

Growth of Uniform CNT Layer on Copper Foil-the Effect of Synthesis Methods/Conditions

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ABSTRACT

Carbon nanotubes (CNTs) with unique thermal and electrical properties, and inherently large surface area are an attractive candidate for integration into thermal structures and for a flexible thermal interface material in power electronics packages. However, reproducible and controllable synthesis of CNTs on reactive substrates such as metals, ceramics and carbon materials has been a challenge compared to growth on conventional, inert substrates such as SiO₂. In this study two different growing methods, pre-coated catalyst thermal chemical vapor deposition (THCVD) and floating catalyst thermal chemical vapor deposition (FCCVD), were used to investigate direct growth of high quality CNT layers on copper foil substrates. SEM images and initial testing results indicated that the synthesis method, growth conditions and especially substrate surface treatment significantly impact CNTs growth, and structure/morphology, as well as interfacial strength and thermal performance. Using either THCVD or FCCVD with Fe as the catalyst, only sparse, poorly-aligned CNT forests were grown on Cu foil substrates. In contrast, uniform, dense, aligned CNT layers were successfully formed with both THCVD and FCCVD under optimized processing conditions when a thin buffer layer of Al₂O₃ was deposited on the Cu foil by atomic layer deposition (ALD) prior to CNT growth. Furthermore, the length, alignment and areal density of CNTs could be controlled by varying the thickness of the Al₂O₃ layer.

Keywords: Carbon nanotubes (CNTs), copper substrate, chemical vapor deposition (CVD), atomic layer deposition (ALD), Al₂O₃ buffer layer

1 INTRODUCTION

As future power electronics operate at higher temperatures, and electronic devices become smaller and faster, heat sinking and thermal transport will become increasingly important. Unless developments in thermal management technology occur in parallel, the continued enhancements in the electrical performance of these devices will be hindered. To address this important thermal management concern, nano-engineered materials are being investigated. Carbon nanotubes (CNTs) with unique properties and inherently large surface area are an attractive

candidate for integration into thermal structures and for a flexible thermal interface material in power electronic packages.

Although vertically-aligned CNT (VA-CNT) synthesis on silicon substrates has been widely investigated and has shown great promise [1-3], the high temperature needed for CNT growth would ruin most conventional Si based electronic devices. Hence, trying to grow CNTs directly on the back of a Si die would be ill-advised. Instead, growth of CNTs directly onto one of the metallic substrates typically used for packaging would be preferred [4, 5]. Copper is one of the most common of these metallic components and has been used in many applications. The direct growth of CNTs on Cu or other metal substrates would not only provide a thermally conductive transition layer, but it would also eliminate some processing steps. Furthermore, these CNTs/metal composite structures could be used as a conductive support for different applications such as energy storage, sensing, and nano-electronics, etc. [4].

Compared to CNT growth on conventional inert substrates (such as SiO₂), controlling CNT growth on active metallic substrates is much more of a challenge. This is because the diffusion between metallic catalyst and metallic substrate under CNT synthesis conditions will reduce catalyst activity. Although VA-CNT direct growth on various metal substrates has been reported by several groups [6-9], growth of CNTs directly on copper substrate is still a challenge on controlling their structure and quality. For example, Yin et al. reported growing multi-walled CNTs on an oxygen-free copper substrate with a poor CNT alignment [7]. VA-CNTs made in Fisher's research group by PECVD for thermal management [8, 9] exhibited different average diameters, diameter distributions and CNT coverage on the growth substrates even though the same synthesis conditions were used. Overall, quality, alignment and reproducibility of CNTs with desired structure are main issues which must be addressed for direct growth CNTs on metal substrates.

In this study, pre-coated catalyst thermal chemical vapor deposition (THCVD) and floating catalyst thermal chemical vapor deposition (FCCVD) were used to directly synthesize high quality CNT layers on copper foil substrates. In order to better understand the mechanism of CNT growth, the effect of synthesis methods and growth conditions on CNTs morphology and quality has been investigated.

2 EXPERIMENTAL METHOD

2.1 Cu substrate preparation

The 99.99% pure copper foil (Cu) (~400 μm thick, purchased from Vortex metals, Inc.) was cut into 6 x6 mm and 12.2 x 12.2 mm samples. The Cu samples were then cleaned via ultra-sonication in acetone. The dried Cu substrates were then loaded into either a RF sputtering or an ALD system for thin film deposition. The sputter coating system (DV-502A) was employed to deposit a thin catalyst (Fe) layer when applicable onto either bare Cu or Al_2O_3 coated Cu. The Al_2O_3 buffer layer was applied to the Cu substrates with an ALD system (Savannah S-100).

