Electrophoretic Deposition of Carbon Nanotubes on Heat Spreader for Fabrication of Thermal Interface Materials (TIM)
(Pengendapan Elektroforesis Karbon Tiub Nano ke atas Penyebar Haba untuk Fabrikasi Bahan Antara Dua Muka Haba (TIM))

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ABSTRACT

Thermal interface materials (TIMs) are applied in packaging of electronic devices for heat dissipation purposes. Carbon nanotubes (CNTs) are promising material due to their high thermal conductivity properties which will give optimum performance as TIMs. In this research study, electrophoretic deposition (EPD) is used which enables the deposition process conduct at room temperature with simple equipment setup which beneficial for CNTs deposition. As-produced CNTs was purified and directly deposited on heat spreader using direct current (DC) electricity. Dimethylformamide (DMF) was used as suspension medium for CNTs and the effect of suspension concentration was studied. From the screening of suspension concentration, 0.50 mg/mL yielded good deposition with thickness of 4.78 µm of CNTs deposited on heat spreader at applied voltage of 150V and 10 min deposition time. Further studied in different applied voltage and voltage of 250 V shows the maximum thickness of 15.01 µm with 2.0 mg weight of deposited CNTs which is suitable for fabrication of TIM.

Keywords: Carbon nanotubes; electrophoretic deposition; thermal interface materials

INTRODUCTION

The developments of product in the Electrical and Electronics (E&E) industry is proportional with the improvement in the design, applications and software of the products. Most of the products will be designed to fit the requirement of consumers such as thinner, faster and smaller but at the same time increasing the power density in electronic devices to a higher level that will affect the overall performance of the devices. These requirements are related to the thermal management system which focuses on heat dissipation from the critical component or system hot spot to the surrounding through improvement of cooling technologies (Fu et al. 2012). Passive thermal management is one of the design strategies in cooling technologies and it relies on thermodynamics of heat transfer processes. For example heat sinks, heat spreaders, heat pipes and thermal interface materials, they are also commonly used due to inexpensive and easy to implement.

Thermal interface materials (TIMs) are materials used for backcuping heat sink to remove heat from the heat sources that are mostly applied for electronic equipment. TIM helps in strengthening the mechanical link and being a good adhesive between surfaces (Fabris et al. 2011; Gwinn & Webb 2003; McNamara et al. 2012). There are various types of materials used as TIM, for example, thermal greases, solder, phase change materials (PCMs). Recently, most studies are switching to the use of nanomaterials because of their ability to perform in nanoscale.

Carbon nanotubes (CNTs) are well-known for having excellent mechanical, electrical, thermal, optical and chemical properties where the properties are different due to the nanotube formations (Boccaccini et al. 2006; Mehrnoush et al. 2015). They are tubular cylinder constructs of carbon atoms, which can be present in many forms such as single-walled, double-walled and multi-walled CNTs. Single-walled nanotubes are generally
figured as a single sheet of graphene rolled and formed in a hollow cylindrical shape whereas multi-walled CNTs consisted of multiple concentric sheets with typically 5-50 nm in diameter and 10 μm in length (Yeoh et al. 2012). CNTs are electrically conductive with great thermal conductivity compare to diamond and have extended too many applications such as thermal interface materials (Xu et al. 2008), solar cells (Song et al. 2016), batteries (Kim et al. 2010) and energy storage (Cott et al. 2013).

Most of the nanomaterials are introduced as TIM due to their excellent thermal performance; however, depositing the materials on heat spreader in the package assembly becomes a challenge. There are various methods to coat the nanomaterials on heat spreader such as chemical vapor deposition (CVD) (Yeoh et al. 2012), spin coating (Llobet 2013), electroplating (Boccaccini & Zhitomirsky 2002) and electrophoretic deposition (Kumar & Ando 2010).

