

Elasticity modulus, hardness and fracture toughness of Ni₃Sn₄ intermetallic thin films

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Abstract

Intermetallic compounds (IMCs) are present in microelectronic solder interconnects as a result of interfacial reaction between the solder and the metallization materials. Their mechanical properties are of great interest for the prediction of joint reliability of electronic packages. In this work, thin film Ni₃Sn₄ IMCs were formed by co-sputtering of Sn and Ni, followed by annealing at different temperatures. Elasticity modulus and hardness of the films were investigated by nano-indentation. It was found that measured hardness decreased with increasing residual tensile stress in the film. The elasticity modulus of the Ni₃Sn₄ thin films was measured to be around 134 GPa by nano-indentation. The fracture toughness of these Ni₃Sn₄ thin films varied considerably with the annealing temperature. It ranged from $2.11 \pm 0.15 \text{ MPa m}^{1/2}$ for 100 °C annealing to $5.75 \pm 0.25 \text{ MPa m}^{1/2}$ for 200 °C annealing. Densification during annealing is believed to be the cause of the increase in toughness. © 2006 Elsevier B.V. All rights reserved.

Keywords: Thin film; Intermetallic compound; Fracture toughness; Elasticity modulus; Indentation hardness

1. Introduction

Solder joints provide electrical connection, mechanical support and thermal dissipation routes for microelectronic devices. An important constituent of a solder joint is the intermetallic compound (IMC), which is formed between the solder and metallization pads during soldering. The physical properties of IMCs, including elasticity modulus, hardness, fracture toughness, coefficient of thermal expansion, thermal conductivity and heat capacity have been focus of numerous research efforts [1–10]. As the down-scaling of feature sizes of microelectronic devices continues, the volume fraction of the IMC in a solder joint will increase further, making it an indispensable component to be considered in determining the device performance and reliability. In the past, work on IMCs in electronic packaging was mainly focused on Cu–Sn system (Cu₆Sn₅, Cu₃Sn) because of the predominant use of Cu as metallization material [11]. With the wide-spread use of lead-free solders in recent years, there is an increasing concern about the reliability of packages with Cu metallization. This is because that most of the popular lead-

free solders contain higher percentage of Sn and their melting temperatures are usually 30–40 °C higher than eutectic Sn–Pb solder [12–14]. Both these factors contribute to faster solder reaction with Cu forming a thicker IMC layer, which may eventually cause solder joint failure due to the brittleness of the layer. However, Ni based metallization have slower rate of reaction compared to Cu [12], and therefore extensive research has been carried out in recent years on the interaction between various types of solders and Ni-based metallization [15–23]. Therefore investigating the mechanical properties of the IMCs formed with Ni-based metallization is crucial.

Existing data on IMC properties were mainly obtained from measurements on bulk samples, prepared either by powder metallurgy [2] or by casting [4]. However, there is no established method to measure thin film IMC fracture toughness. The only work that has been reported is our early work on fracture toughness of thin films of co-sputtered Cu–Sn IMCs using controlled buckling test [10]. This technique has several advantages compared to the indentation technique typically used on bulk specimens. Firstly, the grain size and the thickness of thin films are closer to the one in real electronic packages where the IMC thickness is at the order of micron. Moreover, the grain size in bulk specimens obtained by casting and annealing was at the order of tens of micron [4]. Secondly, the thin film fracture

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toughness measurement enjoyed better accuracy and narrower scatter. It was well known that the indentation induced fracture experiment has to be interpreted based on some pre-assumed fracture patterns. Accordingly, there are many calibration equations derived based on various types of model. The choice of these empirical equations may give rise to the large discrepancy among reported values. Thirdly, the thin film measurement presents isotropic “bulk” properties, while the measurement on large grain sized IMCs may suffer from the uncertainty of crystallographic orientation at the particular point of indentation [4]. All these features make the buckling test [10] an attractive alternative for thin film fracture toughness measurement. So far there has not been any report known to us on the fracture toughness of thin film Ni_3Sn_4 . On the other hand, use of co-sputtered thin film specimens has its own concerns as well. The subsequent annealing of the thin films that have been deposited on a substrate usually causes in-plane stresses due to densification. The induced residual stress may affect the measured mechanical properties. Fortunately residual stress can be superimposed in the calculation of fracture toughness; therefore the measurement will not be affected as long as both the film and substrate remain elastic throughout the test. However, the quantitative correction to hardness and elasticity modulus is not yet established. In this paper, we report three fundamental mechanical properties, i.e., elasticity modulus, hardness and fracture toughness of Ni_3Sn_4 thin films. In addition, we also discuss the effect of residual stress induced during annealing on the measured properties.

