

Effect of Carbon Nanotubes as Thermal Interface Materials on Thermal Conductivity Using Electrophoretic Deposition

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ABSTRACT: *Thermal interface materials (TIM) involve heat removal from electronic devices. It is used to remove heat sink from the heat sources to prolong the operation system of a device. It normally replaces the thermally insulated air between the two surfaces and uses it as a secondary thermal conductive material. The current thermal conductivity of TIM is considered to be a limitation for the development of advance electronic devices. In this study, the performance of carbon nanotubes (CNTs) which were used as TIM was investigated by using electrophoretic deposition method. The deposition of CNTs was varied from one to six layers and the performance of deposition was evaluated. The stable suspension of CNTs in DMF with zeta potential reading of -35.87 mV give rise to a smooth and uniform deposition on nickel plated copper substrate (heat spreader) with the usage of electrophoretic deposition (EPD). Maximum layers of CNTs deposition were obtained at six layers with 56.95 μm of deposition thickness and 11.0 mg of deposition weight. Thermal conductivity was measured using a thermal analyser while the thickness of deposition was observed using scanning electron microscope (SEM). The employment of CNTs improved the heat removal of TIM with thermal conductivity reading of 27.08 $\text{W m}^{-1} \text{K}^{-1}$. Optimisation studies revealed that EPD operated at an applied voltage of 175 V coupled with 10 min deposition time produced a single layer deposition with the thickness of 14.14 μm .*

Keywords: Carbon nanotubes, electrophoretic deposition, thermal interface materials, thermal conductivity

1. INTRODUCTION

To date, the growth of electrical and electronics industry are significantly contributed by the semiconductor products. The semiconductor products are designed to fit the overall specifications demand which includes possessing higher power density with the means of producing a thinner, faster and smaller electronic device.¹ Consequently, as the specification of electronic system becomes more complex, the power densities in the electronic design needs to be increased as well. Complex system which involves many components such as microprocessor will generate more energy. This eventually leads to overheating of the electronic system. Therefore, proper heat management is required to effectively transport the heat away to the ambient environment through cooling processes.²

There are few cooling technologies that are available in the industries such as heat spreader and thermal interface materials (TIM). Among the cooling technologies, TIM garners great attention especially in improving their fabrication system where currently it is moving towards application of nanomaterials. Generally, TIM materials were used as a backup heat sink to remove heat from the heat sources of multiple electronic equipments. It replaces the thermally insulated air in between the two surfaces and uses it as a secondary thermal conductive material. Besides that, TIM also helps in strengthening the mechanical link of electronic equipments where it acts as a good adhesive material between surfaces.^{2,3} The main criteria's for producing a good TIM are high thermal conductivity, good surface contact and good mechanical properties. Nowadays, the application of TIM is moving towards exploring the compatibility of nanomaterials such as carbon nanotubes (CNTs), graphene and others to be used to produce TIM.⁴⁻⁶

CNTs are one of the leading candidates to be considered for interface materials usage due to its high thermal conductivity of $6000 \text{ W m}^{-1} \text{ K}^{-1}$ and high aspect ratio which helps to provide high thermal transport properties through a network of CNTs.^{4,7-9} These properties are very much beneficial in promoting the CNTs to be considered as TIM in order to improve the performance in terms of heat removal. Besides that, CNTs are well known of having excellent mechanical, electrical, thermal and chemical properties and it differs according to the types of nanotube.^{10,11} Therefore, most of the applications of CNTs are related to thin film deposition either individually or in a composite formation.

Thus, this research focuses mainly on the fabrication of CNTs as TIM using electrophoretic deposition (EPD) method and it was operated at room temperature with simple and easy-handling set up as reported in the previous literatures.^{7,12-14} The aim is to mainly study on the thickness of CNTs deposition which will be used as TIM where the thermal conductivity of the developed TIM for successful heat

removal will be monitored. The output from this study will be used to optimise the deposition method for CNTs in regard to TIM applications and heat removal performance of TIM.

