15031) to obtain Ag films with thickness of 20–300 nm, followed by a post-treatment below 373 K for 2 min. Here, the thickness of Ag films was calculated by the mass gain before and after Ag electroplating, measured by a precise

balance (A & D Co. Ltd., HR-100 AZ: accuracy - 0.1 mg) and calculated with the Ag density of 10.49 g cm⁻³. For confirmation, the thickness of Ag films below 100 nm was also checked by X-ray fluorescence measurement and EDS analysis. The post-treatment was adopted to inhibit the migration phenomenon of Ag electrodeposits, which was determined by a preliminary experiment in previous studies [25, 27]. As for Ag electroplating, two kinds of plating baths, *i. e.*, an industrial cyanide bath containing Ag⁺ ions of 5.0 g dm⁻³ (denoted as C-Ag) and an industrial cyanide-free bath containing Ag⁺ ions of 30.0 g dm⁻³ (denoted as CF-Ag), were adopted in the Ag electroplating.

2.2 Characterization of electrodeposited films

The surface morphologies and chemical composition of multilayered Sn/Ag-based films and reference specimens were observed by field emission scanning electron microscopy (FE-SEM: JEOL-JSM-7001F) with X-ray energy-dispersive analysis (EDS) at accelerated voltages of 10–15 kV. The crystalline structures of the specimens before and after heating at 373 K for 120 h were determined by a powdery X-ray diffractometer (XRD: Rigaku-2200, 35 kV/ 30 mA, Cu K α). Moreover, the cross sections of the multilayered Sn/Ag-based films before and after heating were observed by a transmission electron microscope (TEM: JEOLJEM-2100) equipped with X-ray energy-dispersive detector at an accelerated voltage of 200 kV. The specimen for the TEM observation was prepared by focused ion beam (FIB) after evaporation of carbon and Pt layers on the film surface. Moreover, the micro-area surface roughness and topography of the multilayered Sn/Ag-based films were measured by atomic force microscopy (AFM: Nanocute, SII). Furthermore, the chemical states of the Sn/Ag₃Sn films before and after heating were analyzed by an X-ray photoelectron spectroscope (XPS: ULVAC-PHI- 5600CIM, Al K α). The

binding energy of the spectra was corrected by the C 1s signal at 284.5 eV, with an accuracy of within 0.1 eV.

2.3 Reflective characterization

The reflectance, including total reflectivity (SCI) and diffusive reflectivity (SCE), of various electrodeposited films before and after reliability tests as described later was measured by a spectrophotometer (Konica Minolta – 2500d) at an incident angle of 10°, with a standard white plate as reference of 100% reflectivity. Moreover, the specular reflectance of the films in the ultraviolet-visible light wavelength range was measured by a spectrometer (Hitachi-U3500) at an incident angle of 5° and at a resolution of 2 nm, with a standard Al sheet as reference of 100% reflectivity.

2.4 Accelerated tests of thermal stability and sulfidizing resistance

The accelerated test on the thermal stability of multilayered Sn/Ag-based films on Cu alloy sheets at high temperature circumstance was carried out at 373 K for 120 h in the air, which referring to the Class-I standard of The United States Council for Automotive Research (USCAR). The corrosion resistance against sulfidization of the coating materials mentioned above was evaluated by immersing the specimens in 0.2 mL/L (NH₄)₂S_x solution (Japan Industrial Standard JIS-H 8621) at 298 K for 3–60 min. Moreover, a combinatorial accelerated test on thermal stability and sulfidizing resistance was performed by first heating at 373 K for 120 h in the air and then immersing in 0.2 mL/L (NH₄)₂S_x solution at 298 K for 3–60 min successively.