2. Experiment

Thin metallic films of Ni and Sn were co-sputtered onto polyetherimide (Ultem) stripes and silicon wafers using a DC magnetron sputtering machine at room temperature without intentionally heating the substrates. The dimension of the Ultem stripes was $48 \text{ mm} \times 3 \text{ mm} \times 0.175 \text{ mm}$. The glass transition temperature, elasticity modulus and Poisson's ratio of the Ultem substrate are 247°C , 2.6 GPa and 0.36 , respectively. The stoichiometric composition was maintained during co-deposition by controlling the deposition rates of individual targets. In order to form Ni_3Sn_4 IMC, the deposition rate of Ni to Sn was maintained at 3:4 ratio by controlling the sputtering power to the individual Ni and Sn targets (75:70 W). The working pressure was 5.3 mTorr and the Ar flow rate was 25 sccm . After sputtering, the samples were annealed in inert N_2 ambience for 24 h at $50, 100, 150, 200, 250$ and 300°C . The thickness of the film deposited after the annealing was 420 nm , as-measured using with a surface profilometer. X-ray diffraction (XRD) and energy dispersive spectroscopy were used to identify the phase and composition of the film, respectively.

Table 1
Elasticity modulus, hardness, residual stress and fracture toughness of Ni_3Sn_4 thin films

Annealing temperature ($^\circ\text{C}$)	Hardness (GPa)	Elasticity modulus (GPa)	Fracture toughness ($\text{MPa m}^{1/2}$)	Residual stress (MPa)
100	7.0	134.0	2.11 ± 0.15	0
150	6.5	119.4	4.08 ± 0.21	342
200	6.1	123.4	5.75 ± 0.25	564

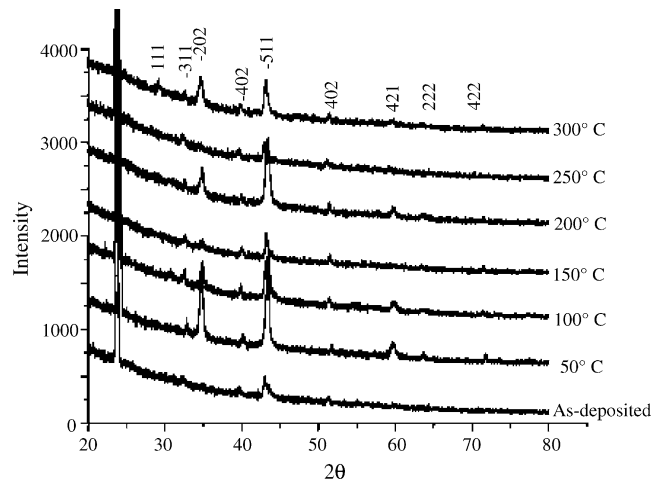


Fig. 1. XRD patterns of the Ni_3Sn_4 films annealed at different temperatures.

Elasticity modulus and hardness were measured using a nano-indenter (NanoTestTM) on films deposited on silicon wafers. The film fracture toughness was evaluated by the controlled buckling test using specimens prepared on Ultem substrates. Preliminary experiments indicated that surface morphology of the films on Ultem stripes and Si wafers are similar. The details of the buckling testing were reported elsewhere [24–26]. Seven to nine specimens were tested for each condition. The residual stress caused by annealing was calculated by the method published elsewhere [27].

