Interfacial Reactions between Liquid Indium and Nickel Substrate

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The morphologies and growth kinetics of intermetallic compounds for the interfacial reaction between liquid In and solid Ni substrate in the temperature range from 225 to 500°C are examined in this study. Experimental results showed that the thickness of intermetallic compounds formed during the Ni/In interface reaction increased with the reaction temperature and the square root of reaction time. The X-ray diffraction pattern revealed the formation of intermetallic compounds Ni10In27 (T<300°C) and Ni2In3 (T>300°C). Moreover, the activation energies for the interdiffusion of Ni and In atoms in the Ni10In27 and Ni2In3 are 94.74 and 33.51 kJ/mol, respectively. Using the Ta thin film as a diffusion mark, the formation mechanism of intermetallic compounds during interfacial reaction was clarified.

Key words: Activation energy, indium, intermetallic compound, nickel

INTRODUCTION

Soldering is a low-temperature joining process commonly used for electronic packaging.1 During soldering, the solder alloy melts and reacts with the substrate to form intermetallic compounds at the joining interface. The formation of intermetallic phases at the solder joint could cause mechanical failure during thermal or power cycling.2 Therefore, a knowledge of intermetallic phases produced by soldering in electronic packaging is essential. Among many solder alloys, Pb-Sn solders have been most commonly used.3 However, since Pb will induce environment pollution,4 the development of Pb-free solders should thus be of vital importance for the electronic industry in the future. Several Pb-free solders4,5 have been developed for electronic packaging. Jin et al.6 developed a Bi-43%Sn solder containing Fe dispersoid particles, which had better microstructure stability and superior creep resistance compared to the Pb-Sn eutectic solder. The growth kinetics of Ni-Sn intermetallic phases at the liquid Sn and solid Ni interface has been investigated by Kang et al.7 In their work, both Ni3Sn4 and Ni5Sn3 were observed and parabolic kinetics was obeyed for the growth of intermetallic compounds.

The In-alloy solders possess a longer fatigue life than conventional Pb-Sn solders for flip-chip interconnections in thermal shock tests between room temperature and liquid nitrogen.8 Some studies have been performed on the interfacial reactions between In and Cu. Kao9 found that Cu11In9, Cu7In3, and Cu2In formed in the solid Cu/liquid In interface. Manna et al.10 studied the interdiffusion between In and bulk Cu and Cu-In alloy isothermally annealed at 373, 398, and 423K for varying lengths of time. They found the growth rates of intermetallic layers to follow parabolic kinetics. The activation energy for Cu (In) interdiffusion was 26.07 kJ/mol and for Cu-In (In) was 26.42 kJ/mol. With the exception of these efforts, no other information is yet available on the interfacial reaction between In and Ni.

In the present work, the morphologies and growth kinetics of intermetallic compounds during the reaction of liquid In with solid Ni were analyzed in the temperature range from 225 to 500°C. For the identification of intermetallic compounds, both electron microprobe (EPMA) and X-ray diffraction (XRD) were employed.

EXPERIMENTAL

Nickel substrates (15 mm × 15 mm) were cut from a 0.8 mm thick high-purity Ni plate (Ni-99.5%). Their surfaces were prepared by grinding with 1500 grit SiC paper and polishing with 0.3 μm Al2O3 powder.
Indium plates (In-99.99%) with dimensions of $3 \times 3 \times 3$ mm$^3$ were laid on the Ni substrates. The SMQ TACFLUX 005 flux was used in this test. Table I lists the characteristics of this flux.

Interfacial reactions were carried out at temperatures ranging from 225 and 500°C in an infrared furnace for various periods of time in a vacuum of $10^{-3}$ Torr. After the reactions, In was selectively etched from the Ni/In specimens using an aqueous solution of $7\text{g NH}_4\text{F} + 10\text{ml H}_2\text{O}_2$. The intermetallic compounds were analyzed using XRD. In order to examine the growth kinetics of intermetallic compounds during interfacial reactions, the cross sections of all specimens were observed with a scanning electron microscope (SEM) and average thicknesses of the intermetallic layer were given for the analyses at five points. The In contents in intermetallic compounds were further examined by EPMA. The measurements are known to be within $\pm 0.05$ at.%. Combining the results of XRD and EPMA analyses, the intermetallic compounds that form through the interfacial reactions between liquid In and Ni substrate were identified. For further clarification of the formation mechanism of intermetallic compounds in the interfacial reaction, the original Ni$_n$/In$_l$ interfaces were marked by sputtering-deposition of a Ta thin film on the partial region of Ni substrates. From the phase diagram, it can be seen that Ta will not react with Ni and In, the deposition of Ta thin film acted as a diffusion barrier at Ni$_n$/In$_l$ interface. The original Ni$_n$/In$_l$ interface can thus be identified.

**RESULTS AND DISCUSSION**

When the specimens were heated above the melting temperature of In (157°C), the molten In reacted with Ni substrate and immediately formed intermetallic compounds (Ni$_x$In$_y$) at the Ni$_n$/In$_l$ interface. According to the Ni-In phase diagram, several intermetallic phases such as Ni$_3$In, Ni$_2$In, Ni$_3$In$_9$, NiIn, Ni$_{13}$In$_9$, and Ni$_{10}$In$_{27}$ could form. However, the x-ray diffraction patterns only revealed the phases Ni, In, and Ni$_{10}$In$_{27}$ for the samples reacting below 300°C (Fig. 1a). When the reaction temperatures increased above 300°C, Ni, In, and Ni$_2$In$_3$ were detected (Fig. 1b). The chemical compositions of interfacial reaction products were also analyzed by using EPMA, the results are shown in Table II. In Table II, average data were given for the analyses at five points, revealing that the primary intermetallic compound formed below 300°C was Ni$_{10}$In$_{27}$, and above 300°C changed to Ni$_2$In$_3$.

The typical morphologies of Ni$_n$/In$_l$ interfacial microstructure in dependence of reaction temperatures and times are shown in Fig. 2. Small nuclei of intermetallic compounds are found randomly along the Ni/In interface at 250°C for 15 min, which revealed the early step of interfacial reaction (Fig. 2a). A continuous intermetallic layer grew slowly with the increase of reaction time (Fig. 2b). At 450°C, the continuous intermetallic layer formed even after a

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**Table I. The Characteristics of SMQ TACFLUX 005 Flux**

<table>
<thead>
<tr>
<th>Flux Type</th>
<th>Flash Point</th>
<th>Solid Content</th>
<th>Viscosity (25°C)</th>
<th>Max. use Temp.</th>
<th>Residue Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMA</td>
<td>66°C</td>
<td>14%</td>
<td>68,000±10% cps</td>
<td>300°C</td>
<td>Water</td>
</tr>
</tbody>
</table>

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Fig. 1. Typical x-ray diffraction patterns of the Ni$_n$/In$_l$ interfacial reaction products formed below and above 300°C: (a) 300°C, and (b) 450°C.

Fig. 2. Typical morphologies of the Ni$_n$/In$_l$ interfacial reaction products formed under various temperatures at various times: (a) 250°C, 15 min, (b) 250°C, 135 min, (c) 450°C, 15 min, and (d) 450°C, 135 min.