3. Results and Discussion

3.1 Microstructures of multilayered Sn/Ag-based films formed in different plating baths

Fig. 1 shows the surface morphologies of the Sn/Ag-based films with different Ag thickness that formed in cyanide and cyanide-free electroplating baths, and a Sn-RF film before Ag electrodeposition. For comparison, a commercial Ag plating film (2.1 μm thick) on Cu alloy, which was normally made in an industrial cyanide bath, was adopted as a reference sample. In case of the cyanide plating bath with low concentration of Ag^+ ions was adopted, a uniform Ag film with smooth granular surface was achieved at a thin thickness of 100 nm (Fig.1a), remaining the smooth morphology of the underlying Sn-RF film (Fig.1e). With increasing film thickness to 300 nm (Fig.1b), an uneven film with coarse grains around 100–200 nm across was formed, which is similar to a typical strike Ag electroplating. In contrast, the Ag film that formed in the cyanide-free bath with high Ag^+ concentration composed of fine grains around 50–100 nm across, almost irrespective of film thickness (Fig.1c, d). This means that the composition of plating baths determined the morphology or grain growth of the plating films. In all cases, the Sn/Ag films exhibited smoother surface than a commercial bright Ag film (Fig.1f), giving a mirror-bright appearance similar to the underneath Sn-RF film on Cu alloys.

Fig. 2 demonstrates the crystalline structures of multilayered Sn/Ag-based films formed in different plating baths through XRD analysis. In all cases, strong peaks corresponding to Sn, Cu_6Sn_5 , and Cu are detected, which were attributed to the Sn-RF films on Cu substrates due to the thin thickness of Ag electroplated films. For the Sn/C-Ag-100 nm film that formed in cyanide plating bath, all of the peaks that related to Ag at $2\theta = 34^\circ$, 37.5° , and 39° were indexed to be the (110), (002), and (111) facets of $\varepsilon\text{-Ag}_3\text{Sn}$ phase with a hexagonal close-packed structure ($a = 2.995 \text{ \AA}$, $c = 4.780 \text{ \AA}$, $c/a = 1.596$; JCPDS card: 00-004-0800), respectively. This indicated that

the Ag was completely alloyed with Sn during the post-treatment followed by Ag electroplating. With the Ag thickness increased to 300 nm, a small peak corresponding to Ag <111> facet was detected out beside of ϵ -Ag₃Sn phase, which can be attributed to the surplus Ag deposits to stoichiometric Ag₃Sn alloy and/or insufficient Ag-Sn alloying treatment, thus leading to a multilayered Sn/Ag₃Sn/Ag film. In contrast, the Sn/CF-Ag-100 nm film which formed in a cyanide-free bath only exhibited a peak corresponding to Ag <111> facet. This indicates that the CF-Ag electrodeposits possessed good crystalline structure stability and difficult to be alloyed with Sn even experienced the same post heat treatment, probably due to the additives in the cyanide-free bath.

The cross-sectional morphology and the crystalline structure of the Sn/Ag-based films that obtained in different plating baths were further investigated by TEM observation and EDS analysis, and the results are shown in Fig.3 and Table 1. The Sn/C-Ag film comprised of a granular top-layer with uneven thickness of 150–200 nm on the Sn-RF film (Fig.3a), which is much thicker than the calculated thickness of Ag film. Referring the EDS result at point No.1, the atomic percentage ratio of Ag and Sn was close to the stoichiometric Ag₃Sn intermetallic compound instead of pure Ag film. In addition, the high-resolution TEM image (Fig.3a') revealed a zigzag interface boundary between Ag and Sn films, which can be attributed to the interdiffusion between Ag and Sn films and/or the Ag-Sn alloying reaction during post-treatment of Ag electroplating. Moreover, the corresponding selected area diffractive electronic pattern of the top-layer (see inset in Fig.3a) revealed a typical spotted pattern for a highly crystalline structure, which was indexed to the Ag₃Sn phase, thus indicating the formation of multilayered Sn/Ag₃Sn film, consistent to the result of XRD analysis (pattern a, Fig.2). On the other hand, the Sn/CF-Ag film (Fig.3b) delivered a dense and continuous film with uniform thickness of 100 nm

