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Carbon nanotube thermal interface material for high-brightness light-emitting-diode cooling

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Abstract
Aligned carbon nanotube (CNT) arrays were fabricated from a multilayer catalyst configuration by microwave plasma-enhanced chemical vapor deposition (PECVD). The effects of the thickness and annealing of the aluminum layer on the CNT synthesis and thermal performance were investigated. An experimental study of thermal resistance across the CNT array interface using the modified ASTM D5470 standard was conducted. It was demonstrated that the CNT-thermal interface material (CNT-TIM) reduced the thermal interfacial resistance significantly compared with the state-of-art commercial TIM. The optimized thermal resistance of the CNT arrays is as low as 7 mm² K W⁻¹. The light performance of high-brightness light-emitting diode (HB-LED) packages using the aligned CNT-TIM was tested. The results indicated that the light output power was greatly improved with the use of the CNT-TIM. The usage of the CNT-TIM can be also extended to other microelectronics thermal management applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Challenges in the thermal management of an electronic package arise from the continued increase in power dissipation and power density of higher-power devices [1]. One such example is solid state lighting using a high-brightness light-emitting diode (HB-LED) which is an attractive candidate for future general illumination applications. However, the efficiency, reliability and color of the solid state lighting devices strongly depend on successful thermal management of the package. With the increase of input power and the applications of high-density HB-LED packaging, the requirements of improving the performance and reliability impose a significant challenge on the thermal design of HB-LED packages and the application of novel materials. The luminance of HB-LEDs will reduce linearly while the life will reduce exponentially with the increasing junction temperature [2, 3]. Therefore, proper thermal design is imperative in keeping the LED package below its rated operating temperature. With the multilayer structure of HB-LED packages, the thermal resistance across material interface remains the bottleneck in heat transfer from the LED junction to the cooling system [4]. The thermal conductivity of conventional TIMs used in the interface is relatively low because the TIMs normally make up of polymer matrix with thermally conductive fillers.

The carbon nanotube (CNT) is a promising candidate to improve the thermal performance of TIM due to its low thermal resistance as well as the ultra-high thermal conductivity, about 600–3000 W m⁻¹ K⁻¹ for an individual multi-walled carbon nanotube (MWNT) [5, 6] and 15–250 W m⁻¹ K⁻¹ for bulk vertically aligned CNT (VACNT) films [7–9].
CNT composites with CNTs randomly dispersed in matrix material possess thermal conductivity no more than 10 W m^{-1} K^{-1} [10–12]. Fan et al filled polymer in aligned CNT arrays, and the thermal property of the CNT array composite was found to be better than that of random CNT composite [13]. They further used an aluminum thin film to reduce the thermal interfacial resistance of the CNT array composite [14]. However, the thermal interfacial resistance was still higher than 50 mm² K W^{-1}. It should be further improved to reach the thermal performance target of TIM of 5 mm² K W^{-1} [15]. Xu et al [16] and Cola et al [17] prepared some dry CNT arrays. The thermal resistance was measured using different methods and the results were 20 mm² K W^{-1} and 16 mm² K W^{-1}, respectively. Tong et al [18] also measured the thermal conductance of the CNT array as 9 × 10^4 W m^{-2} K^{-1}. All these experimental results indicated that a vertically aligned CNT array without polymer matrix is a good candidate of TIM.

In this paper, a process of CNT-TIM synthesis by microwave PECVD is presented. The thickness of the aluminum thin film was optimized, and the effect of annealing the aluminum thin film to minimize the thermal interfacial resistance of the CNT-TIM was studied. The CNT-TIM was used in HB-LED packaging and the optical performance was evaluated. The result showed that CNT-TIM can maintain the output light power of LED devices at high input current. It indicated the effectiveness of the CNT-TIM in facilitating the heat dissipation of HB-LED packages.