In this study, electrophoretic deposition (EPD) method is proposed for CNTs deposition which is easy in equipment handling and are able to operate at room temperature (Besra & Liu 2007; Sarkar 2013; Sarkar & Nicholson 1996). EPD is essentially a two-step process. In the first step, particles suspended in a liquid medium are forced to move towards an electrode by applying an electric field (electrophoresis). In the second step, the particles are collected at the electrode and will form a coherent deposit (deposition) (Besra & Liu 2007; Corni et al. 2008; Dickerson & Boccaccini 2012; Sarkar & Nicholson 1996). The deposition occurs only on conducting surfaces, but non-conductive substrates can be infiltrated by using EPD (Boccaccini & Zhitomirsky 2002). The method can be applied, in general, to any solid in particulate form with small particle sizes (less than 30 μm) and colloidal suspensions (Sarkar & Nicholson 1996; Van der Biest & Vandeperre 1999).

There are various solvents used for dispersion of CNTs such as distilled water, organic and surfactant. The suitable solvent is selected based on solvent type, high suspension stability, low ionic conductivity, low viscosity, zeta potential reading and performance for EPD. The EPD method is widely used for CNTs coating but the application is not focused on TIM fabrication. The TIM required higher thickness of CNTs with good deposition adhesion besides offering excellent thermal conductivity (Fabris et al. 2011; Wang et al. 2006; Xu et al. 2008). The aim in this study was to have the maximum heat dissipation by getting the maximum thickness of deposition with the purpose of understanding the EPD mechanism of CNTs coatings.

**MATERIALS AND METHODS**

**MATERIALS**

Carbon nanotubes (CNTs) (Outer Diameter: 21 nm) produced from catalytic chemical vapor deposition (CCVD) method, Dimethylformamide (DMF) from Fisher Scientific, electroless nickel oxide-copper plate designed from AMKOR, Thailand, ethanol from Merck, nitric acid, HNO₃ (65%) from Fisher Scientific and distilled water.

**ELECTROPHORETIC DEPOSITION**

The as-produced CNTs via catalytic chemical vapor deposition (CCVD) (Yeoh et al. 2012) were purified to remove the impurities before EPD method utilization. The CNTs were weighed and suspended in DMF (volume 50 - 90 mL) using sonic dismembrator (Fisher Scientific) for 10 min at different suspension concentrations of 0.50, 0.56, 0.63, 0.71 and 0.83 mg/mL. DMF is chosen because of its high dielectric constant (k = 36.71) which is sufficient to perform EPD. This is due to the ability of DMF to keep the CNTs suspension stable for a long period of time. The suspended CNTs were kept at room temperature for 36 h undisturbed to examine the stability of the solutions.

The stability of suspended CNTs was analyzed using zeta potential, Malvern Instruments Nano Series Zetasizer (model: ZEN 3600) at different concentrations of CNTs suspension. The stabilized CNTs in suitable suspension concentration was deposited on heat spreader using EPD, which was prior cleaned with ethanol. All EPD experiments were carried out by applying 150V of voltage with 10 min of deposition time (Dickerson & Boccacin 2012). The distance between two parallel electrodes were kept constant at 10 mm apart and they are connected to a power supply (KIKUSUI Regulated DC Power Supply, model PAS500-0.6) as shown in Figure 1. The effect of voltage applied during EPD was investigated by varying between 125 and 250V at constant 10 min and 10 mm EPD process conditions. The samples were weighed before and after deposition and the coating area was measured in order to determine the yield of the process (Corni et al. 2009). They were dried at room temperature after the deposition process had completed (Sarkar 2013). The surface and thickness of deposited CNTs were analyzed using scanning electron microscopy (SEM; FEI, model Quanta 450 FEG).

**RESULTS AND DISCUSSION**

**ZETA POTENTIAL MEASUREMENT**

In this research, DMF was chosen as suspension for medium CNTs because the CNTs can be stably suspended and deposited in this solvent (Inam et al. 2008; Mohamed et al. 2016). Figure 2 shows the zeta potential for different CNTs suspension concentrations. The zeta potentials for concentration of CNTs suspensions are -36.8, -31.5, -30.0, -41.8 and -42.0 mV for 0.50, 0.56, 0.63, 0.71 and 0.83 mg/mL, respectively. The standard deviation for all concentrations did not exceed ±6 mV and these indicated that the measured data are relatively good (Tantra et al. 2010).