on the Sn-RF film. The EDS result (Spot No.4 in Table 1) confirmed that the top-layer consisted in pure Ag. Moreover, the high-resolution image (Fig.3b') disclosed that the CF-Ag film composed of fine grains and that no Ag-Sn alloy layer or grains formed at the Ag/Sn interface. The corresponding SADE pattern exhibited a ring-like pattern that indexed to pure Ag, which was consistent to the XRD analysis (Fig.2, pattern c), thus leading to a multilayered Sn/Ag film. In addition, the underlying Sn-RF films delivered regular spotty SADE patterns, indicating their highly crystalline structure that formed by resolidification from high temperature above Sn melting point.

3.2 Surface roughness and grain size of multilayered Sn/Ag₃Sn and Sn/Ag films on Cu alloys

Fig. 4 shows the effects of plating bath and Ag thickness on the micro area roughness and grain size of Sn/Ag-based films measured by AFM. The AFM images in Fig.4a demonstrated the granular surface of Ag₃Sn (C-Ag) and Ag (CF-Ag) top layers on Sn-RF films, with the grain size increasing with Ag thickness, consistent to the FE-SEM observation (Fig.1). As for the surface roughness that calculated from the AFM images (Fig.4b), Sn-RF films before electroplating possessed a low roughness around 6 nm due to the smooth surface of molten Sn film. After Ag electroplating, the roughness for both the Sn/Ag₃Sn and Sn/Ag films increased compared to the Sn-RF because of the deposition of granular Ag film (Fig.1a-d), in proportional to the Ag thickness. Therefore, in order to diminish diffusive reflection of Ag films and to save costive noble Ag, it is preferred to set the thickness of Ag films be low 100 nm.

3.3 Reflectance of multilayered Sn/Ag₃Sn and Sn/Ag films on Cu alloys

Fig. 5 shows the total reflectivity of as-deposited multilayered Sn/Ag₃Sn (C-Ag) and Sn/Ag (CF-Ag) films with different Ag thickness. For references, a conventional Sn-RF film and commercial Ag (2 μm-thick) and Au (50 nm-thick) films for LED lead frames were also given in Fig.5. As a base material, the Sn-RF film shows a high total reflectivity of 80% at a wavelength of 480 nm (close to blue light wavelength), which is ascribed to the metallic glister and the water-like smooth surface that formed by melting and resolidification (refer to Fig.1e). After Ag electroplating, the reflectance of multilayered Sn/Ag films was dependent greatly on the electroplating conditions. As the Ag electroplating performed in a cyanide bath with low Ag⁺ concentration (Fig.5a), the reflectivity of the film dropped to around 70% (480 nm), which can be mainly attributed to the formation of Ag₃Sn alloy layer with less reflective nature than pure Ag. With increasing Ag thickness, the reflectivity slightly decreased to around 65%, which can be ascribed to the increase of surface roughness of Ag₃Sn grains (Figs.1b and 4b). Apparently, the reflectance of multilayered Sn/Ag₃Sn films were lower than the commercial bright Ag film due to the reflective nature of Ag₃Sn intermetallic compound, but it is definitely much high than that of a commercial Au film (24% - 480 nm). Whereas for the Sn/Ag films formed in a cyanide-free bath with high Ag⁺ concentration (Fig.5b), the film with Ag thickness as thin as 50 nm demonstrated a higher reflectivity around 94% that equivalent to pure Ag film of 2 μm. This can be attributed to the phase stability of CF-Ag with low alloying ability to Sn (see XRD pattern c in Fig.2 and TEM image in Fig. 3b) and the smooth underlying Sn-RF film, as well as the good throwing property of the cyanide-free plating bath. As the Ag thickness increased above 100 nm, the multilayered Sn/Ag films possessed a high reflectance around 96% (480 nm), even higher than the commercial bright Ag film, which can be attributed to the small surface roughness and fine grain film of CF-Ag film (see Fig.4b).