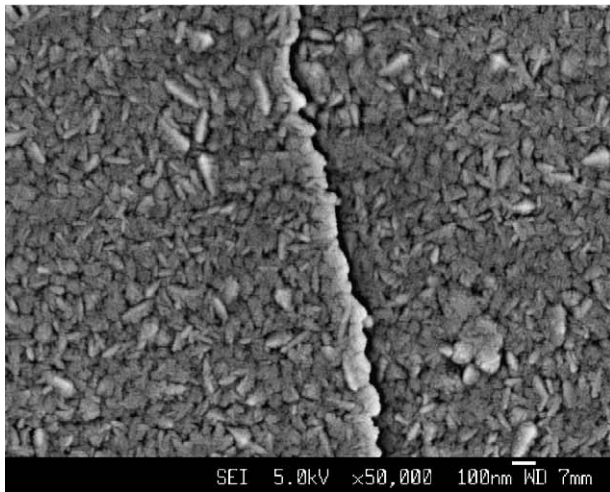
3. Results and discussion

3.1. Phase formation and microstructure

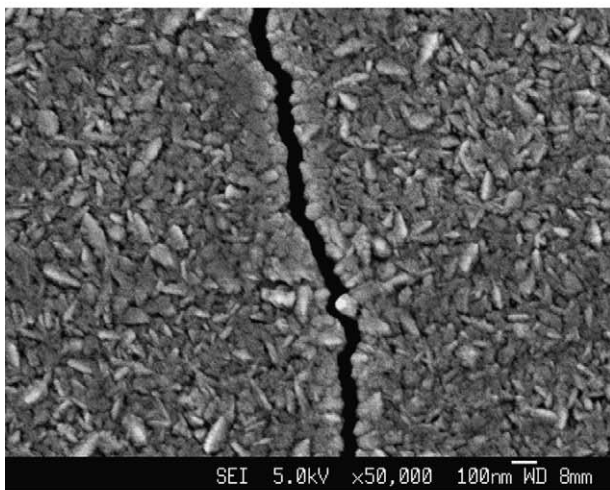
Fig. 1 shows the XRD patterns of the as-deposited specimen, together with those annealed at various temperatures. Composition analysis by EDX confirmed that ratio of Ni to Sn was 3:4. The SEM images in Fig. 2 show the grain size to be about 100 nm for all the specimens annealed between 100 and 200°C . From the XRD patterns, Ni_3Sn_4 compound seem to be formed even in the as-deposited state, although we could not tell whether there were any un-reacted Ni and Sn from the XRD result. After annealing for 24 h at 50°C and above, Ni_3Sn_4 peaks were sharp and clear, indicating complete formation of the compound.

3.2. Hardness, elasticity modulus and residual stress

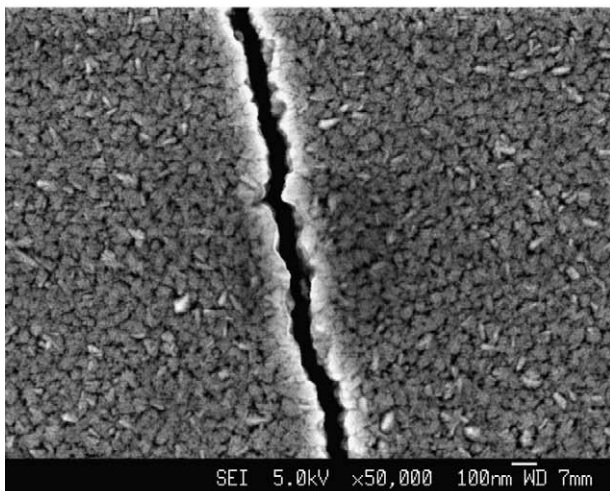
Table 1 lists the elasticity modulus, hardness, residual stress and fracture toughness of Ni_3Sn_4 thin films. At 100°C anneal-



(a)



(b)



(c)

Fig. 2. SEM images showing the film cracking patterns after the fracture toughness test. Grains of about 100 nm are clearly visible from these pictures. Specimens are annealed at (a) 100, (b) 150 and (c) 200 °C for 24 h.

ing, the residual stress was very small. Significant tensile stress has developed after 150 and 200 °C annealing, most likely caused by densification of the films. Since the co-deposition is carried out without substrate heating, the mobility of the adatoms are relatively low, and there will inevitably exist some internal defects, such as vacancies and interstitial voids, etc. During annealing the elimination of these defects densifies the film. However the film is constrained by the substrate so that it cannot densify by shrinking. As a result, tensile stress in the film will be induced [27]. Since such a process is thermally activated, stress can only build up when the temperature is high enough.