2. EXPERIMENTAL

The CNTs were synthesised via catalytic decomposition of methane over bimetallic Co-Mo/MgO catalyst.¹⁵ It was later purified using 3 M nitric acid (HNO₃) in order to remove the impurities (i.e., catalyst particles and amorphous carbon used in deposition). The deposition of CNTs took place when the CNTs were being suspended in dimethylformamide (DMF) using sonic dismembrator (Fisher Scientific) at 50% amplitude for 20 min. The final solution concentration obtained was 0.5 mg ml⁻¹. The CNTs suspension was kept at room temperature undisturbed to examine the stability of the solution. The solution was analysed using Malvern Instruments Nano Series Zetasizer (model: ZEN 3600) to obtain the zeta potential value. The CNTs suspension was deposited using EPD (KIKUSUI Regulated DC Power Supply, model PAS500-0.6) on nickel plated copper substrate (heat spreader) at conditions of applied voltage of 175 V and 10 min of deposition time with a constant 10 mm electrode gap. The heat spreader was weighed before and after deposition in order to measure the weight of CNTs that has been deposited on the heat spreader. This procedure was repeated for three times for each deposition processes. The effects it had on the thickness of CNTs deposition on heat spreader that will be packaged as TIM were studied. In addition, maximum layers of deposition were obtained in order to have maximum TIM thermal conductivity. The thickness of the deposited CNTs will be analysed using scanning electron microscopy (SEM; Zeiss Supra 35 VP) and the thermal conductivity of CNTs was analysed using thermal analyser (Hot Disk Thermal Constant Analyser).

3. RESULTS AND DISCUSSION

3.1 Carbon Nanotubes Suspension

The suspension of CNTs in DMF will be evaluated using zeta potential where observations on well suspended CNTs in the solution will be recorded because it is important for successful EPD method to take place. Zeta potential value for 0.5 mg ml⁻¹ CNTs suspension was recorded at -35.87 mV. This result signified the suspension stability of the solution with high absolute charge (more than 30 mV). This hence promotes the sufficient mutual repulsion of stable suspension particles.¹⁶ The mixture of CNTs in DMF showed a moderate range of stability

with a strong zeta potential which particularly provides good deposition. Besides that, the introduction of acid during the CNT purification process also contributed to the formation of functional groups on the wall of CNTs and the presence of this carbonyl and hydroxyl group contributes to the existence of negative charges.¹⁷ Figure 1 shows the FTIR spectra of the wave-number ranging from 500 cm^{-1} to 4000 cm^{-1} for the as-produced and purified CNTs. The band at 3450 cm^{-1} refer to the hydroxyl (-OH) group and band at 1636 cm^{-1} refer to the carbonyl (C=O) group which overlapped with C=C bonds.¹⁸ The intensity of C=O and -OH peaks increased after the purification of CNTs. The process involved covalent modification where the functional group will be attached to the side wall or end caps of the CNTs. The end cap has higher reactivity due to its higher pyrimidisation angle and the walls of CNTs have lower reactivity.¹⁹

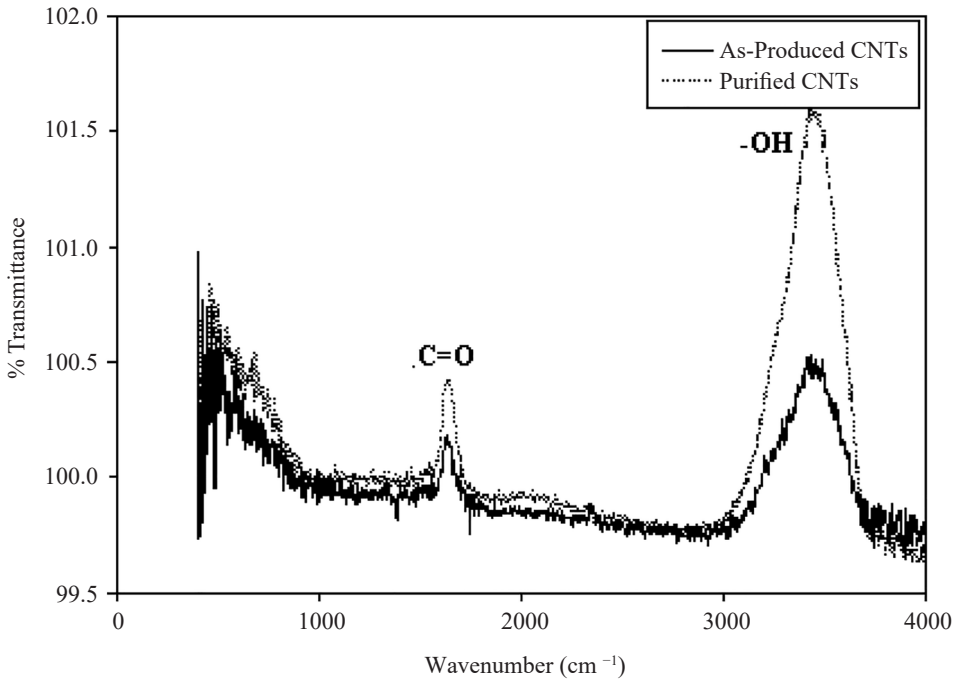


Figure 1: FTIR spectra of the as-produced and purified CNTs.

