Mechanical properties of intermetallic compounds in electrodeposited multilayered thin film at small scale by nanoindentation

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ABSTRACT

Mechanical properties of intermetallic compounds (IMCs) which were formed in electrodeposited Cu/Sn and Cu/Ni/Sn multilayered thin film have been investigated. The layers of Cu, Sn and Ni were formed by electrodeposition technique using copper pyrophosphate, tin methanesulfonic and nickel Watts baths, respectively. After synthesis, samples were subjected to high temperature aging at 150 °C for 168 h. Two different types of intermetallics Cu_3Sn and Cu_6Sn_5 were formed in Cu/Sn. After adding ultra-thin layer of Ni (70 nm) in between Cu and Sn layers, $(Cu, Ni)_6Sn_5$ was formed after aging at similar condition to that of Cu/Sn. Tin whisker growth was not observed in both samples after preserving the samples in air for 365 days. Hardness and elastic moduli of all three different types of IMCs were measured by using a Hysitron Triboindenter 750 Ubi system. Hardness of the three IMCs Cu_3Sn, Cu_6Sn_5, $(Cu, Ni)_6Sn_5$ and Cu were found to be 5.99, 6.61, 7.43 and 1.55 GPa, respectively. The addition of Ni suppressed the growth of Cu_3Sn greatly. This is expected to lead to better reliability of electronic interconnections as Cu_3Sn is often associated with void formation.

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1. Introduction

Growth of tin whisker has detrimental effect on electrical devices. Although effect of tin whisker in electronics is known since the early 20th century, growth mechanism is still not well understood. Rapid growth of tin whisker on lead-free Sn solder alloy has been reported elsewhere [1–4]. Recently, Sun et al. suggested the mechanism of tin whisker growth [5]. Traditionally, lead was used to suppress the growth of tin whisker. However, lead was banned due to its detrimental effects on human health by European Union. Many electronic devices failed because of tin whisker growth which causes short-circuit as it can conduct electricity to the neighboring parts within the device. It may cause major havoc in large facility such as nuclear reactor and satellite [6]. As future microelectronics inevitably moves toward nano-scale devices, this could be one of the important issues to be addressed to ensure reliability of the electronic devices. Multilayered thin film interconnects could be one possible solution to this problem. This could be applicable in miniature devices with a possibility to prevent tin whisker growth.

We used electrodeposition technique to synthesize Cu/Sn and Cu/Ni/Sn multilayered thin film [7]. Reliability of the interconnects greatly depends on the mechanical properties of the IMCs. Therefore, it is very important to understand the mechanical properties of these IMCs in thin film. Thus we investigated mechanical properties of the IMCs by using nanoindentation technique [8]. To the best of our knowledge, there is no study which reports on the mechanical properties of IMCs formed on electrodeposited Cu/Sn and Cu/Ni/Sn multilayered thin film at small scale by nanoindentation.

2. Experimental

The layers of Cu, Sn and Ni were formed by electrodeposition using copper pyrophosphate, tin methanesulfonic and nickel Watts baths, respectively [9]. Deposition current density was set at 10 mA/cm^2 for the copper bath and 20 mA/cm^2 for tin and nickel baths. Cu/Sn and Cu/Ni/Sn thin films were prepared in the sequence of Cu/Sn/Cu/Sn/Cu and Cu/Ni/Sn/Ni/Cu/Ni/Sn/Ni/Cu, respectively. After preparation, short reflow was done in a FT-02 convection reflow oven at 250 °C for 60 s followed by high temperature aging at 150 °C for 168 h in a Memmert oven. Samples were then mounted in epoxy resin for microstructure investigation. Progress of solid state reaction in the multilayered films was monitored by using a FEI Quanta 450 field emission scanning electron microscope (FESEM) and energy dispersive x-ray spectroscopy (EDX). Mechanical properties of intermetallic compounds (IMCs) were obtained by using a Hysitron Triboindenter 750 Ubi system at ambient temperature. A Berkovich diamond indenter tip was used to measure hardness and elastic moduli of the IMCs. Indenter tip was held at the peak load, 4 mN for 20 s at each indent spot maintaining

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minimum drift rate at ≤ 0.05 nm/s. Hardness, H, was defined by

$$H = \frac{P_{max}}{A} \quad (1)$$

where P_{max} is maximum indentation load and A is the resultant area of contact that corresponds to that load. The reduced elastic modulus, E_r, was defined as

$$E_r = \frac{S\sqrt{\pi}}{2\sqrt{A}} \quad (2)$$

where S is the stiffness of unloading curve and A is the projected area. Initial unloading stiffness contact can be defined as

$$S = \frac{dP}{dH} \quad (3)$$

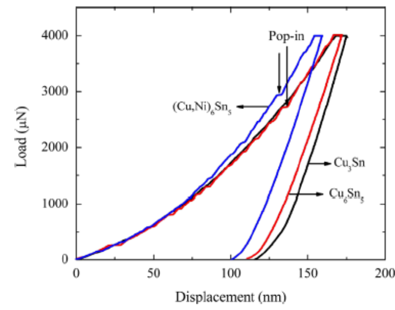

Fig. 2. Representative load–displacement curves from nanoindentation on the cross-section of IMC layers.

