In situ formation of Cu–Sn–Ni intermetallic nanolayer as a diffusion barrier in preplated lead frames

In the electronic industry, the manufacturing of semiconductor devices requires a lead frame as a support for mounting semiconductor chips and as an electrical connection between the chip and the wiring board. The widely used preplated lead frames (PPFs) comprise a Cu alloy base plated with Ni, Pd, and Au sequentially. The Ni layer is to provide the lead frame with oxidation and corrosion resistance by impeding Cu outdiffusion to the lead frame surface because Cu outdiffusion to and oxidation at the lead frame surface is the most severe failure mechanism of PPFs. In general, increasing the thickness of the Au/Pd/Ni layers improves the quality and reliability of PPFs, but increases the cost as well. The technical challenge is how to reduce the thickness of the Au/Pd/Ni layers while maintaining or even enhancing the PPF quality and reliability. In a previous work, an electrodeposition technique has been developed, which enables the production of low defect, continuous, and epitaxial Ni/Pd layers atop the Ni layer. The thicknesses of Pd and Au layers are reduced to 10 and 3 nm, respectively. The PPFs have 800–1000 nm thick Ni layers adhering to industry standards. A viable approach to reduce the Ni layer thickness with satisfied PPF quality and reliability would carry a definite advantage to the electronic packaging industry.

Introducing a nanometer-thick intermetallic-compound (IMC) layer is an effective means to meet such a requirement. The diffusivity of guest species in an IMC is in general much lower than that in respective metallic constituents due to the covalent bond of IMC that exhibits a higher energy barrier for the diffusive species to overcome. A typical example of utilizing IMC as a diffusion barrier is the Ni–Cd IMC (NiCd₂/NiCd₃) for protection of steel parts from oxidation. Furthermore, a 20 nm thick Cu₃Sn IMC overlayer on Cu interconnect surfaces was found to effectively block dominant surface diffusion paths, thus resulting in an increase of electromigration lifetime close to ten times. Tin easily forms IMCs in a wide temperature range with Cu or Ni. In the present work, a cold rolled sheet of Cu alloy was used as the base with composition of 2.35 wt % Fe, 0.12 wt % Zn, 0.07 wt % Sn, 0.03 wt % Cu, 0.03 wt % Ni, 0.01 wt % Fe, and 0.01 wt % Mg, while the Ni layer consists of 99.99% Ni. In what follows, a plating technique is developed for PPF manufacturing, by which a nano-Sn layer is introduced in between the Cu base and the Ni layer to form a Cu–Ni–Sn IMC interlayer. The resultant IMC layer is a more effective diffusion barrier than the bare Ni layer; thereby the oxidation and corrosion resistance of the PPFs is boosted.

A technique for impeding Cu outdiffusion in Cu alloy based preplated lead frames has been developed by electroplating a 3–4 nm thick Sn layer on a Cu alloy base prior to electroplating a Ni layer. A 10–14 nm thick epitaxylike and dense (Cu,Ni)₃Sn intermetallic-compound (IMC) layer is automatically formed en route of diffuse reaction, which leads to a drastic reduction in Cu outdiffusion and hence improves significantly the protection of the lead frames against oxidation and corrosion attack. The estimated Cu diffusion coefficient in the IMC interlayer is about 1.6 × 10⁻²² m²/s at 250 °C. © 2006 American Institute of Physics. [DOI: 10.1063/1.2352803]
P, and Cu in balance. Sn, Ni, Pd, and Au layers were plated in sequence on the base alloy by using the epitaxy electrodeposition technique. Conventional PPF samples without the Sn layer were prepared in the same way. The thicknesses of the Ni, Pd, and Au layers were measured after deposition by using the x-ray fluorescence technique with a film thickness measuring system (Micron X of Thermo NORAN). The measured results were tabulated in Table I. The effectiveness of the introduced nano-Sn layer in the enhancement of the PPF oxidation resistance was examined by a consecutive annealing and testing experiment, in which a sample was annealed at 250 °C in air for a period of time, then taken out for composition analysis, then annealed at 250 °C again, and so on.