Therefore, the efficiency of CNTs suspension towards the EPD process in regard to the intensity of repulsive interaction between particles and kinetic stability can be gathered in terms of relationship between prepared suspension particle and electrical double layer (EDL) particles.^{12,20} In fact, the high dielectric constant of DMF (36.71) provides high ionic concentration to promote good dispersing agent for CNTs.¹²

3.2 EPD and Thermal Measurement

Stable suspension of CNTs ensures successful development of EPD. In this study, the operating condition for EPD using purified CNTs was fixed at 175 V of applied voltage, 10 min of deposition time and 10 mm of electrode gap. Figure 2 shows the SEM images of CNTs deposited at different layers of EPD conditions. The overall thickness of CNT deposition after the layer addition was observed and measured. From the EPD process, the thickness of CNTs deposited were measured using SEM for one, two, three, four, five and six layers. The thickness of layers one, two, three, four, five and six were 14.14 μm , 22.13 μm , 23.75 μm , 30.33 μm , 47.66 μm and 56.95 μm , respectively. The deposition was stopped at layer 6 as it achieved the minimum thickness required for TIM (50 μm). From the observations, the thickness of CNTs increases when the deposition layers increases as shown in Figure 3. The error bar was not added in this measurement since the measurement was only taken once for each deposition. The deposition image clearly showed the adhesion between CNTs and heat spreader whereby the CNTs deposition performance was sufficiently shown. In fact, the interaction between the deposited CNTs and suspended CNTs gave rise to good increment values of thickness throughout the deposition layers increment.

The process of deposition by layers showed the interaction between CNTs on the deposited surface and those suspended in the solution. Initially, the CNTs interacted with the surface of heat spreader and form the first layer of deposition. The substrate and deposited particles which has good thermal properties is important in order to have a higher rate and uniform deposition.¹² Therefore, in this study, the interaction between nickel in heat spreader and CNTs helps to form a smooth deposition. For the second layers of deposition, the interaction is mostly in between the deposited CNTs and suspended CNTs. The layer of deposited CNTs readily serves as a substrate with good conductivity. Thus, the process of second and following layers of deposition is implied from the first layer of deposition. This phenomenon affects the deposition weight and thickness of the deposited layers. Even though the measurements of the average thickness were not consistent for every layer, there was still an increment for each additional layer deposited. This was justified by the movement of suspended CNTs towards the deposition. Moreover, the deposition of CNTs until six layers proved that the deposition adhesion is good which is important to achieve high performance of heat removal.

