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Formation of $PtSn_4$ and PtSn in the initial reaction between Pt and molten Sn

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ABSTRACT

The initial reaction between Pt and molten Sn has been studied by dipping tests of 1 and 2 s. It was found that both PtSn and $PtSn_4$ formed in the first second of contact. PtSn formed 7 nm (1 s) and 20 nm (2 s) thick layers on top of the Pt substrate but $PtSn_4$ formed scattered particles in the liquid Sn. No orientation relationship was found between Pt and PtSn. PtSn nucleates heterogeneously on Pt by its larger energy of formation than $PtSn_4$ and $PtSn_4$ nucleates in liquid Sn by the very low solubility of Pt in molten Sn.

1. Introduction

Platinum is a noble metal and can be used as a base metal or metallization layer on integrated circuits because of its high oxidation resistance, low dissolution rates [1–4] and acceptable wetting properties [1] in molten solders. However, experimental studies of its reaction with Sn or Sn-containing solders are very limited. In reflow process, the intermetallic compound (IMC) $PtSn_4$ was observed to form first [1,2,5,6] and Pt_3Sn and Pt_2Sn_3 formed afterward with further exposure [1]. In solid/solid reaction only the formation of $PtSn_4$ was reported [4,7]. Clearly, the understandings of the sequence and the mechanisms of the formation of the Pt-Sn IMCs are far from complete. Further detailed research work is necessary for the application of Pt in microelectronic industries.

The purpose of this research was to study the very early stage reaction between Pt and molten Sn. The IMCs formed and the possible orientation relationships at their interfaces were studied using transmission electron microscopy (TEM) and high-resolution TEM. The reactions were performed by dipping tests of very short time, only 1 and 2 s. The formation mechanisms of the observed IMCs at the Pt/Sn interface were discussed.

2. Experimental details

Pt foil (99.9% pure) 0.1 mm thick was cut into 15 mm × 5 mm rectangles and was fully annealed in vacuum at 1200 °C for 6 h to enlarge its grain size. The Pt foils were degreased with acetone and the cleaned by dipping in a 7 ml HCl + 1 ml HNO_3 + 8 ml H_2O solution for several minutes. Then the Pt foils were then cleaned with acetone, methanol and deionized water and were immediately dipped into a molten Sn bath (99.97% pure) at 240 ± 1 °C for 1 or 2 s and followed by quenching in ice water. The specimen surfaces were studied with a scanning electron microscope (SEM, JEOL JSM–6330, 5–10 kV). X-ray diffraction (XRD, Simens D5000) was conducted by using a Cu target and scanned at a step rate of 0.04° per second. The Sn on the specimen surface was removed.

The layer of Sn and IMCs on the surface of the reacted specimen were first thinned by polishing with abrasive papers. The remaining Sn was then carefully partially removed by electrochemical reduction with K–50 solutions (Kokico., Tokyo, Japan). The partial removal of Sn was important because some IMC particles could be retained for observation by the small amount of Sn left on the surface. Otherwise only the IMCs directly attached to the Pt surface could be studied. TEM specimens were prepared by focused ion beam. Selected area diffraction (SAD), bright and dark field images, and high-resolution lattice-fringes images by TEM (Philips, CM200, operating at 200 kV) were used for analysis.

3. Results

Fig. 1 is the XRD pattern of the specimen surface dipped in liquid Sn for 2 s. Weak peaks of $PtSn_4$ were detected. A typical SEM micrograph of the specimen surfaces after dipping is shown in Fig. 2. The surface is already densely covered with IMCs and the larger ones are plate-like. These are $PtSn_4$, as has been reported in the literature [1,2,5,6], and was confirmed by X-ray diffraction (results not shown) and the following TEM analyses. The characteristic plate-like morphology was

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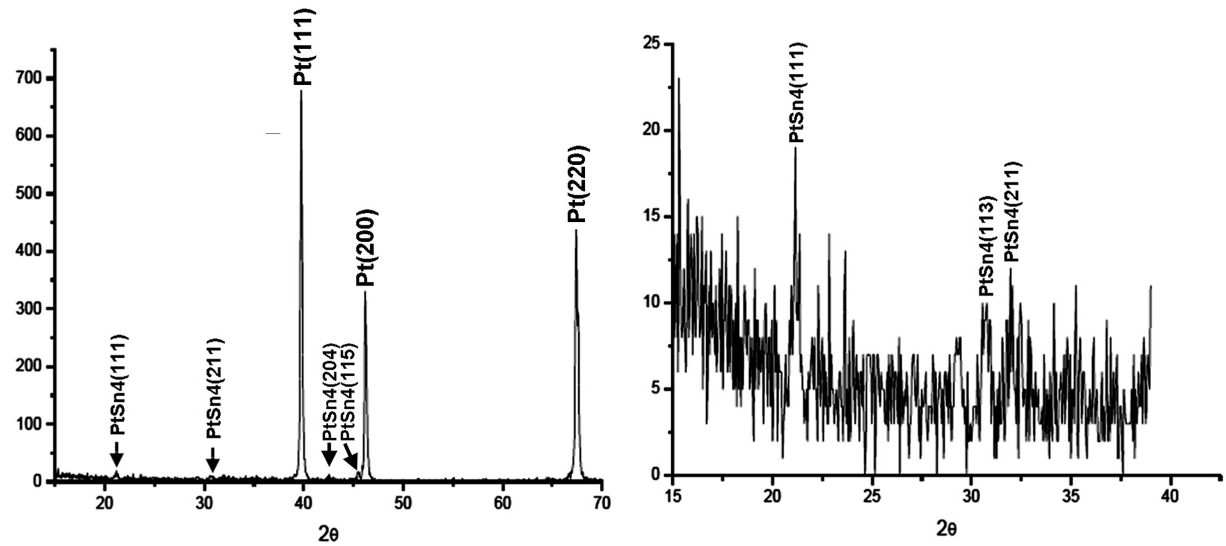

Fig. 1. XRD pattern of the specimen surface dipped in liquid Sn for 2 s.