2. Experimental testing of CNT-TIM

2.1. CNT-TIM fabrication

CNTs were synthesized by the microwave PECVD process. Microwave power of 300 W was used. Zhang et al has shown that better CNT–substrate bonding and better CNT synthesis quality resulted in improved thermal performance [19]. A 20 nm titanium buffer layer was sputtered on the silicon substrate to improve its adhesion with the catalyst layer and the eventual aligned CNT-TIM. An aluminum layer was further sputtered on top of the titanium layer to help activate the catalyst particles. The thickness of aluminum layer was optimized, and the effect of aluminum layer annealing by e-beam evaporation on the top of the aluminum layer. In the CNT fabrication process, the substrate with catalyst was first introduced to the chamber and subjected to 40 sccm H₂ and 10 sccm N₂ plasma treatment at 850 °C for 1 min. CNTs started to grow with further introduction of 10 sccm CH₄ at the same temperature for 5 min. The plasma and the heater were turned off after the CNT growth. The whole system was then cooled down naturally to room temperature. Figure 1 shows the processing procedure of CNT synthesis.

2.2. Thermal resistance measurement

The thermal performance of the TIM is affected by the bulk material and the interfacial conditions of the HB-LED packages. Therefore, the thermal performance of CNT-TIM in this study was evaluated by the thermal resistance measurement system designed in accordance to ASTM D5470. The testing procedure was modified by adopting a lower contact pressure 0.15 MPa as compared with the 3 MPa stipulated in the ASTM D5470 standard. This modification is in line with the practice adopted in electronic packaging processes [20]. The testing setup is shown in figure 2(a).

Figure 2. (a) Schematic system of thermal resistance measurement; (b) sample package; (c) SEM image of grown CNT-TIM; (d) TEM of grown CNT.
The CNT-TIM sample package, shown in figure 2(b), has the aligned CNT array grown on a 1 inch by 1 inch Si substrate coupled with an aluminum alloy plate by mechanical pressure. A load cell was used to control the mechanical contact pressure at 0.15 MPa. Using this measurement technique, both the thermal resistance of bulk CNT-TIM \( (R_{TIM}) \) and the thermal interfacial resistances \( (R_{Si-TIM} \text{ and } R_{Al-TIM}) \) can be evaluated. The test sample configuration was designed to assimilate that of the real packages.

In order to compare the thermal performance of CNT-TIM with other state-of-art TIMs, three other kinds of TIM samples were prepared. The first is ‘air’, representing the direct attachment of a silicon substrate to an aluminum alloy surface with air entrapped in between. The second is ‘commercial silver epoxy’ having a layer of 25 \( \mu \text{m} \) thick commercial silver epoxy pasted and cured between a silicon substrate and an aluminum alloy surface. The third is a ‘metal system’ formed by a reflow process consisting of sputtered 80 nm titanium, 300 nm copper and 10 \( \mu \text{m} \) electroplated eutectic lead/tin solder on both the silicon substrate and the aluminum alloy surface.

### 2.3. HB-LED testing with CNT-TIM

The thermal management capability of the CNT-TIM was tested in HB-LED packages and the optical performance of the HB-LED packages was tested against packages with commercial TIM. A blue color 1 mm by 1 mm LED chip was assembled on a silicon-interposer with flip-chip technology. Figure 3 shows the cross-section of the LED package with CNT-TIM. The flip-chip bonded LED device was first assembled to a heat slug. Then the module was tested in HB-LED packages and the optical performance of the HB-LED packages was tested against packages with CNT-TIM and assembling it to an HB-LED package is described elsewhere [21].

The output light power of different samples was measured using a PMS-50 spectrometer from Everfine Company Limited. The input electrical current was varied from 150 to 900 mA. Measurements were taken after the samples were turned on for 6 min to ensure that the sample reached a thermal equilibrium state.

