Preplating Process Characterization by Atmospheric Ultraviolet Photoelectron Counting

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大気中紫外線光電子計数法によるめっき前処理プロセスの評価

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Introduction

Many of the defects arising in plating technology are attributed to insufficient preplating treatment¹⁾; such treatment is selected empirically. It thus becomes essential to clarify the condition of the preplating-treated surface to develop a process that enables a stable production line.

We analyzed metal surfaces by using atmospheric-ultraviolet photoelectron counting (a-UPC)²⁾. This does not limit sample size, and enables rapid photoelectron measurement in the air. We then studied the surface change in the IC leadframe preplating process, focusing on degreasing.

Experiments

a-UPC measurement counts the photoelectrons emitted by the ultraviolet light in the air atmosphere. A comparison of photoelectron measurement in air and in a high vacuum agreed closely³⁾.

Using a surface analysis machine AC-1 (Rikken Keiki Co. Ltd.), the sample is illuminated by an ultraviolet beam grated by the monochrometer between 344 and 200 nm, corresponding to a light excitation energy between 3.4 eV and 6.2 eV. The plot of the photoelectron yield versus light energy reveals the rising photoelectron level (Fig. 1, arrow) which starts at the optical work function specific to the material (4.5 eV).

Plotting the square root of the yield of photoelectrons from metal versus energy usually shows

Fig. 1 Photoelectron intensity change versus ultraviolet light energy in preplating. Intensity increases with treatment (■ → □ → △ → + → ●), showing the removal of oil and the oxide layer. ■ As-stamped sample; □ After degreasing, △ After electropolishing, + After acid treatment. Measurement error is within 1.5 times of the size of each symbol. Light source power: 10nW, temperature: 22.4°C, relative humidity: 23%; light cross-section: 2 mm² at sample surface.

a linear trend. The thicker the contamination layer, the lower the gradient. It is thus possible to estimate surface cleanliness.

Stamped copper leadframe material MF-202 (Cu, Sn 2.0, Ni 0.2) was chosen as the sample.

Preplating was divided into four treatments: soak degreasing (silicate salt and potassium hydroxide solution), electropolishing (pyrophosphoric acid solution), acid pickling (sulfuric acid solution), and alkaline soak (cyanogen solution). The sample was rinsed with pure water between each treatment. Successive treatments were conducted using an autostrip plating machine. Sampling was done after each treatment, and ultra-dry room-temperature air was used to dry samples. An experiment was also conducted to determine degreasing liquid life. Here, each sample was taken only after soak degreasing with a controlled oil concentration. All a-UPC measurements were made within 20 minutes

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Fig. 2 Photoelectron intensity change versus ultraviolet light energy in copper oxide powder alone. The high-energy copper oxide plot corresponds to the high-energy metal plots in **Fig. 1** ($\square$, $\triangle$, and $+$).

after the sampling.

Results and Discussions

Untreated samples showed a low gradient due to the thick adhesion of the stamping oil (**Fig. 1**). After degreasing treatment, more electrons were counted, displaying a large gradient. After electropolishing, the plot showed a kink at about 5.4 eV. Acid treatment thus shows little change after electropolishing.

The plot after alkaline treatment shows a linear line beginning at 4.5 eV, coincident with the work function of copper⁴⁾. At this state, the surface is almost like the bare copper itself. Such a surface would tightly contact the plating metal.

The electropolished and acid-treated samples have the same work function as those alkaline-treated (**Fig. 1**). The change in gradient between 4.6 and 5.5 eV reflects exposure of the metal copper base.

In a-UPC measurement, the homogeneous contamination layer has a constant gradient; if the layer has two types of photoactive materials, the plot has a kink. To identify high-energy portions of plots exceeding 5.5 eV, we measured copper oxide samples (extra-reagent powder copper oxide I, copper oxide II, Kanto Kagaku Co. Ltd.). The high energy-portion begins at 5.1 eV and rapidly increases with the high energy-portion of the electropolished and acid-treated sample plots (**Fig. 2**). The high energy-parts of the electropolished and acid-treated plots are due to the existence of the copper oxide. Above 5.1 eV, the copper oxide provides enhanced photoelectron emission relative to the bare copper sample, but acts as an impediment between 4.5 and 5.1 eV (**Fig. 1**, $\triangle$ and $+$). The surface change in this preplating is as follows: First, the oil layer is removed by soak degreasing, then the oxide layer is removed after the alkaline soak.

Fig. 3 Photoelectron intensity change of soak degreased copper samples. With increased oil in the solution, degreasing power decayed above 0.2%.

The change due to electropolishing and acid pickling, however, remains unclear, and must be investigated further.

In the degreasing liquid life test, from no oil concentration to 0.20%, the same degreased surfaces are obtained (**Fig. 3**). Above 0.3%, the high energy-portion of the plot shifted to 4.9 eV and photoelectron yield decreased. These results indicate that the liquid's degreasing power decreased rapidly when oil content exceeded 0.2%. This data provides useful information on plant operation conditions. The difference in the photoelectron yield between **Fig. 1** and **3** is due to the difference in the base material. It should be noted that absolute measurement of photoelectrons by a-UPC is difficult, but the technique shows a precise relative surface change.

Even though surface change is not fully understood, this experiment shows that a-UPC can accurately characterize the preplating surface. a-UPC in combination with other methods, together with more data, will become a valuable tool in further surface finishing development.

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