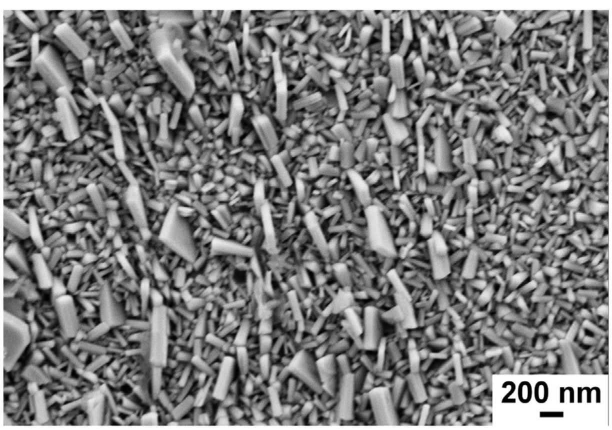

Fig. 2. SEM micrograph of the specimen surface dipped in liquid Sn for 2 s.

analyzed and the plate surface was shown to be the (001) plane [8].

Fig. 3 shows the cross-sectional view of the specimen dipped for 1 s. Above the interface, marked as C, many IMC particles were successfully retained by Sn. TEM SAD pattern confirmed that these particles are

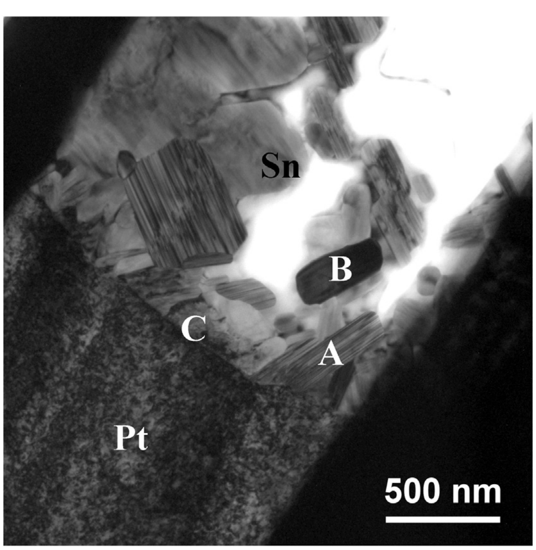

Fig. 3. Cross-sectional view of the Pt interface of the specimen dipped for 1 s.

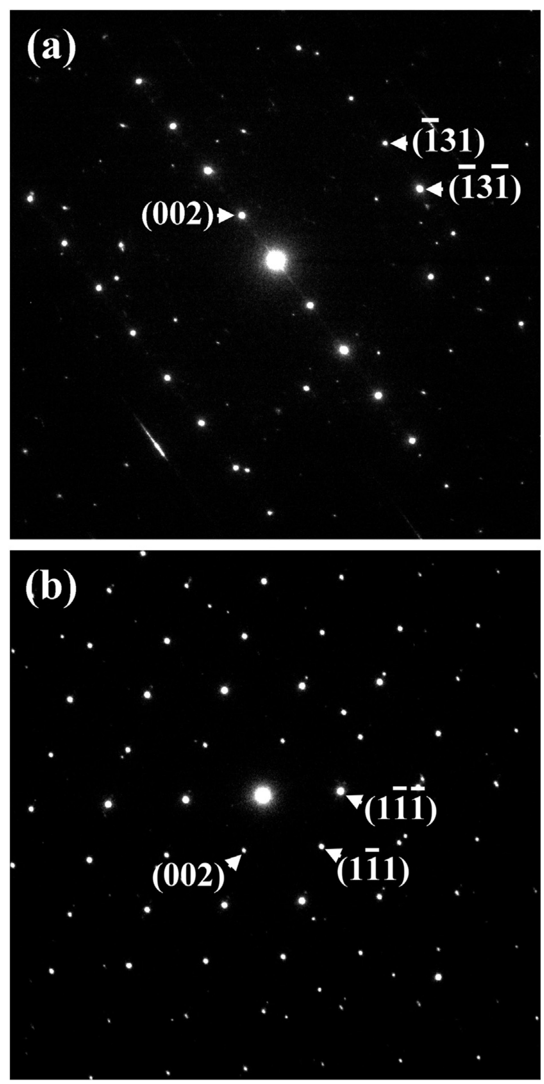

Fig. 4. (a) TEM SAD pattern of particle A in Fig. 3, showing it is $PtSn_4$ in the [310] zone. (b) The same of particle B in the [110] zone.