Correspondingly, the dependence of diffusive reflectivity of the multilayered Sn/Ag₃Sn (C-Ag) and Sn/Ag (CF-Ag) films on Ag thickness was illustrated in Fig.6a, compared to the commercial bright Ag film. All of the multilayered Sn/Ag-based films with Ag thickness below 300 nm delivered lower diffusive reflectivity than that of commercial Ag film, though the diffusive reflectance increased slightly with the thickening of Ag plating. Especially, the Sn/Ag₃Sn films with thin Ag thickness of 30–80 nm delivered extremely low diffusive reflectivity around 0%, which was the same as the underlying Sn-RF film with smooth surface (refer to Fig.1a). Fig.6b gives the specular reflective spectra in a wide light wavelength throughout ultraviolet and visible light range for multilayered Sn/Ag₃Sn films with thin Ag thickness of 30–80 nm. It can be seen that the multilayered Sn/Ag₃Sn films exhibited higher specular reflectance than the conventional pure Ag film. Because the diffusive and specular reflectance is greatly affected by the surface roughness and the grain sizes of the films, the multilayered Sn/Ag-based nano-films are expected to deliver enhanced extraction efficiency. In addition, it should be noticed that the multilayered Sn/Ag₃Sn exhibited higher reflectivity in the ultraviolet light range than both Au and Ag films (0%), indicating a promising application to substitute commercial Au films for UV-type LED lead frames.

3.4 Thermal stability of multilayered Sn/Ag₃Sn and Sn/Ag films on Cu alloys

The structural stability of Ag-based films at high temperature circumstance is an essential prerequisite to achieve necessary thermal and sulfidizing resistance for as LED lead frame usages, especially for automotive LED headlamps that are mounted in the engine rooms. Fig. 7 displays the cross sections of TEM images near the surface regions of Sn/Ag₃Sn (C-Ag-100 nm) and Sn/Ag (CF-Ag-100 nm) films after heating at 373 K for 120 h. The EDS analytic results

corresponding to the spots in TEM images were listed in Table 2. Similar to the specimens before heating in Fig.3, the Sn/C-Ag film (Fig.7a and a') composed of a granular top layer on Sn-RF film, which was identified to be Ag_3Sn from the SAED pattern and EDS analysis. The Ag_3Sn top layer exhibited a zigzag grain boundary at the Ag/Sn interface due to the aggregation at prolonged high temperature circumstance, but still reserved the smooth surface of the film. In contrast, the Sn/CF-Ag film (Fig.7b and b') remained as a continuous Ag layer without discernable agglomeration, indicating the excellent structural stability at high temperature circumstance. The SAED pattern with faint rings also indicated the fine crystalline structure of CF-Ag film reserved. Moreover, some tiny particles can be observed at the interface between Ag and Sn-RF films (see white arrows in Fig.7b and b'), which can be attributed to the formation of intermetallic compound of Ag-Sn alloy during the heating process.

Fig. 8 shows the corresponding XRD patterns of multilayered Sn/ Ag_3Sn and Sg/Ag films after heating at 373 K for 120 h. The Sn/Ag film exhibited a similar XRD pattern to the as-deposited film (Fig.2), indicating a stable crystalline structure of CF-Ag film, consistent to the TEM observation. No apparent peak corresponding to Ag_3Sn or Ag-Sn alloy observed in the TEM image was detected, which can be ascribed to the small amount of Ag-Sn alloy or its low crystallinity. Whereas for the Sn/C-Ag-300 nm film, the Ag peak disappeared compared to the as-deposited film (Fig.2), indicating the progress of Ag-Sn alloying reaction at prolonged high temperature circumstance. Moreover, the relative strength of peaks corresponding to Sn and Cu_6Sn_5 phases almost unchanged compared to those before heating, indicating its good thermal stability.

