Evaluation of Corrosion Resistance of Multilayered Sn/Ag_3Sn Electroplating on Cu Alloys for Electric Connectors

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Introduction. Recently, with the development of electronic systems equipped on automobiles, the sensors and/or connectors of the various electronic devices are increasingly being mounted close to the engine room or exhaust system. This required that the connectors must withstand higher temperature and more corrosive circumstance than usual throughout the whole life of vehicles. The conventional coating materials for electric connectors in automobiles mainly included various Sn films like electroplated Sn and hot-dip Sn, and the noble metal coatings like Au and Ag films. The Sn films are mostly used as general connectors because of the low cost and good soldering ability, but the temperature for stable electric contact resistance is usually not higher than 150 ºC. The noble metal coatings are usually used as special connectors for high reliability, though the cost is much higher than the Sn films.

In this study, we will report a novel multilayered Sn/Ag_3Sn film on copper alloy with low cost and high reliability, which is expected as a promising coating material for various electric connectors and terminals.[1-2] The present investigation focused on the evaluation of the corrosion resistance, *i.e.*, sulfuring resistance and anti-oxidation, of the multilayered Sn/Ag films compared to a commercial Ag film in 2-μm thick and a reflowed Sn film. The surface states and microstructures of the multilayered Sn/Ag films before and after corrosion tests were investigated by various analyzing methods, and the possible mechanisms were proposed according to the analyzing results.

Experimental. Multilayered Sn/Ag_3Sn films with Ag thickness in 30–80 nm were used as starting materials. A conventional Ag film in 2 μm thick and a reflowed Sn film in 1 μm thick were used as reference samples.

The high temperature oxidation resistance of the coating materials mentioned above was investigated by heating at 200 ˚C up to 3000 h. The corrosion resistance against sulfidation was evaluated by immersing in a 0.2 ml/L $(NH_4)_2S_x$ solution at 25 ˚C for 30 min – 100 h. The electrical contact resistance of the specimens before and after corrosion tests was measured by an electric contact simulator in a 4 terminal method vs. Au wire, with a sliding distance of 0.5 mm at low load from 0 to 50 g.

The specimens of the multilayered Sn/Ag_3Sn films before and after various corrosion tests were observed and analyzed by means of field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) with x-ray energy-dispersive analysis (EDS), x-ray photoelectron spectroscopy (XPS), glow discharge optical emission spectrometry (GDOES), Auger electron spectroscopy (AES), and time-of-flight secondary ion mass spectrometer (Tof-SIMS).

Results and Discussion. Fig. 1 exhibits a representative cross-sectional FE-SEM image of multilayered Sn/Ag_3Sn electroplating on Cu alloy. The Sn/Ag_3Sn film consisted of an Ag-Sn alloy film with 50 nm-thick ε–Ag_3Sn covered on a 1-μm-thick Sn film on Cu substrates, which is different from Sn-Ag alloy electroplating[3] and Sn-Ag hot-dip coatings[4]. The Sn/Ag_3Sn films exhibited low and stable electrical contact resistances of ~1 mΩ even after ageing at 200 ˚C for 3000 h, which is equivalent to those of as-plated samples, indicating an excellent electrical conductive stability. On contrast, the conventional reflowed Sn film and the Ag film showed every-increasing electrical contact resistance since 500 h and finally failed after ageing for 2000 h, beyond the measuring range of 2 Ω. The excellent stability of electrical contact resistance for the multilayered Sn/Ag_3Sn films can be mainly ascribed to the good oxidizing resistance of the Ag_3Sn and the inhibiting effect of the Ag from Ag_3Sn alloy against the Cu diffusion from the substrate materials.

Moreover, the multilayered Sn/Ag_3Sn films succeeded the accelerated sulfuring test, with unchanged appearance and stable electrical contact resistance, even lasting for 100 h. While the conventional Ag film and reflowed Sn film failed the sulfuring test, losing the glossy into a dark brown and delivering an ever-increasing contact resistance with prolonged immersing period. The excellent sulfuring resistance and durability of the Sn/Ag film can be mainly ascribed to the chemically stable Ag_3Sn alloy covered with a thin Sn oxide film, which enhanced the corrosion resistance of Ag-Sn alloy film and hindered the chemical reaction between the Ag and the S outside.

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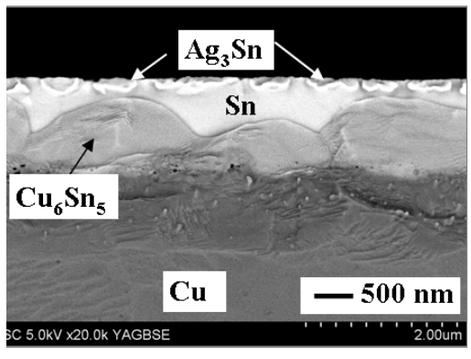

Fig.1 Cross-sectional FE-SEM image of a multilayered Sn/Ag_3Sn film on Cu alloy.