### 3. Results and discussion

#### 3.1. Thermal performance of CNT-TIM

The total measured thermal resistance of each TIM sample, \( R_{TIM} \), included the thermal resistance of bulk TIM \( (R_{TIM}) \) and two thermal interfacial resistances \( (R_{Si-TIM} \text{ and } R_{Al-TIM}) \). It was obtained in three steps, as shown in figure 4. First, the whole sample package was put in the thermal resistance measurement system. The measured thermal resistance, \( R_{package} \), was the sum of a whole series of thermal resistances, including \( R_{Cu-Si}, R_{Si}, R_{Si-TIM}, R_{TIM}, R_{TIM-Al}, R_{Al}, \) and \( R_{Al-Cu} \). Second, a Si chip was put in the thermal resistance measurement system. This measured thermal resistance, \( R_{Si} \), covered \( R_{Cu-Si}, R_{Si}, \) and \( R_{Si-Cu} \). Among them, \( R_{Cu-Si} \) was assumed equal to \( R_{Si-Cu} \) as the surface roughness conditions of the two Cu block surfaces and the two Si surfaces are the same. Similarly, the measured thermal resistance \( R_{Al} \) can be obtained inclusive of \( R_{Cu-Al}, R_{Al}, \) and \( R_{Al-Cu} \). With the assumption that \( R_{Cu-Al} \) equals \( R_{Al-Cu} \), the total thermal resistance of the TIM, \( R_{TIM} \), can be calculated as follows:

\[
R_{TIM} = R_{Si-TIM} + R_{TIM} + R_{TIM-Al} = R_{package} - \frac{R_{Si}}{2} - R_{Si} - \frac{R_{Al}}{2} - \frac{R_{Al}}{2} \tag{1}
\]

where the thermal resistance of bulk Si \( (R_{Si}) \) and bulk aluminum alloy \( (R_{Al}) \) can be calculated directly from their

---

**Figure 4.** Three steps to obtain the total thermal resistance of TIM.
In order to minimize the error of measurement, several samples were prepared and tested to obtain the average total thermal resistance, $R_{\text{TIM}}$, and standard deviation for each of the four kinds of TIM, as shown in figure 5. As for CNT-TIM, five samples were prepared and measured. The thermal resistance, $R_{\text{TIM}}$, ranged from 2 to 13 mm$^2$ K W$^{-1}$. The data deviation resulted from the error of temperature measurement ($\pm 0.3 \degree C$) by using class A platinum resistance temperature detectors and copper bar fabrication (5 $\mu$m). In addition, the samples were not exactly the same even though we used the same preparation method for each one. The resulting average thermal resistance of CNT-TIM is 7 mm$^2$ K W$^{-1}$ with a standard deviation of 5 mm$^2$ K W$^{-1}$. This is about 10% of that of the commercial silver epoxy TIM samples. It is also much lower than that of the metal system samples. This indicates that the aligned CNT array is a promising base material for TIM.

The total thermal resistance of TIM, $R_{\text{TIM}}$, depends not only on the thermal property of TIM itself, but also on the thermal and physical properties of the contacting members, the contact geometry, and the contact pressure [17]. The low thermal resistance of CNT-TIM in this study was achieved by having better bonding between the CNT-TIM and the substrate. In the process of heating the substrate to the CNT synthesis temperature, 850 $\degree$C, the supporting materials and the catalyst melt to form alloys or compounds because the melting point of nanoscale particles is typically much lower than that of the bulk material [22]. Therefore, the catalyst adhered better to the substrate and thus provided better adhesion at the roots of the CNT array. Furthermore, the flexible nanoscale tips of CNT arrays can possibly penetrate into the troughs on the rough interfacial surface, thus building more phonon flow paths. In addition, the high CNT density made the CNT array an effective heat conduction pathway and a strong structural support system. These facilitated phonon heat transfer from the silicon chip to the aluminum alloy plate via the CNT array along its axial direction. As a result, the total thermal resistance of CNT-TIM was much lowered.

### 3.2 Effects of annealing of substrate and catalyst

We investigated the effect of annealing of substrate in O$_2$ on CNT synthesis. Substrates with supporting layers of 20 nm titanium and 10 nm aluminum were annealed in O$_2$ at 550 $\degree$C for 30 min before the 10 nm nickel catalyst layer was deposited. Figures 6(a) and (b) are AFM images of substrates (Si/Ti/Al) with and without annealing of substrate in O$_2$, respectively. It was shown that after annealing the surface of the substrates changed from a thin film structure (with average roughness of 1.524 nm) to a relatively rough configuration (with average roughness of 5.168 nm). High-density uniform sized small protrusions were observed on the substrate. The interaction surface area of the substrate was significantly increased.