The stability of reflective property of Ag-based films is critical for LED lead frames. Fig.9 illustrates the variation of the total and diffusive reflective spectra of multilayered Sn/ Ag_3Sn and

Sn/Ag films before (dotted lines) and after annealing at 373 K for 120 h in air (solid lines). As reference, the reflective spectra of a commercial bright Ag-2.1 μm film before and after heating were also given in the Fig.9a. The reflectivity of the commercial Ag film decreased significantly, especially in the short wavelength, which can be attributed to the agglomeration of Ag grains at high temperature as described in many studies [5-10]. In contrast, the reflectivity of Sn/Ag₃Sn films after heating varied little in the short wavelength but decreased slightly in the long wavelength. Remembering the partial agglomeration of Ag₃Sn grains from TEM observation in Fig.7a, it can be deduced that the variable reflective performance of multilayered Sn/Ag₃Sn films after heating may be attributed to the mixed reflection of Sn and Ag₃Sn regions. Moreover, it is noteworthy that the multilayered Sn/CF-Ag films (Fig.9b) exhibited remarkable stability of reflective performance throughout the visible light range, remaining a high reflectivity around 96% (480 nm) and low diffusive reflectance below 10%. This can be attributed to excellent structural stability of CF-Ag films as indicated in Fig. 7b and Fig.8.

3.5 Sulfidizing resistance of multilayered Sn/Ag₃Sn films

Fig. 10a shows the reflectivity of as-deposited multilayered Sn/Ag₃Sn films with Ag film thickness of 20–100 nm and a commercial bright Ag-2 μm film after immersing in 0.2 ml/L (NH₄)₂S_x solution for 3 min (solid lines) and 60 min (circle mark). It can be seen that the reflection of multilayered Sn/Ag₃Sn films is inversely proportional to the thickness of top Ag layers. In case of thin Ag thickness of 20 and 40 nm, Sn/Ag₃Sn films exhibited stable reflection throughout the visible light wavelength, remaining a high reflectivity around 70% and 66% (480 nm), respectively. Especially, the Sn/Ag₃Sn-20 nm film maintained the initial reflectivity even after immersion for 60 min, indicating the excellent sulfidizing resistance. As the

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4 thickness of top Ag layer increased to 100 nm, the reflectivity decreased in the whole
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6 wavelength range. In contrast, the reflectivity of the pure Ag-2.1 μm film decreased rapidly
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8 from 95% to 69% (480 nm) even after 3 min immersing. From the appearance of the films, the
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10 multilayered Sn/Ag films kept their mirror-like luster throughout the sulfidizing test, whereas
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12 the Ag films changed from silvery to yellow and lost the metallic luster. Moreover, it was also
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14 found that a tarnish phenomenon occurred for the Sn/CF-Ag film, which can be ascribed to the
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16 pure Ag top-layer on the film surface (refer to Figs.2 and 3b). This means that the completion
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26 Fig. 10b gives the reflective spectra of multilayered Sn/ Ag_3Sn films with Ag thickness of
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34 throughout the visible light wavelength after the severe combinatorial accelerated test, compared
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47 In order to clarify the mechanism of superior sulfidizing resistance of multilayered
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49 Sn/ Ag_3Sn films to pure Ag films, Fig.11 shows the XPS spectra at Sn 3d region for multilayered
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55 oxide in form of SnO and a shoulder peak close to metallic Sn, consistent to our previous study
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4 heating, the main peak of Sn/Ag₃Sn-20 nm film shifted toward the binding energy of SnO₂.
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8 of oxidization of Sn in Ag₃Sn alloy and/or thickening of tin oxide film. This suggested that
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14 film on the surface, thus inhibiting the chemical reaction of Ag and S²⁻ ions.
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23 **4. Conclusions**

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28 reflowed Sn layer on Cu alloy sheets as promising coating materials for LED lead-frames. The
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30 morphology, surface roughness, and crystalline structure of multilayered Sn/Ag-based films are
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32 mostly affected by the compositions of plating baths, in addition to the Ag electrodeposition
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34 conditions or film thickness. Multilayered Sn/Ag₃Sn films were achieved by using a cyanide
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36 electroplating bath with low Ag⁺ concentration and multilayered Sn/Ag films were formed from
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38 a cyanide-free plating bath with high Ag⁺ concentration. The multilayered Sn/Ag₃Sn film formed
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FIGURES and CAPTIONS

Table 1 EDS analysis results for the spots in TEM images in Fig.3.