The characteristic of zeta potential in relation to suspension stability was investigated by Riddick (1968) as shown in Table 1. Riddick (1968) reported when the potential is small, attractive forces may exceed this...
repulsion and the dispersion may break and flocculate. Thus, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate. The charge of particles that are more than absolute 30 mV represent good suspension stability and from the zetasizer measurements, all suspension concentrations have good stability with no tendency to form agglomeration (Tantra et al. 2010). The results showed that the CNTs suspension is stable for EPD.

ELECTROPHORETIC DEPOSITION
EPD method of CNTs suspension with different CNTs concentration was carried out to deposit CNTs on nickel plated copper substrate (heat spreader). The experiments were set as in Figure 1 and the current intensity was monitored during suspension. From the zeta potential results, the deposition occurred at positive electrode (anode) because the zeta potential CNTs suspension gave negative values, which show that the CNTs are negatively charged and the process is called anodic electrophoretic deposition (Besra & Liu 2007). The samples with uniform deposition were characterized using scanning electron microscopy (SEM) in terms of microstructure and deposition thickness.

Figure 3 shows the cross section SEM images for CNTs deposited on heat spreader at different suspension concentrations and the top surface of deposited CNTs. The deposition condition was set at 150 V and 10 min of deposition time for all the suspension concentrations. Figure 3(a) to 3(e) shows the thickness of deposited CNTs from cross section view of heat spreader for suspension concentrations 0.50, 0.56, 0.63, 0.71 and 0.83 mg/mL which gave 4.78, 2.84, 2.30, 3.57 and 1.58 μm, respectively. From this observation, the suspension concentration at 0.50 mg/mL gives the maximum thickness of 4.78 μm of CNTs deposited on heat spreader. The same suspension concentration is reported to have also been used by other researchers when using DMF as dispersing agents in EPD (Boccaccini et al. 2006; Lee et al. 2005).

Figure 4 shows the thickness profile of deposited CNTs of different suspension concentrations. The thickness

![FIGURE 1. Schematic diagram of electrophoretic deposition set up](Image)

![FIGURE 2. Zeta potential of different concentration of CNTs suspension](Image)
of deposited CNTs decreased when the concentration is increased to 0.56 and 0.63 mg/mL. This is because the CNTs in the suspension medium have lower charge which make them difficult to deposit as compared to the CNTs in 0.71 mg/mL which have higher charge (Besra & Liu 2007; Ferrari & Moreno 2010; Sarkar & Nicholson 1996) but most colloidal processes are limited by the complexity of preparation of highly concentrated and stable suspensions of nanoparticles and their fast ageing. Electrophoretic deposition (EPD). Therefore, the thickness fluctuates within this range of concentration. For the case of 0.83 mg CNT/mL DMF, the charge of CNTs is close to 0.71 mg CNT/mL DMF concentration, but the thickness of CNTs deposition is the lowest among others which is 1.58 μm. This situation is due to high zeta potential CNTs in the stable suspension that possess strong repulsion forces between CNTs that were impossible to overcome by electric field during EPD and thus, resulted in less deposition (Besra & Liu 2007).

Applied voltage is one of the important parameters in EPD method. In this research, the CNTs suspension concentration of 0.50 mg/mL was chosen to further study the effect of applied voltage on the deposition of CNTs on
heat spreader via EPD method to determine the optimum condition of deposition. The range of applied voltage studied is between 125 and 250V. Figure 5 shows the SEM image for cross section view of deposited CNTs at different applied voltages. The thickness of deposition increases proportionally with increasing of applied voltage as shown in Figure 6. The voltage applied at 125V had almost no CNTs deposition and the thickness of deposition was less than 1 µm. The applied voltages of 150, 175, 200 and 250V show high deposition thickness of 4.78, 10.17, 12.8 and 15.01 µm of single component of CNTs, respectively. Whereas other researchers have reported the optimum deposition thickness to be of less than 10 µm of CNTs composite with existing of other components (Boccaccini

FIGURE 4. Profile for thickness of deposited CNTs for different suspension concentration at deposition condition of 150V of applied voltage, 10 min of deposition time and 10 mm of gap between electrodes

