Fabrication of Carbon Nanotube/Copper and Carbon Nanofiber/Copper Composites for Microelectronics

Leila Ladani^{1*}, Ibrahim Awad², Ying She³, Sameh Dardona³ & Wayde Schmidt³

1. Department of Mechanical and Aerospace Engineering, University of Texas at Arlington

2. VEXTEx Corporation

3. United Technologies Research Center, East Hartford, Connecticut, USA

Abstract

Carbon Nanotubes (CNTs) and Carbon Nanofibers (CNFs) exhibit high ampacity, the key property needed for next-generation interconnects, at miniaturized scales. Copper (Cu), the current state-of-the-art material used in interconnects, faces reliability issues at further miniaturized scales. This is due to high current density causing electromigration of Cu atoms. Therefore, CNTs and CNF were proposed to replace Cu in next-generation microelectronics. Using standalone CNT or CNF structures is very challenging and achieving the same properties as an individual CNT or CNF is difficult. The difficulty arises because the electrical properties of a grown forest depend on characteristics of the forest including self-alignment, density and mechanical stability. Thus, in this study, Cu is used to densify self-aligned CNTs and CNFs so that the mechanical stability and high density can be achieved. Parameters that impact the quality of the final Cu-CNT composite layer including the CNT qualities and fabrication techniques, CNT underlayer effect and different Cu deposition techniques are investigated. Different Cu deposition techniques on the as-grown CNTs are also experimented including electroplating, electroless plating and physical vapor deposition (PVD). The experiments show that although CNFs were successfully coated with Cu using electroless plating, CNTs are found to be fragile and are dissolved during the process of electroless plating. Furthermore, it was found that CNTs cannot act as seed layer for Cu. Other underlayer material such as Ti and TiN were found difficult to work with due to several reasons. Ti and TiN were not found a good material to grow vertically aligned CNTs using CVD. However, PECVD combined with TiN underlayer was successful in obtaining vertically aligned CNTs, although with a much slower growth rate compared to CNTs grown on Al₂O₃ underlayer. However, TiN was not successful in terms of electroplating.

1. Introduction

Next-generation of microelectronic devices require new candidate materials that will increase their reliability, performance and functionality. Carbon nanostructures exhibit promising thermal, mechanical and electrical properties [1] that make them good candidate materials to replace some key components of silicon-based devices. Carbon Nanotubes (CNTs) and Carbon Nanofibers (CNFs) are among those nanostructures that have been investigated vastly to replace the materials of some microelectronics' key components such as transistors [2–4] and interconnects [5–8]. According to International Technology Roadmap for Semiconductors (ITRS) [9], Cu, would not be able to meet the miniaturization requirements of the next-generation microelectronics due to its low current carrying capacity (ampacity) and electromigration. Electromigration is the transport of materials by gradual movement of ions in a conductor due to momentum transfer between the electrons and the atoms [10]. The mass transfer due to electromigration is directly related to the current density. As the size of the conductors decreases, their cross section area decreases accordingly. Therefore, to carry the same current, the conductors have to bear larger current density. This results in a higher mass transfer in smaller interconnects. Thus, novel materials with higher ampacity need to be developed.

CNT and CNF are believed to be good candidate materials, since their ampacity is higher than Cu's by four and one orders of magnitude, respectively [11,12]. If used with current technologies, CNTs and CNFs will have to be interfaced with other materials including other interconnect materials such as Cu. For instance, CNTs can be used in vertical interconnects such as Through Silicon Vias (TSVs) in microelectronics [13–16]. Issues associated with fabricating standalone CNTs and CNFs include low mechanical stability, interface resistance and low

density. In order to facilitate interfacing these materials with other Cu interconnects, a composite forms of materials such as CNT/Cu-composites have been proposed.

Fabrication of these interconnects in a composite form is believed to overcome some of these issues. Recent studies on CNT/Cu-composites have shown great improvements in conductivity and ampacity [17]. It was shown that CNT/Cu-composite has the same conductivity as that of Cu and two order orders of magnitude higher ampacity than Cu's [17]. Furthermore, Cu's addition is believed to densify the interconnects and enhance the mechanical stability.

CNF/Cu composite is used as general on-chip interconnects. It can be used in different forms of interconnect such as lines, interposers or vias. CNF-interconnects have been investigated extensively in the literature as replacement to Cu-interconnects [6,8,12,18]. The reliability of CNF-interconnects was compared with ITRS requirements for next-generation microelectronics and they were found viable for future implantation in on-chip interconnects [6,12]. However, the resistivity of individual CNF was found to be higher than that of Cu by two orders of magnitude.

The morphology of CNTs and CNFs are different in a sense that CNTs are formed by parallel graphene layers, while CNFs graphene layers are slanted as shown in Fig. 1. CNTs tunneling effect cannot be fully implemented in CNFs due to discontinuity of these slanted graphene layers.