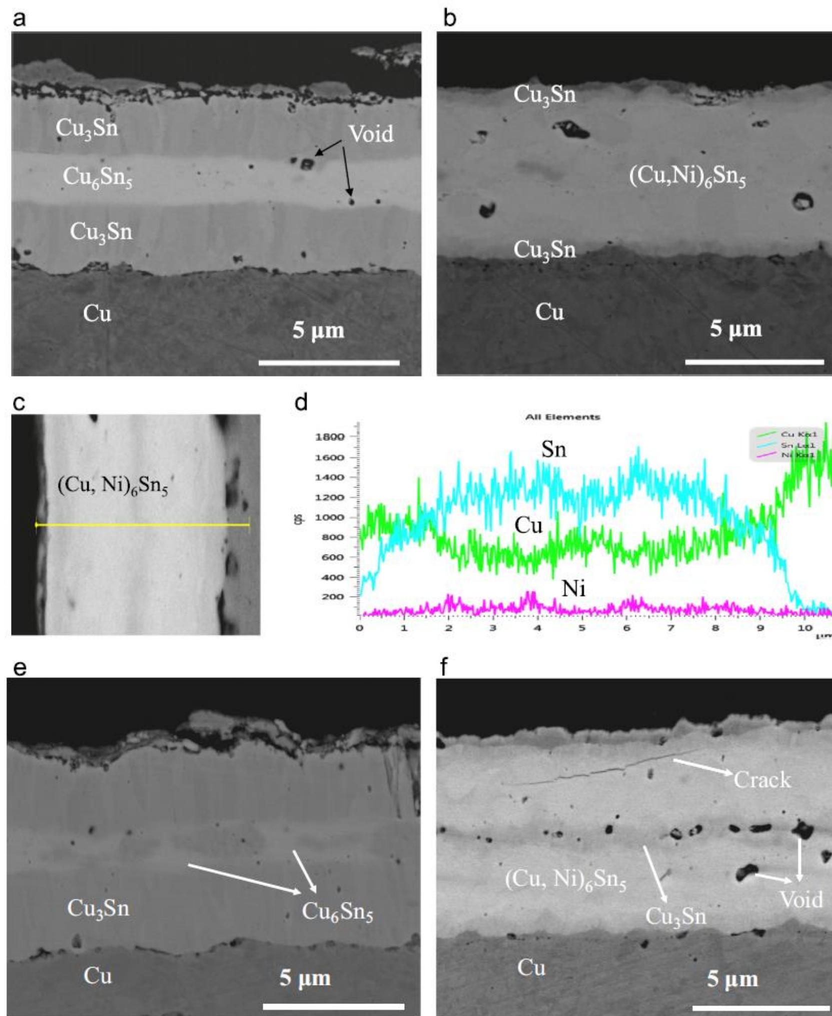

Fig. 1. FESEM cross sectional images of electrodeposited Cu/Sn (a) and Cu/Ni/Sn (b) multilayer thin film after 168 h of solid state aging at 150 °C. Elemental analysis on a line (c) of IMC layer in Cu/Ni/Sn system by EDX (d). FESEM images of Cu/Sn (e) and Cu/Ni/Sn (f) after 365 days of preservation in air.

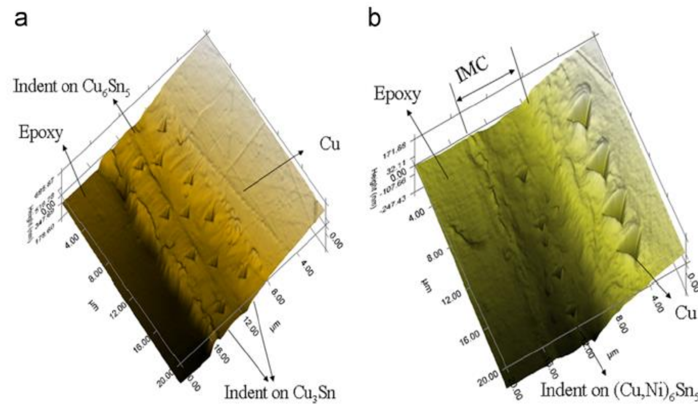

Fig. 3. Typical 3D SPM images of (a) Cu_3Sn, Cu_6S_5 and (b) (Cu, Ni)$_6$Sn$_5$, Cu after nanoindentation.