2.2 Syntheses of CNTs on Cu substrate: Pre-coated catalyst thermal chemical vapor deposition (THCVD)

For THCVD growth of the CNTs, The general experimental processing (scheme) is shown in Figure 1. A tube furnace was set up as a horizontal CVD reactor for use in both annealing (catalyst thin film) treatment and CNT growth. First, the Cu substrates were loaded on a quartz tray and put in the middle of the tube. The tube was pumped down to 7 mTorr, The furnace was then ramped to the desired annealing temperature with floating Ar + H_2 (5%) at 90 Torr. The samples were annealed in-situ at the desired temperature (700°C, 750°C or 800°C). When the annealing time was reached, the sample was cooled down. Upon cooling, the CVD system was reheated to the desired growth temperature and a Ar + C_2H_2 (10%) precursor mixture was introduced; the pressure was kept at 90 Torr for 30 minutes. The precursor mixture was then turned off, and Ar + H_2 (5%) was used to purge the tube of any residual carbon contaminants while holding at temperature for 5-10 minutes. The samples were then cooled to room temperature under the same purge gas flow conditions.

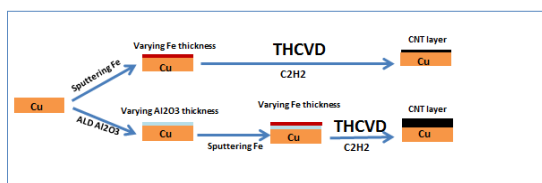


Figure 1: Scheme of processing for CNTs grown on Cu substrate by THCVD (not to scale)

2.3 Syntheses of CNTs on Cu substrate: Floating catalyst thermal chemical vapor deposition (FCCVD)

For FCCVD growth of the CNTs, the general experimental processing (scheme) is shown in Figure 2. A tubular furnace was also set up as a horizontal CVD reactor, and Cu substrates were placed in the middle of the quartz tube on the quartz tray. Ar and H_2 (flow rate ratio=2:1) were used as the carrier gas. A mixture of ferrocene/*m*-xylene (0.012g/ml) was used as the iron catalyst and carbon

source, and was continuously fed into the furnace via a digital syringe pump at a desired feed rate during the reaction (at 750°C). After the reaction, the samples were cooled to room temperature in flowing Ar and then removed from the quartz tube for characterization.

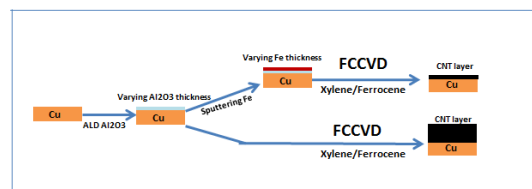


Figure 2: Scheme of processing for CNTs grown on Cu substrate by FCCVD (not to scale)

2.4 Characterization of CNTs on Cu substrate

Systematic characterization of CNTs on Cu substrates is important for improving the growth methods and techniques. The structure and morphology of CNTs grown on the Cu substrates at different method/conditions was studied using scanning electron microscopy (Jeol JSM-6060). Raman spectroscopy was performed using a Renishaw inVia Reflex Spectrometer System to determine the quality of the CNTs grown on Cu substrates (CNTs/Cu) by D/G peak ratio. The interfacial thermal impedance is determined by ASTM D5470 Thermal Interface Material (TIM) Testing System. A peel off tester was used to quantify CNTs/substrate interfacial adhesion.

3 RESULTS AND DISCUSSIONS

3.1 Synthesis of CNTs by THCVD

3.1.1. Cu as substrate without buffer layer

It has been reported that Cu alone can act as an effective catalyst for CNT growth under certain conditions [10, 11]. However, compared to Fe, or Ni, etc., the catalytic activity of Cu is much lower, and the grown CNTs catalyzed by Cu are “spaghetti-like” [12]. Therefore, to grow dense aligned CNTs on Cu substrates, a more active catalyst needs to be introduced on the Cu surface. In order to eliminate processing steps and hopefully minimize contact resistance between CNT and Cu substrate, in our early experiments, Fe thin film catalyst was directly sputter deposited onto the Cu substrates. The studies were focused to investigate the effect of annealing/growth temperature and thickness of catalyst (Fe) layer on CNT quality. The SEM results of CNTs growth under different annealing/growth temperatures and varying catalyst layer thicknesses indicated that through an optimized THCVD process, CNTs could be grown on Fe coated Cu substrates. As expected, the quality and morphology of CNTs was affected by annealing/growth temperature and the thickness of catalyst. When annealing temperature or catalyst layer thickness was increased, the CNTs areal density increased,