Transmission electron microscopy (TEM) was employed to characterize the microstructure of the PPFs. Figures 2(a) and 2(b) are cross-sectional TEM images, showing the

<table>
<thead>
<tr>
<th></th>
<th>Sn</th>
<th>Ni</th>
<th>Pd</th>
<th>Au</th>
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</thead>
<tbody>
<tr>
<td>Developed PPF sample</td>
<td>3–4</td>
<td>182</td>
<td>10.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Conventional PPF sample</td>
<td>Nil</td>
<td>190</td>
<td>10.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Au/Pd/Ni/Cu and Au/Pd/Ni/IMC/Cu microstructures, respectively, of the conventional and developed PPF samples. Clearly, a 10–14 nm thick, dense, and continuous IMC interlayer is formed between the Cu base and the Ni layer after annealing the developed PPF sample at 250 °C for 810 min. Outside the Au flash there is a layer with a thickness between 57 and 100 nm for the conventional PPF sample, as shown in Fig. 2(a), while its thickness is around 5 nm, which is barely seen in Fig. 2(b), for the developed PPF sample with the Sn interlayer. Energy dispersive x-ray (EDX) analysis with a 1 nm electron beam size proved the most outside layer to be a CuO layer with a near 1:1 Cu/O atomic ratio, which was consistent with the prediction of the Cu–O phase diagram. The EDX analysis was also conducted to investigate the composition of the IMC interlayer, resulting in a (Cu,Ni)/Sn atomic ratio of 73.29:26.71 and a Cu/Ni atomic ratio ranging from 1/2 to 2. Thus, the interlayer must be a mixture of Cu<sub>2</sub>NiSn and CuNi<sub>2</sub>Sn IMCs. A high-resolution TEM micrograph of the Ni/IMC/Cu layered structure is shown in Fig. 3, where the beam axis is along the (111) direction with respect to the Cu substrate. The inset is the FFT diffraction pattern of the IMC interlayer. Energy dispersive x-ray (EDX) analysis with a 1 nm electron beam size proved the most outside layer to be a CuO layer with a near 1:1 Cu/O atomic ratio, which was consistent with the prediction of the Cu–O phase diagram. The EDX analysis was also conducted to investigate the composition of the IMC interlayer, resulting in a (Cu,Ni)/Sn atomic ratio of 73.29:26.71 and a Cu/Ni atomic ratio ranging from 1/2 to 2. Thus, the interlayer must be a mixture of Cu<sub>2</sub>NiSn and CuNi<sub>2</sub>Sn IMCs. A high-resolution TEM micrograph of the Ni/IMC/Cu layered structure is shown in Fig. 3, where the beam axis is along the (111) direction with respect to the Cu substrate. The fast Fourier transformation (FFT) diffraction pattern of the IMC interlayer is also given as inset in Fig. 3, indicating that the (Cu,Ni)<sub>2</sub>Sn IMC resembles an L2<sub>1</sub>-type super lattice.

In the consecutive annealing and testing experiment, the samples were annealed at 250 °C in air for a series of durations from 10 to as long as 810 min. The composition analysis was conducted by EDX incorporated in a scanning electron microscope. An acceleration voltage of 7.5 kV and a working distance of 10 mm were maintained unchanged during all tests to ensure that the detected Cu content was totally from the surface and the probed volume could be treated as a constant provided that the penetration depth of the electron beam and the gain of the resultant x-ray do not vary significantly with the increasing oxide thickness. The EDX composition analysis further verified that Cu was oxidized into CuO at 250 °C in air. The Pd and Au layer thicknesses were 10.7–10.5 and 1.6–1.7 nm, respectively, which were unchanged during the annealing at 250 °C in air such that the Pd or/and Au absolute quantity per unit area was taken as a reference to estimate the absolute value of CuO thickness from the EDX analysis.
results. The determined thickness of the oxide layer is illustrated in Fig. 4 as a function of annealing time for both developed and conventional PPF samples.