FIGURE 5. SEM for 0.50 mg/mL CNTs suspension concentration deposited on heat spreader (a) 125 V, (b) 150 V, (c) 175 V, (d) 200 V and (e) 250 V at 10 min deposition time and 10 mm of gap between electrodes
et al. 2010; Lee et al. 2005; Su & Zhitomirsky 2013). The increment of thickness is small as the voltage increased due to the limitation of CNTs movement at high voltage that will affect the quality of deposition formation. This is because the CNTs packing in deposition will be influenced by the rate of CNTs accumulation (Besra & Liu 2007). The thickness for TIM fabrications, usually in range of 10 to 200 μm, depends on the type of materials with excellent thermal properties (Kim et al. 2015; Peacock et al. 2016; Prasher 2006). Higher TIM thickness will provide higher thermal conductivity for excellent heat dissipation by considering the uniformity and packing density of the TIM. Therefore, the thickness of CNTs deposited in range 150 to 250 V of applied voltage is suitable for fabrication of TIM.

WEIGHT OF DEPOSITED CNTS DURING EPD

The mechanism of CNTs coatings is determined by measuring the weight of CNTs deposited in EPD method. The amount of particle deposited correlates to other parameters in the EPD method. Hamaker equation is a kinetic model used for analyzing EPD method in planar geometries as shown in (1) (Besra & Liu 2007; Sarkar & Nicholson 1996):

\[ w = (C_s)(\mu)(S)(E)(t), \tag{1} \]

where, \( w \) is the deposition weight per unit area (g/cm\(^2\)); \( C_s \) is the solids (CNTs) loading (g/cm\(^3\)); \( \mu \) is the electrophoretic mobility (cm\(^2\)/Vs); \( S \) is the deposition area (cm\(^2\)); \( E \) is the electric field per unit cm (V/cm); and \( t \) is the deposition time (s). Figures 7 and 8 show the profile of CNTs deposition weight per unit area for experimental and theoretical weight. The theoretical weight of deposited CNTs was calculated based on Hamaker equation which takes into consideration of other parameters in the EPD method. The weight of experimental CNTs deposition for suspension concentrations of 0.50, 0.56, 0.63, 0.71 and 0.83 mg/mL are 0.90, 0.50, 0.35, 0.60 and 0.10 mg, respectively. The large difference between theoretical and experimental weight observed is due to the real condition of EPD method affected by the environmental condition and type of CNTs used as the Hamaker equation is generally designed for
charged particles (Sarkar & Nicholson 1996). Meanwhile in Figure 8, the theoretical and experimental weights are not so much different except for the deposition at applied voltage 125V. This result indicates the optimum deposition condition of CNTs is in range of voltage 150 to 250V to keep good quality of deposition and adhesion, as too high voltage applied may introduce cracks on the deposition which will eventually affect the performance of TIM in heat dissipation (Besra & Liu 2007; Corni et al. 2009).

For the validation of CNTs as TIM, the thermal conductivity measurement was conducted for sample of 175V applied voltage. The thermal conductivity is important in the determination of heat dissipation performance of TIM where the heat is transferred through materials by heat conduction mechanism. From the measurement, 5.291 W/m.K of thermal conductivity was recorded and this result is comparable with commercially existing TIM that have thermal conductivities ranging between 1 to 10 W/m.K (Bergman et al. 2011; Tong et al. 2007).

CONCLUSION
This study successfully uses EPD method for deposition of CNTs on heat spreader. DMF is used as suspension medium to prepare CNTs suspension prior for EPD method. The operating condition of EPD method is optimized in terms of suspension concentration and applied voltage to maximize the thickness of CNTs deposition. The investigation confirms that the 0.50 mg/mL suspension concentration is good for electrophoretically deposited CNTs compared to other concentrations. The SEM result shows the maximum thickness deposited on the heat spreader, which is 4.78 μm deposited at 150 V and 10 min and 0.50 mg/mL of suspension concentration. For different applied voltage, study shows maximum thickness of 15.01 μm of CNTs deposition was observed at 250 V for 10 min with the CNTs suspension concentration 0.50 mg/mL. Higher amount of CNTs is required in fabrication of TIM to successfully dissipate the heat in cooling system of microelectronics devices. Thus, the identification of the suitable range of applied voltage is important in further study other parameters that correlate in the EPD method.

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