The indentation hardness decreased steadily with the increase of annealing temperatures. This was believed to be related to the tensile stress in the film. Indentation measures the resistance to compressive intrusion by the indenter tip. Tensile stress in the film reduces the penetration resistance to the indenter, and thus reduces the measured hardness. The elasticity modulus fell slightly with the residual stress but it did not seem to follow the steady trend as the hardness did. Our reported modulus at stress-free state (100 °C annealing) agreed very well with the reported value of 133.3 GPa by Fields et al. [2] but was higher than 118.4 GPa reported by Ghosh [4]. In Ghosh's work, the average grain size was 32 μm and the indentation was made inside a grain. Therefore the reported value in his work was an average of values from many single grains with unknown crystallographic orientations. While in our current work, the grain size was small so that the indentation likely reflected contribution from multiple grains. We suppose that the difference could be due to the difference in crystallographic orientation.

3.3. Fracture toughness

The fracture toughness measured is reported in Table 1 with its standard deviation. Since our measured elasticity modulus was very close to one by Fields et al. [2], the modulus (133.3 GPa) and Poisson's ratio (0.33) recommended by Fields et al. were used in our calculation of fracture toughness. Residual stress was superimposed on the stress induced by the buckling test, therefore the influence from the residual stress was well accounted for. The cracking patterns in Fig. 2 show that the fracture was mainly intergranular, which is similar to the thin film cracking in Cu–Sn IMCs [10]. It is interesting to note that the cracks remained open after the release of the loading for the 150 and 200 °C annealed specimens. The gap could not be caused by residual plastic deformation since the film and the substrate remained elastic during the fracture test. We believe it is due to the release of residual tensile stress of the film at the vicinity of crack. This view is supported by comparing Fig. 2(a)–(c): the gap was wider with the 200 °C, which has the highest residual tensile stress.

There was a considerable increase in fracture toughness with annealing temperature from $2.11 \pm 0.15 \text{ MPa m}^{1/2}$ for 100 °C annealing to $5.75 \pm 0.25 \text{ MPa m}^{1/2}$ for 200 °C annealing. The scatter in our experiment was smaller than what one would expect from a conventional fracture of bulk, brittle materials.

The increase in toughness was, again, due to the densification of the film by annealing. Densification reduces the number of flaws and the critical flaw size in the film, which improves the fracture resistance. Besides the current work, there were only two reports on the fracture toughness of Ni_3Sn_4 that were known to us, but both are measurements from bulk samples. Ghosh [4] reported the value to be $4.22 \pm 0.45 \text{ MPa m}^{1/2}$ when the indentation load was 100 g and $3.65 \pm 0.47 \text{ MPa m}^{1/2}$ when the load was 200 g. The values should be compared, if a comparison needs to be made, with our result of $5.75 \pm 0.25 \text{ MPa m}^{1/2}$ obtained from the 200 °C specimens, because the treatment temperature is close to the annealing temperature of 222 °C used in Ghosh's work [4]. Our reported value is clearly higher. The microstructural difference could be responsible for such a difference. In our specimens, fine grain sized film fractured by intergranular mode (Fig. 2). While in the case of Ghosh [4], the grain size was very large (32 μm). Under both loads (100 and 200 g) the cracks induced by the indentation were mainly contained inside an individual grain [4]. Both Ghosh's work and our current work reported much higher values of fracture toughness than the one by Fields et al. [2], which was $1.2 \pm 0.1 \text{ MPa m}^{1/2}$. The specimens used in Fields et al.'s work were prepared by powder metallurgy. The fracture toughness of sintered specimens is highly dependent on the porosity; the lower value obtained in the work of Fields et al. [2] could be due to its relatively large pore size.

4. Conclusion

In this work, Ni_3Sn_4 IMC thin films of 420 nm thick were prepared by co-sputtering and subsequent annealing. The hardness and elasticity modulus measured by nano-indentation were 7.0 and 134 GPa, respectively. Residual stress developed during annealing affected the measured hardness and elasticity modulus. Densification of the film during annealing significantly increased the fracture toughness. The fracture toughness of the Ni_3Sn_4 thin film measured by controlled buckling test was,

respectively, 2.11 ± 0.15 , 4.08 ± 0.21 and $5.75 \pm 0.25 \text{ MPa m}^{1/2}$ for specimens annealed at 100, 150 and 200 °C for 24 h.

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