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Effect of the size of carbon nanotubes (CNTs) on the microstructure and mechanical strength of CNTs-doped composite Sn0.3Ag0.7Cu-CNTs solder

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A B S T R A C T

Carbon nanotubes (CNTs) with three different diameter ranges (10–20, 40–60, and 60–100 nm) were doped into tin-silver-copper (SAC) solder, to study the performance of the composite SAC-CNTs solder materials – as well as the effect of the size of the CNTs. It was found that all the CNTs-doped composite solder samples displayed refined microstructure, inhibited interfacial intermetallic compound (IMC) growth, and reinforced mechanical strength – while the melting point of the composite solder was close to that of the pristine solder. The reinforcement in mechanical strength was due to the doped CNTs pinned at the solder grain boundaries, which acted as second-phase particles that refined the microstructure and increased the dislocation density. The adsorbed CNTs destroyed the integrity of the interfacial IMCs, leading to reduced growth rate. Among these composite solders, CNTs with a diameter of 40–60 nm provided superior performance in refining the microstructure, lowering the IMC growth rate by 30.9% – and reinforcing the ball shear strength by 15.3% and the hardness by 16.1%. This size effect on the performance of composite solders was due to the various surface energy values for CNTs – that led to the agglomeration and adsorption of CNTs in the solder matrix and interfacial IMCs.

1. Introduction

To meet the demand for miniaturization and high performance, the microelectronics industry has utilized flip chip (FC) technology to enable a greater number of inputs/outputs (I/Os) – and has used solder balls for interconnection [1,2]. Solder joints were subjected to a mixture of the electric, thermal and mechanically coupled stresses that make solder joints vulnerable during service [3,4]. The reliability of solder joints is of great importance for electronic products, since any failure of the millions of interconnects may induce the breakdown of the operation of entire device [5].

Doping nanoparticles (NPs) into solder joints has been studied and has proven to be useful in reinforcing the mechanical strength, as well as controlling the evolution of the microstructure [6–11]. Generally, three distinct types of NP have been studied: type I – metal NPs such as Ag, Cu and Ni [9,12,13]; type II – metallic oxide NPs such a ZrO_2, TiO_2 and Al_2O_3 [6,8,10,14]; type III – nonmetallic NPs such s graphene, fullerene and carbon nanotubes (CNTs) [11,15–17]. The NPs were pinned at the grain boundaries and resulted in refined grain structure, which increased the dislocation density [18]. As a result, the mechanical strength of the composite solder joints was reinforced. Some NPs precipitated on the interfacial IMC layer destroyed the integrity of the IMC layer and inhibited the reaction between the solder pad and the solder matrix, which led to controlled microstructure evolution and IMC growth - as well as strong resistance to electromigration (EM) and thermomigration (TM) [11,12,19]. Ag NPs have been doped into various solder materials, in order to study the performance of the composite solder [12,20–24]. The wettability of Ag-doped Sn0.7Cu solder on Cu pads was reported to improve, with an increased spreading area and decreased wetting angle [23]. A thinner Bi-rich layer was obtained in the Ag-doped Sn58Bi solder joint, as compared to the plain Sn58Bi solder joint under current stressing, due to the Ag_3Sn formed blocking the atomic diffusion [24]. A composite under-bump metallization (UBM) structure, which incorporated NPs into the UBM layer through electroless plating, has been proposed by Hu et al. [6,14,25]. The shear strength and tensile strength of the solder joints on the WO_3 doped Ni-P UBM was reinforced significantly, while the IMC layer growth was controlled and reduced by around 28.6% [6]. Reinforcement was also reported for Ni-P-TiO_2 and Ni-P-ZrO_2 composite UBM layers [14,25]. The 0.1 wt% addition of graphene nanosheets into Sn8Zn3Bi solder joints showed a 10.2% increase in ball shear strength and a 9.1% increase in hardness, as compared to the plain solder joints [15]. The

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incorporation of C60 & C70 into Sn3.0Ag0.5Cu solder joints contributed to reinforced micro-hardness and shear strength, as well as enhanced resistance to TM, as reported by Chen et al. [11,26]. Research on NP-reinforced solder joints can be divided into the following topics: NP types, NP weight percentages, addition methods, and addition sites. However, the size of the NPs can also have an impact on the effectiveness of nano-doping, as reported by Li et al. [27], who has found that the Ag-NPs with a diameter of 75 nm showed better control over phase coarsening, IMC growth and mechanical strength degradation than the smaller or larger sized Ag NPs.

CNTs have the advantages of large current carrying capacity, high electric conductivity, and high thermal conductivity – and have been regarded as a potential candidate for next-generation interconnects [28]. Previous studies on solder materials doped with CNTs have confirmed that the incorporation of CNTs inhibits IMC growth and phase-rich grain growth. The CNTs-doped SAC solder also displayed a slower EM rate, in comparison with the plain SAC solder. It has been reported that the particular CNTs used – metal composite materials – displayed superior mechanical performance through four mechanisms: 1) load transfer from the matrix to the CNTs, 2) increase in dislocation density, 3) homogeneous dispersion of CNTs, 4) refined matrix size [29]. In contrast with Ag, which can react with Sn to form Ag_3Sn IMCs, CNTs are inert and will be physically embedded in the solder matrix. In the present work, we have studied the performance of three composite solders doped with three different sized CNTs.