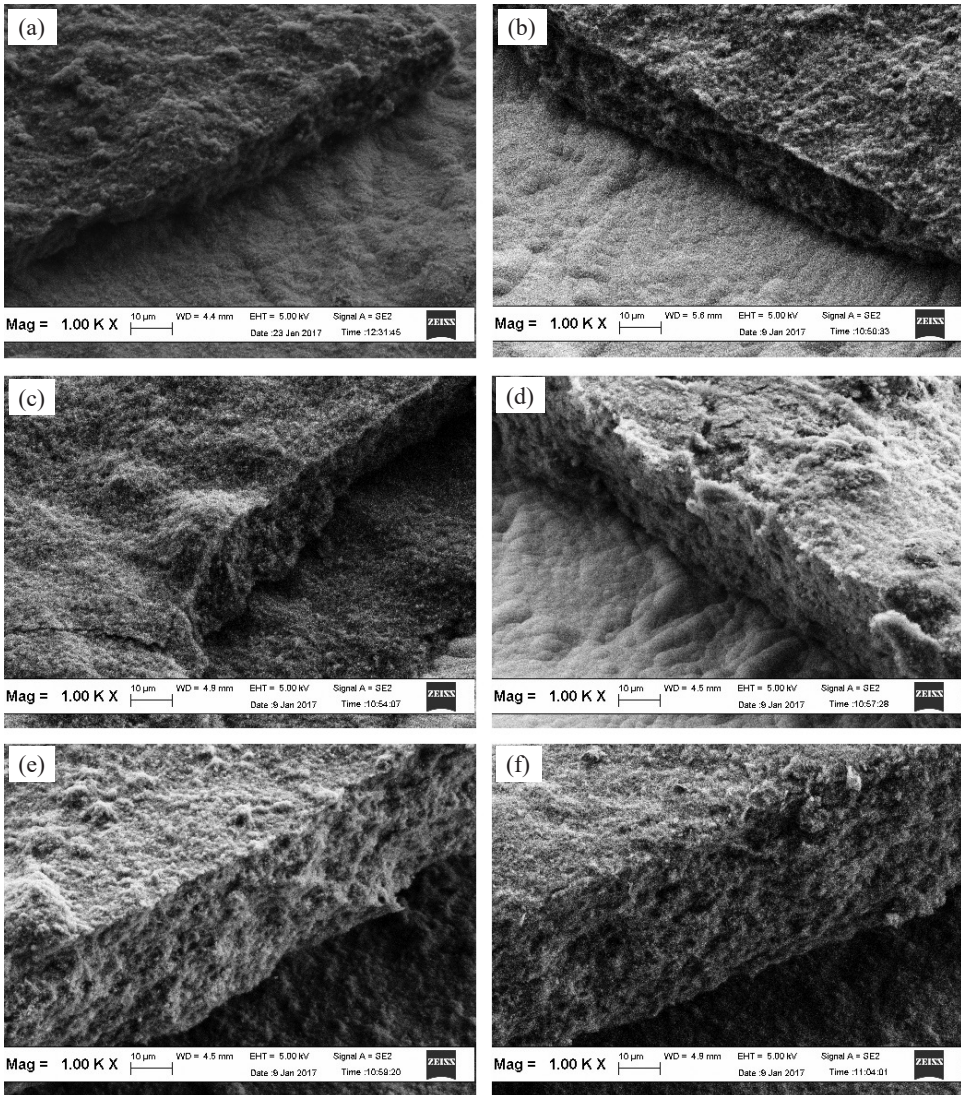


Figure 2: SEM images for 0.5 mg ml^{-1} CNTs suspension concentration deposited on heat spreader with (a) one layer, (b) two layers, (c) three layers, (d) four layers, (e) five layers, and (f) six layers. The EPD process conditions were maintained at 175 V of applied voltage, 10 min of deposition time, and 10 mm gap of electrode.

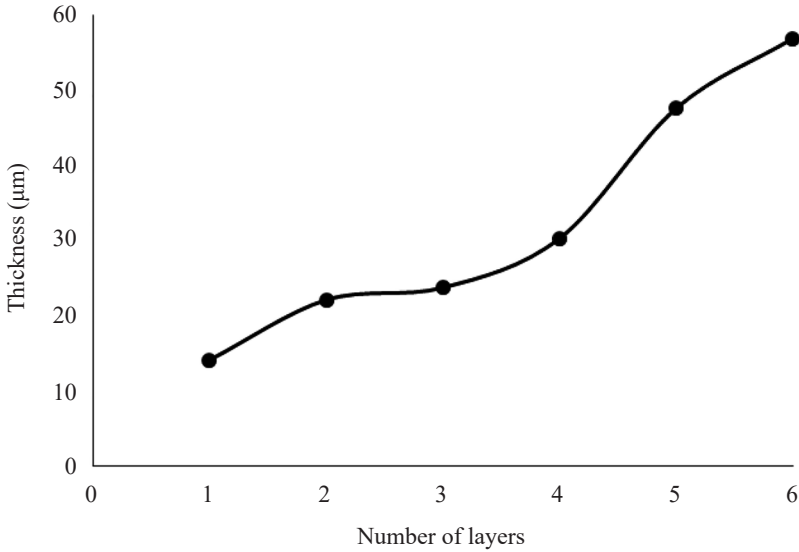


Figure 3: Thickness profile for deposited CNTs in regard to different layer. The EPD process conditions were 175 V applied voltage, 10 min deposition time and 10 mm gap of electrode.