We also investigated the effect of additional annealing of catalyst-coated substrates in H$_2$ microwave plasma. After the 10 nm nickel catalyst layer was evaporated on the top, the substrates were put in the PECVD chamber and heated to 850 $\degree$C. The catalyst-coated substrates were then annealed for 1 min in H$_2$ microwave plasma at this temperature and 720 Pa. Figures 6(a) and (b) are AFM images of catalyst-coated substrates (Si/Ti/Al) without annealing in H$_2$ microwave plasma. Figures 6(c) and (d) are AFM images of catalyst-coated substrates (Si/Ti/Al/Ni) with annealing in H$_2$ microwave plasma. It is shown that the average roughness of catalyst-coated substrates after annealing in H$_2$ microwave plasma is higher than those without annealing.

Figures 6(e) and (f) show the results of CNT growth on substrates with and without substrate (Si/Ti/Al) annealing in O$_2$, respectively. It is obvious that there is no CNT growth on the substrate without annealing in O$_2$, while there are vertically aligned CNTs grown on the annealed substrate. It is more conducive for CNT growth on relatively rough surfaces because the neutral gases are decomposed into ions or radicals in the plasma region with the intense high-energy electron impact, and the ions are more reactive with the larger catalysts where electric fields are preferentially concentrated [23]. Therefore, both annealing of substrates and annealing of catalyst-coated substrates are good for aligned CNT growth.

The thermal resistances of CNT-TIM grown on substrates with and without annealing were measured to determine the effect of annealing on the thermal performance of CNT-TIM. It is shown clearly in Table 1 that the thermal resistance of CNT-TIM on substrates with annealing in O$_2$ is much lower than that of CNT-TIM on substrates without annealing in O$_2$. In conclusion, substrate annealing is helpful not only to CNT synthesis but also to thermal performance improvement of synthesized CNT-TIM.

### 3.3 Effects of aluminum buffer layer thickness

It was found from experiments that the growth of CNTs is sensitive to the thickness of the aluminum buffer layer. The effect of aluminum thickness on CNT growth under the same synthesis conditions was investigated, and the result is shown.
Figure 6. Effect of substrate and catalyst annealing on CNT growth. (a) AFM image of substrate with Si/Ti/Al annealing in O₂ but without Si/Ti/Al/Ni annealing in H₂ plasma; (b) AFM image of substrate without Si/Ti/Al annealing in O₂ and also without Si/Ti/Al/Ni annealing in H₂ plasma; (c) AFM image of substrate with Si/Ti/Al annealing in O₂ and with Si/Ti/Al/Ni annealing in H₂ plasma; (d) AFM image of substrate without Si/Ti/Al annealing in O₂ but with Si/Ti/Al/Ni annealing in H₂ plasma; (e) CNTs grown on substrate with Si/Ti/Al annealing in O₂ and also with Si/Ti/Al/Ni annealing in H₂ plasma; (f) CNTs grown on substrate without Si/Ti/Al annealing in O₂ but with Si/Ti/Al/Ni annealing in H₂ plasma.

Table 1. Thermal resistances of CNT-TIM on substrates with and without annealing.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Thermal resistance (mm² K W⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT-TIM with annealing in O₂</td>
<td>7 ± 5</td>
</tr>
<tr>
<td>CNT-TIM without annealing in O₂</td>
<td>61 ± 7</td>
</tr>
</tbody>
</table>

Table 7. Figure 8 shows the relationship between the density and the average length of grown CNTs with the thickness of aluminum layer. It shows that 10–15 nm is the best range of aluminum layer thickness for growing dense and vertically aligned CNT arrays with uniform length.

The thermal resistances of CNT-TIM on substrates with different aluminum thickness were tested. The results, given in table 2, show that the thermal resistance of CNT-TIM on a substrate without aluminum layer is 44 mm² K W⁻¹. It is much higher than that of CNT-TIM synthesized on substrates with a 10–15 nm aluminum layer, which is only about 5–10 mm² K W⁻¹. With a 10–15 nm aluminum layer, high-density and vertically aligned CNT arrays with uniform length were synthesized. Higher CNT density is beneficial to heat dissipation by providing more heat conduction paths and minimizing the air gaps. Uniform CNT length will facilitate more CNT tip contact with the mating surface to reduce the thermal interfacial resistance. Therefore, this indicates that an aluminum layer with proper thickness should be used to synthesize CNT-TIM with low thermal resistance.