and the CNTs were more likely to grow individually rather than as bundles. Although a uniform, non-aligned CNT layer was achieved at 750°C with 15 nm Fe, the most of CNTs were randomly distributed and tangled yielding a non-uniform film on the majority of the Fe/Cu substrates. The reason for this outcome was because the diffusion between catalyst and copper substrate inhibited catalyst activity and the resulting CNT growth. To overcome this problem, an effective method would be to deposit a thin barrier layer to restrain the diffusion reaction between catalyst and substrate [13].

3.1.2. Buffer layer coated Cu as substrate

A proper combination of the catalyst and the buffer layer material can result in uniform and dense catalyst islands for seeding CNT growth [14]. In our study, the Al₂O₃ buffer layer was deposited on the Cu surface by ALD. The effect of both Al₂O₃ and Fe layer thickness on CNTs growth, morphology, and overall quality was investigated. The experimental results indicated that a uniform CNT layer could be grown on a bilayer (a thin layer of Fe on a support Al₂O₃ layer) coated Cu substrate by using THCVD, and the morphology of the CNTs was affected by the thicknesses of both the Fe and Al₂O₃ layers. For example, at a set Al₂O₃ layer thickness, when the Fe thickness was increased from 2 nm to 5 nm, the areal density/uniformity and the alignment of CNTs layer increased. Similarly, at a constant Fe layer thickness (5 nm), when the Al₂O₃ thickness was increased from 5 nm, to 10 nm, to 15 nm, and to 30 nm, we observed several trends. First, as shown in Figure 3, there was an overall increase with the height of CNT forest; however, the highest CNT forest corresponded to the 15 nm Al₂O₃ coated sample as opposed to the 30 nm. Secondly, as the buffer layer thickness increased, the morphology of top surface seemed to change (Figure 3). This was more likely due to changes in CNT length and areal density. Finally, the diameter of the CNTs tended to remain constant regardless of the thickness of the buffer layer.

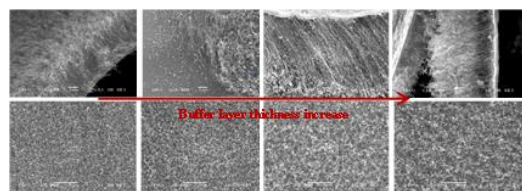


Figure 3: CNT growth on Fe/Al₂O₃/Cu substrate with varying thickness of Al₂O₃, (Left to right = 5 nm, 10 nm, 15 nm and 30 nm)

3.2 Synthesis of CNTs by FCCVD

In this method, keeping all other CNT growth parameters constant, the effect of Al₂O₃ buffer layer thickness and growth time on CNT morphology/quality was investigated. The thickness of the Al₂O₃ film was either 0 nm (pure Cu substrate without buffer layer), 5 nm, 10 nm,

15 nm or 30 nm; the growth time was either 20 min or 40 min. Based on the SEM results of this set of experiments, several observations were made. First, as expected, the choice of buffer layer certainly played an important role in the growth of a uniform, dense and aligned CNT forest on the Cu substrate as Figure 4 shows. Second, at a growth time of 20 min, when the Al₂O₃ thickness was increased from 5 nm to 10 nm, the CNT layer length is increased from 15 μm to 20 μm. Interestingly, there was no effect on CNTs length when buffer layer was increased to 15 and 30 nm in thickness. Thirdly, at 40 min growth, there was a significant increase in CNTs length when the buffer layer thickness was increased from 5 nm to 10 nm and from 15 nm to 30 nm. For some yet unexplained reason, however there was no noticeable effect on CNTs length when buffer layer thickness changed from 10 nm to 15 nm (Figure 4). Forth, for all thickness except the 5 nm Al₂O₃, an increase in growth time resulted in an increase in CNT length (the maximum length ranged from 22 μm to 80 μm). Fifth, the areal density, CNT layer surface flatness and CNT bundle alignment all increased with increasing Al₂O₃ thickness, regardless of growth time. The alignment improvement was perhaps most noticeable when the buffer layer thickness was increased from 5 nm to 10 nm (Figure 4). Finally, the diameter of the CNTs (d = 40 nm~50 nm) was independent of buffer layer thickness and growth time.