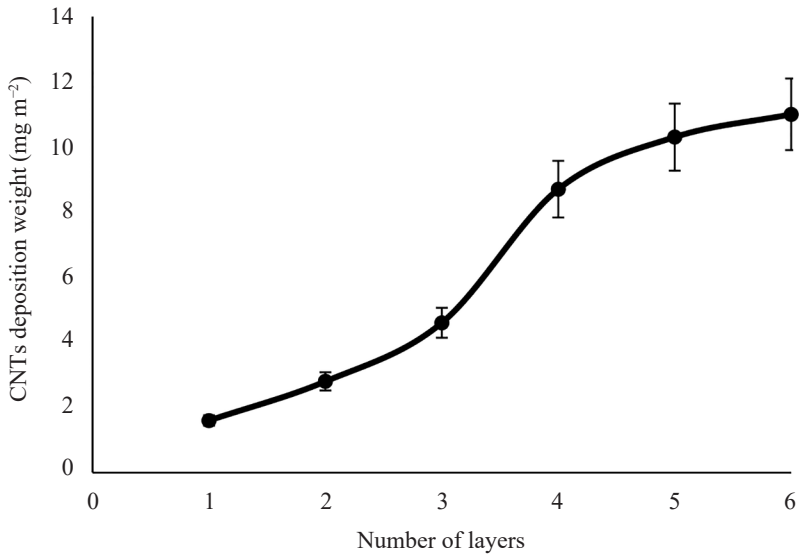


Figure 4: Graph profile of CNTs deposition weight for 0.5 mg m⁻² CNTs suspension concentration at different layers. The EPD process conditions manifested were 175 V of applied voltage, 10 min deposition time and 10 mm gap of electrodes.

Figure 4 shows the profile of CNTs deposition weight for different deposition layers of EPD conditions at 175 V, 10 min deposition time and 10 mm electrode gap. The weights of deposited CNTs for every deposition layers of one, two, three, four, five and six were 1.6 mg m^{-2} , 2.8 mg m^{-2} , 4.6 mg m^{-2} , 8.7 mg m^{-2} , 10.3 mg m^{-2} and 11.0 mg m^{-2} , respectively. The weight of CNTs was measured repeatedly in order to obtain precise deposition rate for the same EPD condition. Therefore, the error bar was added in Figure 3 which indicated minimum error for the measurements done. The error was less than 5% which is considered to be the minimum range. This indicates the uniformity of deposition when the EPD process is repeated. Moreover, the weight of deposited CNTs is important in predicting the thermal conductivity value for the package developed from CNTs that works as TIM and heat spreader. As the used CNTs were purified, the value of thermal conductivity was expected to be higher when compared to the composite CNTs. This happened due to the existence of other components which might affect the measurement of thermal conductivity. Thus, higher weight of deposited CNTs with the maximum layers of deposition was required to undergo successful heat removal process.

For the thermal conductivity measurement, the deposited CNTs were prepared in sets of two and the thermal sensor was placed between the samples. The CNTs deposited layer was facing each other where constant pressure was applied to remove air gap. This would affect the measurements due to poor thermal conductivity when the measurement was obtained at room temperature. Each reading of the thermal conductivity was taken by referring to the thermal conductivity standard of heat spreader which consisted of copper-nickel plate. The measurement was taken for six samples of CNTs layers deposition. Upon the introduction of CNTs deposition, small differences in thermal properties were found in the initial four layers of deposition ($5.88 \text{ W m}^{-1} \text{ K}^{-1}$) in terms of heat spreader thermal conductivity. The thermal conductivities were followed by $5.29 \text{ W m}^{-1} \text{ K}^{-1}$, $6.66 \text{ W m}^{-1} \text{ K}^{-1}$, $6.24 \text{ W m}^{-1} \text{ K}^{-1}$ and $4.98 \text{ W m}^{-1} \text{ K}^{-1}$ for layer one to four of CNTs deposition respectively. The values obtained for layer one to layer four was close to the value measured from the heat spreader. However, the thickness obtained is not sufficient enough for heat conduction to occur within the materials. The measured thermal properties were mostly attributed to the nickel plated substrate particularly. However, the thermal conductivity surprisingly increased to $24.57 \text{ W m}^{-1} \text{ K}^{-1}$ at five layers of deposition and the value was further increased to $27.08 \text{ W m}^{-1} \text{ K}^{-1}$ at six layers of deposition. Consequently, this shows that the CNTs deposition through EPD had greatly enhanced the thermal conductivity when compared to the best commercially available pastes and greases which ranges from $1 \text{ W m}^{-1} \text{ K}^{-1}$ to $10 \text{ W m}^{-1} \text{ K}^{-1}$.²¹

4. CONCLUSION

CNTs performed well as TIM due to higher thermal conductivity ability as shown from the thermal measurement. In this work, the TIM was assembled using EPD method where disposition of CNTs on heat spreader was successful. The CNTs were successfully deposited with repeated layers of deposition with an optimum thickness of 56.95 μm . This was further proved via SEM analysis where it shows good interaction in between CNTs and heat spreader during the fabrication of TIM. This confirms that the CNTs are suitable to be used as TIM due to good thermal conductivity with the value of 27.08 $\text{W m}^{-1} \text{K}^{-1}$ at six layers of deposition. The excellent thermal conductivity of CNTs creates a possibility for it to be considered for TIM usage for heat removal which might contribute towards more future sustainable technology.

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