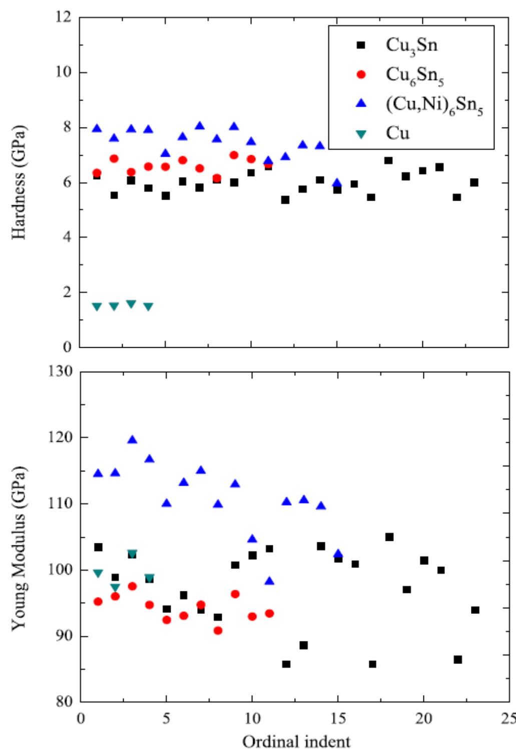

Fig. 4. Hardness and elastic moduli of three different types of IMCs Cu_3Sn, Cu_6Sn_5, (Cu, Ni)$_6$Sn$_5$ and Cu measured for each nanoindent.

Elastic modulus can be obtained from the following equation if the sample and diamond indenter tip are subjected to elastic deformations:

$$\frac{1}{E_r}=\frac{1-\nu_s^2}{E_s}+\frac{1-\nu_i^2}{E_i} \tag{4}$$

where E_s and ν_s are elastic modulus and Poisson ratio of the sample,

Table 1
Elastic moduli and hardness of Cu_3Sn, Cu_6Sn_5 (Cu, Ni)$_6$Sn$_5$ and Cu obtained by nanoindentation.

Material	Elastic moduli (GPa)	Hardness (GPa)	Ref.
Cu_3Sn	97.25 ± 7.34	5.99 ± 0.39	This work
	132.17 ± 3.63	6.34 ± 0.14	[11]
	134.2 ± 6.7	6.12 ± 0.17	[16]
Cu_6Sn_5	94.30 ± 2.36	6.61 ± 0.25	This work
	112.3 ± 5.0	6.38 ± 0.21	[16]
	97.0 ± 3.0	5.7 ± 0.5	[12]
(Cu, Ni)$_6$Sn$_5$	110.80 ± 5.05	7.43 ± 0.57	This work
	160.0 ± 4.9	7.3 ± 1.2	[12]
	157.82 ± 5.69	7.24 ± 0.44	[17]
Cu	99.66 ± 2.02	1.55 ± 0.044	This work
	116 ± 4.7		[16]
	140 ± 9	1.7 ± 0.2	[18]

respectively. E_i and ν_i correspond to elastic modulus and Poisson ratio of the diamond indenter, respectively. For a diamond tip, E_i = 1140 GPa and ν_i = 0.07 [10]. On the other hand, ν_s was assumed to be 0.299 for Cu_3Sn, 0.309 for Cu_6Sn_5 [11], 0.3 for (Cu, Ni)$_6$Sn$_5$ [12] and 0.33 for Cu [13].

3. Results and discussion

Fig. 1a shows the cross-sectional image of electrodeposited Cu/Sn multilayered thin film after 168 h of aging at 150 °C. Regions with the darkest contrast at the bottom shows Cu substrate, while regions with lighter contrast shows two different IMC phases. The IMC phases were identified based on the ratio of concentration of constituent elements measured by EDX. The IMC phase with darker gray represent Cu_3Sn phase while the lighter gray represents Cu_6Sn_5 [14,15]. In Fig. 1b, regions with brighter contrast represents (Cu, Ni)$_6$Sn$_5$ IMC phase. The thin gray layers in between (Cu, Ni)$_6$Sn$_5$ phase and Cu substrate is shown to be Cu_3Sn phase. With the addition of Ni, the thickness of Cu_3Sn decreases considerably as the growth of Cu_3Sn phase seemed to be suppressed with the presence of Ni. Average concentration of Ni was found to be about 5% in the (Cu, Ni)$_6$Sn$_5$ IMC from the EDX analysis (Fig. 1d) which was measured on the line shown in Fig. 1c. Tin whisker growth was not observed in both samples. One of the reasons for tin whisker growth is IMC formation that alter the lattice spacing in the tin plating. This change in lattice spacing could cause stress to the tin plating which form tin whisker as a process to release stress. However,

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