3.4. Light performance of HB-LED packages with CNT-TIM

The output light power of HB-LED packages should ideally maintain a linear relationship with the electrical input current if the heat generated from the LED modules can be effectively
Figure 7. CNT synthesis results with different aluminum thickness: (a) 0 nm, (b) 5 nm, (c) 10 nm, (d) 12 nm, (e) 15 nm, (f) 18 nm.

Figure 8. Effect of the thickness of aluminum layer on the density and average length of grown CNTs.

dissipated. However, as the input power increases, ineffective heat dissipation would degrade the LED optical performance and result in the output light power reaching a saturation value. Figure 9 shows that, up to an input current of 350 mA, the commercial TIM as well as CNT-TIM can dissipate heat well and the output light power of both packages increase linearly with the input current. However, the output light power of the HB-LED packages with the commercial TIM starts to deviate from a linear relationship with the input current approaching 350 mA and attains a peak value at 700 mA. With CNT-TIM, the output light power of HB-LED packages retains a linear profile with increasing input current and does not reach a saturated value even up to 900 mA.

Figure 9 also demonstrates that the HB-LED packages with higher synthesis quality CNT-TIM results in better optical performance. Compared with sample CNT2 and CNT3, CNT1 has a higher CNT density and more uniform length. The tips of CNTs with uniform length can better penetrate into the troughs of the rough aluminum surface and reduce the thermal interfacial resistance. In addition, high-density CNTs will easily maintain their vertically aligned morphology instead of collapsing. Therefore, the thermal performance of CNT-TIM is benefiting from the heat conduction in the CNTs along their axial direction. As a result, the optical performance of the HB-LED package with CNT1 is better than that of the HB-LED package with CNT2 or CNT3. However, there is not much degradation of the optical performance of HB-LED packages with CNT3-TIM, which has the worst quality. This is because the average thermal performance of CNT-TIMs is high, which allows them to meet the requirement of heat dissipation of HB-LED packages at the current power level, even the sample with relatively worse quality. However, with the input power increasing, it is expected that HB-LED packages using CNT-TIM samples with different thermal performance will have more distinctive optical performance.

4. Conclusions

The thermal performance of the CNT-TIM in the HB-LED packages influences their optical performance. It is demonstrated that the quality and morphology of CNT-TIM synthesis are important factors affecting the thermal performance of the CNT-TIM. CNT-TIM synthesis by microwave PECVD was demonstrated and optimized. Both annealing of the substrate and annealing of the substrate with catalyst were found to improve the quality of the grown CNTs. The aluminum layer was shown to help activate the catalyst for CNT growth. The thickness of aluminum layer was optimized to 10–15 nm. The thermal performance of CNT-TIM was evaluated according to the modified ASTM D5470 and compared with commercial TIMs. The total thermal resistance of the CNT-TIM was only 7 mm² K W⁻¹ and was

<table>
<thead>
<tr>
<th>Aluminum thickness (nm)</th>
<th>Thermal resistance of CNT-TIM (mm² K W⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>44 ± 5</td>
</tr>
<tr>
<td>10</td>
<td>7 ± 4</td>
</tr>
<tr>
<td>12</td>
<td>10 ± 3</td>
</tr>
<tr>
<td>15</td>
<td>5 ± 4</td>
</tr>
</tbody>
</table>

Table 2. Thermal resistances of CNT-TIM on substrates with different aluminum thickness.
about 10% of that of commercial silver epoxy TIM. The fabricated CNT-TIM was further used for HB-LED packaging and the measured output light power of LED packages was able to maintain a linear relationship with input current up to 900 mA without reaching saturation. The experimental results illustrated that the aligned CNT array is a promising base material for TIM used in HB-LED packages.

References