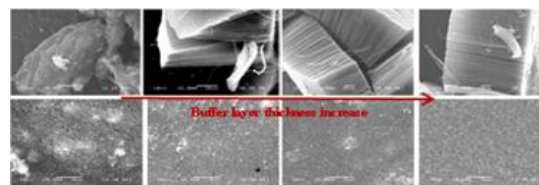


Figure 4: CNTs growth on Al₂O₃/Cu substrate with varying thickness of Al₂O₃ (Left to right = 5 nm, 10 nm, 15 nm and 30 nm)

3.3 The quality of the CNTs grown on Cu

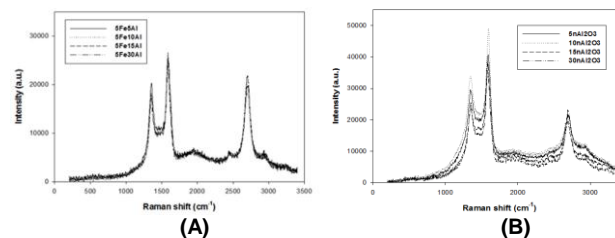


Figure 5: Raman spectroscopy of the CNT/Cu THCVD (A) and FCCVD (B)

The quality of the CNTs in our study was determined by Raman spectroscopy using the D/G peak ratio with green (532 nm) laser radiation. D and G Peak for CNTs were observed at 1354cm⁻¹ and 1588cm⁻¹, respectively. Upon compilation of the results in Figure 5, it was concluded that the CNTs grown on the Al₂O₃ coated Cu substrates via both THCVD and FCCVD resulted in

acceptable D/G ratios (range 0.65-0.74). Compared to FCCVD, CNTs grown by THCVD resulted in a consistent D/G ratio.

3.4 Thermal properties testing

The initial thermal properties test results are shown in Figure 6. As seen in the figure, when CNTs were grown on Cu substrate, the thermal impedance was lower than that of pure Cu foil. The reason for this improvement might be that CNT layer can provide a substantial increase in contact area at the cost of only a slight thickness increase. The experiment results also showed that when areal density and CNT length was increased, the impedance value was reduced. To fully understand these initial testing findings, more indepth studies are required in the future.

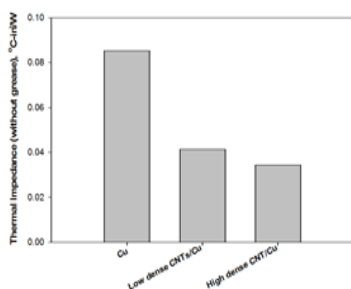


Figure 6: The effect of CNT layer on CNTs/Cu impedance

3.5 Interface adhesive measurement of CNTs/Cu

The measured results of interfacial adhesion between the CNT layers and Cu substrates show that values for shear force was higher than normal force for all samples. The reason for this was that the contact area for the shear force test was larger than that of the normal force test. These initial experimental results also showed that the highest normal force and the highest shear force values corresponded to the with 5 nm and 30 nm Al₂O₃ coated samples, respectively. More research is needed to better understand the effect of buffer layer on interfacial properties.

4 CONCLUSIONS

A CNT layer could be grown on Cu foil by using both THCVD and FCCVD. If Fe was used as a catalyst, without a buffer layer on the Cu foil surface, only sparse, poorly-aligned CNT forests were grown. When Al₂O₃ was used as a buffer layer, uniform/dense /aligned CNT forests could be grown on the Cu substrates via both THCVD and FCCVD. If the thickness of Al₂O₃ layer was increased (from 5nm to 30 nm), the length and alignment of CNTs is increased as well. Additionally, the areal density and uniformity of the CNT forest was also improved. There was almost no effect on CNT diameter when the buffer layer thickness and CNT growth time were varied for both THCVD and

FCCVD. Experiment results indicated that CNT length could be controlled by varying growth time in the FCCVD method. The Raman analysis suggested that the CNTs grown on the Al₂O₃ coated Cu substrates via both THCVD and FCCVD resulted in acceptable D/G ratios. Initial thermal impedance testing results suggest that the CNT layer can improve interface connection and reduce contact resistance. Hence, the CNTs could be used as a promising thermal interface material.

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