2. Experiments

Three types of multi-walled carbon nanotube (CNTs) were obtained from a commercial company (Shenzhen Nanotechnologies Port Co., Ltd, purity ≥ 95%). The lengths of the three types of CNT were in the same range: 1–2 μm, while the diameters were different – since type I CNTs had a diameter within the range from 10 to 20 nm, type II CNTs had a diameter within the range from 40 to 60 nm and type III CNTs had a diameter within the range from 60 to 100 nm, as listed in Table 1. The CNTs firstly underwent a surfactant-assisted process to remove impurities and reduce residual van der Waals forces, according to a method described by Xu et al. [30]. This process avoids the clustering of CNTs and leads to better distribution and dispersion of the CNTs.

CNTs were doped into the Sn0.3Ag0.7Cu (SAC) solder paste with a weight percentage of 0.05%, followed by mechanical blending using a stick for half hour to achieve uniform distribution of CNTs in the solder paste. The four types of solder paste were then printed on a glazed ceramic substrate through a stencil, followed by reflowing in an eight-zone convection reflow oven (BTU Pyramax-100 N) to fabricate the pristine SAC and composite SAC-CNTs solder balls (average dimensions of 600 μm). More detailed experimental settings can be referred in a previous work [12]. A second reflow was applied to fabricate solder joints on metalized substrate, which has a three layer Au(∼ 5 μm)/Ni(∼ 10 μm)/Cu(∼ 20 μm) under bump metallization (UBM) structure, with an opening of 500 μm, covered with solder mask. Fig. 1 illustrated the reflow profile applied in fabricating the solder balls, as well as the solder joints, with a peak temperature of 260 °C (533 K) and a reflow zone of 80 s. The thermal properties of these four types of solder joints were examined with differential scanning calorimetry (TA instrument, DSC-Q10), during which 10 mg samples sealed in an aluminum pan were heated at a ramp rate of 5 °C/min within the scanning interval from 200 to 260 °C.

Table 1
Composition of both the pristine and CNTs-doped composite solder joints.

Solder type	CNTs weight percentage	Length/ μm	Diameter/ nm	Melting point T_m/ °C
SAC	0	–	–	226.4479
SAC-CNTs I	0.05%	1–2	10–20	226.5676
SAC-CNTs II	0.05%	1–2	40–60	226.6082
SAC-CNTs III	0.05%	1–2	60–100	226.7648

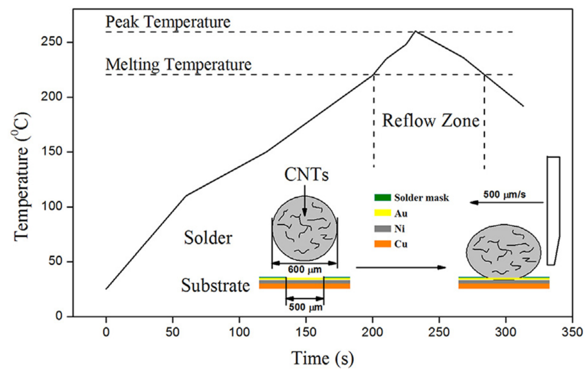

Fig. 1. Schematic drawing of reflow profile applied for solder ball and solder joint fabrication.

The solder joints were then put into aging ovens with temperature set to 100 °C. After various aging times, the solder joints were taken out for study of both the mechanical strength and the microstructure evolution. The shear strength was studied using a ball shear tester (Dage series 4000) with a pendulum weight of 5.0 kg, at a shear speed of 500 μm/s, as shown in Fig. 1. The average shear strength was calculated from the average value of 15 test results, with the maximum and the minimum removed. After shear test, the fracture surfaces were studied using scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis to obtain the change in the shear strength in various types of solder joint. The microhardness was investigated using a Vickers hardness tester (MXTCXT, MATSUZAWA), with an applied load of 200 g-force (gf) for 12 s. The average hardness was calculated from the average value of 15 test results, with the maximum and the minimum removed. The microstructure evolution was studied on the metallurgical samples by cross-sectioning the epoxy-mounted solder joints to the center using various types of grinding sandpaper, followed by polishing and etching. The IMC layers were examined with SEM and the elemental composition was studied with EDX. It should be noted that extensively etching was carried out to study the grain structures, which made the images a bit smeared. The thicknesses of the IMC layers were estimated using ImageJ software [31] by dividing the area of the IMC layer by the length of the IMCs. The CNT morphologies were studied using transmission electron microscopy (TEM) and focused ion beam (FIB).

3. Results and discussion

3.1. Thermal properties of CNTs-doped solder joints

The thermal properties of both pristine and CNTs-doped SAC solder materials were studied using DSC. The DSC curves presented in Fig. 2 show that the addition of CNTs increased the melting point of SAC solder slightly. The pristine SAC solder had a melting point of 226.4479 °C, while melting points for CNTs-doped solders were 226.5676 °C, 226.6082 °C and 226.7648 °C for SAC-CNTs I, SAC-CNTs II, and SAC-CNTs III, respectively. This slight increase was possibly due to the incorporation of CNTs, which have a higher melting point. Meanwhile, the small difference suggested that the same reflow profile could be used for fabricating all four types of solder balls and solder joints.

3.2. Morphologies of CNTs

Multi-walled CNTs were schematically drawn using a nanotube modeler in Fig. 3(a)–(d) are TEM images of three CNTs with the diameter ranges labelled. The three CNTs can be clearly distinguished from