Spot No.	Compositions (at.%)				Notes
	Ag	Sn	Cu	O	
1	70.71	24.45	4.11	0.73	Ag ₃ Sn
2	0	91.67	0.59	7.74	Sn
3	0	42.55	57.00	0.45	Cu ₆ Sn ₅
4	98.51	0	0.44	1.05	Ag
5	0	89.94	0.42	9.64	Sn
6	0.54	59.78	33.96	5.73	Cu ₆ Sn ₅

Table 2 EDS analysis results for the spots in TEM images in Fig.9.

Spot No.	Compositions (at.%)				Notes
	Ag	Sn	Cu	O	
1	75.5	22.76	1.33	0.83	Ag ₃ Sn
2	0.11	96.49	1.79	1.61	Sn
3	0.05	43.30	55.60	1.05	Cu ₆ Sn ₅
4	97.08	0	2.46	0.46	Ag
5	33.85	54.55	0.37	11.23	Sn+Ag ₃ Sn+Ag
6	0	88.27	0.66	11.07	Sn

Fig. 1 Surface FE-SEM images of (a–d) multilayered Sn/Ag films formed in (a, b) cyanide and (c, d) cyanide-free plating baths, and (e) a Sn-RF film before Ag electroplating and (f) a conventional bright Ag film on Cu alloys.

Fig.2 XRD patterns of as-deposited multilayered Sn/Ag films formed in (a, b) a cyanide bath with (a) C-Ag-100 nm and (b) C-Ag-300 nm, and (c) a cyanide-free bath with CF-Ag-100 nm on Cu alloy sheets.

Fig. 3 Cross sectional TEM images of as-deposited multilayered Sn/Ag films with Ag thickness of (a) C-Ag-100 nm and (b) CF-Ag-100 nm on Cu alloys and the corresponding selected area electron diffraction patterns.

Fig. 4 (a) AFM images and (b) roughness and grain size of multilayered various Sn/Ag-based films with different Ag thicknesses.

Fig.5 Total reflective spectra of as-deposited multilayered Sn/Ag films formed in (a) cyanide and (b) cyanide-free plating baths with different Ag thickness compared to conventional Ag, Au, and Sn-RF films on Cu alloys.

Fig.6 (a) diffractive and (b) specular reflective spectra of as-deposited multilayered Sn/Ag-based films with different Ag thickness compared to conventional Ag, Au, and Sn-RF films on Cu alloy sheets.

Fig. 7 Cross sectional TEM images of (a) $\text{Sn}/\text{Ag}_3\text{Sn}$ (C-Ag-100 nm) and (b) Sn/Ag (CF-Ag-100 nm) films after heating at 373 K for 120 h and the corresponding selected area electron diffraction patterns.

Fig.8 XRD patterns of multilayered Sn/Ag films with Ag thickness of (a) C-Ag-100 nm and (b) C-Ag-300 nm, and (c) CF-Ag-100 nm on Cu alloy sheets after heating at 393 K for 120 h.

Fig. 9 Reflective spectra of (a) Sn/Ag₃Sn and (b) Sn/Ag films with different Ag thickness before and after heating at 373 K for 120 h.

Fig. 10 Reflective spectra of (a) as-deposited and (b) posted-heated Sn/Ag₃Sn films with different Ag thickness before (dotted lines) and after immersing in a 2 ml/L (NH₄)₂S_x solution for 3 min (solid lines) and 3 h (circle marks).

Fig.11 High-resolution XPS spectra at Sn 3d energy regions of multilayered Sn/Ag₃Sn films with Ag thickness of (a) 100 nm and (b, c) 20 nm (b) before and (c) after heating at 373 K for 120 h.