The oxidation model proposed by Deal and Grove is slightly modified here for quantitative analysis of the experimental results. In the modified version, Cu atoms or ions diffuse across the copper oxide and oxidize at the surface. For the developed PPF samples, the Cu concentrations at the downward and upward interfaces of the IMC layer are denoted by \( C^* \) and \( C \), respectively. The Cu flux from the Cu alloy base through the IMC layer is then given by \( F_0 = D_{\text{Cu}}^{\text{IMC}} \left( C^* - C \right)/l \), where \( D_{\text{Cu}}^{\text{IMC}} \) is the effective diffusion coefficient of Cu in the IMC layer and \( l \) is the IMC layer thickness. The Cu flux going through the composite Ni/Pd/Au barrier layer is estimated by \( F_1 = h \left( C^* - C_0 \right) \), where \( h \) is an effective Cu transport coefficient and \( C_0 \) denotes the Cu concentration at the vicinity of the interface between the composite layer and the oxide layer. The Cu flux inside the oxide layer is described by \( F_2 = D_{\text{CuO}}^{\text{IMC}} (C_0 - C)/x \), where \( D_{\text{CuO}}^{\text{IMC}} \) is the effective Cu diffusion coefficient in the oxide, \( C_0 \) is the Cu concentration near the oxide surface, and \( x \) denotes the oxide thickness. The rate of oxidation reaction is assumed to be of the first order and given by \( F_3 = k C_1 \), where \( k \) denotes the rate constant. Flux continuity requires \( F_0 = F_1 = F_2 = F_3 = F \). By eliminating \( C_0 \) and \( C_1 \), \( F \) is reexpressed as

\[
F = \frac{C^*}{1/k + 1/h + l/D_{\text{IMC}}^{\text{Cu}} + x/D_{\text{CuO}}^{\text{IMC}}}.
\]  

(1)

The rate of the oxidation reaction indicates the growth rate of the oxide layer to be \( dx/dt = F/N \), where \( N \) is the atomic density of the oxide, thereby leading to an explicit formula to predict the oxide layer thickness as a function of time, i.e.,

\[
x(t) = \left( 1 + \frac{t}{A^2/4B} \right)^{1/2} - 1,
\]  

(2)

with \( A = 2D_{\text{CuO}}^{\text{IMC}} (1/k + 1/h + l/D_{\text{IMC}}^{\text{Cu}}) \) and \( B = 2D_{\text{CuO}}^{\text{IMC}} C^*/N \). For the conventional samples without the Sn interlayer, \( l = 0 \) and \( A \) is reduced to \( A_0 = 2D_{\text{CuO}}^{\text{IMC}} (1/k + 1/h) \). Equation (2) is used to fit the experimental data and the fitting curves are plotted in Fig. 4 also. From the fitting, parameters \( A_0, A, \) and \( B \) are determined to be \( A_0 = 15.6 \times 10^{-10} \) m, \( A = 552 \times 10^{-9} \) m, and \( B = 1.25 \times 10^{-9} \) m²/s.

The above analysis also gives

\[
\frac{l}{D_{\text{Cu}}^{\text{IMC}}} = \frac{C^* A - A_0}{N B},
\]  

(3)

which is used to estimate the effective diffusion coefficient of Cu in the IMC interlayer. The thickness of the IMC can be obtained from TEM observation as \( l = 12.5 \) nm. Simplifying the Cu alloy to be pure Cu gives \( C^*/N = (\rho_{\text{CuO}}/N_{\text{CuO}})/(\rho_{\text{Cu}}/N_{\text{Cu}}) = (8.9/63.5)/(6.3/79.5) = 1.77 \), where \( \rho \) and \( N \) are, respectively, the density and mass number for either Cu or CuO. The effective diffusion coefficient of Cu in the IMC interlayer is then estimated to be \( D_{\text{Cu}}^{\text{IMC}} = 1.6 \times 10^{-22} \) m²/s. On the other hand, the diffusion coefficient of Cu in the CuO can also be obtained, i.e., \( D_{\text{Cu}}^{\text{CuO}} = (BN)/(2C^* + 3.54 \times 10^{-20}) \) m²/s, which is more than two orders of magnitude as large as \( D_{\text{Cu}}^{\text{IMC}} \).

In conclusion, by the introduction of a 3–4 nm Sn layer in between the Cu alloy base and the Ni plating, the \textit{in situ} formed 10–14 nm thick epitaxy like (Cu,Ni)Sn IMC interlayer is an effective barrier against Cu outdiffusion to and oxidation at the lead frame surface due to the low diffusivity of Cu in the IMC interlayer. Although the Cu–Sn–Ni multilayer structure, featured with an ultrathin Sn layer, is studied mainly for the purpose of oxidation protection of PPFs used in the microelectronic devices, the approach can also be extended to more general industrial applications where protection of metals from oxidation and corrosion is required.

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