Fig. 1. Difference between CNT and CNF

CNTs are very stable materials. Carbon has strong sp^2 hybrid bonds with its neighboring carbon atoms and no desire to bond to anything outside of the tube. Furthermore, the large curvature of the surface of the CNTs prevents adhesion of other materials. It was shown previously that CNTs have poor wettability to metals [19]. Metals surface tension plays an important role in this wetting behavior. Liquids with low surface tension such as water or other aquatic solutions can easily wet the CNTs. However, it was discovered by Ebbesen [20] that materials with surface tension higher than 100-200 mN/m generally do not wet the surface of CNTs. Many have suggested chemically treating the CNT surfaces such as oxidation or acid treatments so that it could react with other materials. Using these approaches, researchers have used mostly electroless plating of CNTs [19,21,22]. However, these technologies have yet to achieve optimum results and full use of CNTs extraordinary properties.

At the large scale, most technique involve blending with metal nanoparticles, ball milling, extrusion or other methods [23]. At smaller scale a co-deposition of copper and graphene and CNTs were examined using electrochemical processes [24]. Electrodeposition and electroless chemical processes [25] have always been a technique that is deemed a potentially successful technique for fabricating these composites. However, these technique have not been found repeatable and systematics for successful production of CNT-Cu composites. Due to the novelty of CNT/Cu- and CNF/Cu-composites, a systematic fabrication technique needs to be provided. There are many factors that have to be primarily investigated such as growth technique, types of under-layers and catalysts, growth temperature and Cu deposition technique. These factors have a chief effect on the properties of the as-grown CNTs or CNFs. The sought properties include self-alignment, high density, high growth rate (in order to reduce the fabrication cost) and high adhesion to the substrate to facilitate possible subsequent plating processes. In this study, the

effect of the previous factors on the properties of the CNT- and CNF-forests is investigated. Moreover, different Cu deposition techniques are evaluated.

2. Fabrication

The goal of this research was to evaluate different approaches that could result in a robust technique for fabricating cu-CNT composites for microelectronic devices. Initially, highly dense vertically aligned forest of CNTs are fabricated on the surface of a wafer and subsequently Cu is deposited on the CNTs. A successful approach would result in Cu infiltrating CNTs and creating a fully dense composite material on top of a wafer with CNTs oriented vertically and going through thickness. The CNTs could provide tunneling effect for electrons to transfer and create a high ampacity material in through thickness direction. Several parameters are important in successful fabrication of these interconnects. In order to be able to electrodeposit copper, a seed layer must be deposited under CNTs, although CNTs were also examined as seed layers in this study. The analysis was conducted with Al_2O_3 , Ti and TiN under layers. When Al_2O_3 was used the assumption was that CNTs can perhaps act as seed layers. Ti and TiN are both conductive materials and were deposited as seed layers for Cu. Several different scenarios were tested in this study including different CNT growth techniques, under-layers, catalysts, temperatures and Cu deposition techniques as shown in Table 1. Both Plasma Enhanced and regular Chemical Vapor Deposition PECVD and CVD were used for growth of CNTs as seen in this table. Catalyst used for growing CNTs were Fe and Ni. The fabrication temperature was varied to find the best recipe for obtaining highly dense, highly oriented CNTs.

Table 1. Fabrication scenarios for CNT-Cu

Process	Under-layer (buffer or seed layer)	Catalyst	Temp (C°)
CVD	Al ₂ O ₃	Fe	675
			700
			725
			750
	Ti	Fe	750
	TiN	Fe	750
		Ni	750
PECVD	TiN	Fe	650
		Ni	650

All the processes starts with creating insulation layer of SiO₂ (200 nm) thermally on the surface of the wafer. In a case where CNTs were supposed to be used as seed layer, the underlying buffer layer was selected to be Al₂O₃. A 20-nm layer of Al₂O₃ is deposited as a buffer layer using Electron Beam (E-Beam) evaporation. The buffer layer is deposited prior to catalyst deposition in order to avoid the formation of silicide during the growth process [26–28]. Alumina, in particular, assists to grow aligned CNTs. Another characteristic feature of alumina is that it restricts the surface mobility of the catalyst due to the strong substrate-catalyst interaction [29]. There is another case where Ti and TiN are used as under-layer and a seed layer for the subsequent Cu-electroplating. Ti is deposited as an under-layer using AJA sputtering system in the presence of gaseous plasma (Ar). A 300-nm layer of Ti is deposited at room temperature and 3 mTorr pressure at a growth rate of 10 Å/s. TiN is attempted as an under-layer. A 100-nm layer of TiN is deposited using the sputtering system at room temperature and 3 mTorr pressure at a growth rate of 1.5 Å/s.

2.1 CNT Growth

Two kinds of catalysts (Fe and Ni) are deposited using E-Beam evaporation as listed in Table 1. Thicknesses of 2.5 nm and 7 nm of Fe and Ni are deposited, respectively. Then, both CVD and PECVD CNT growth are conducted on each under-layer/catalyst stack.

Aixtron-Black Magic Pro is used for both CVD and PECVD processes. For the thermal CVD, the wafer is cleaned by 60 seconds of Ar flow at 1000 sccm in the CVD tool. The Fe catalyst is annealed by 500 sccm flow of H_2 for 180 seconds at 700 °C and 25 mBar. Then, the growth process is started by 50 sccm flow of C_2H_2 along with 500 sccm of H_2 for 300 seconds at 25 mBar. Since CNT characteristics i.e. density, growth rate and crystallinity have been found affected by the growth temperature [30], different temperatures (675, 700 725 and 750 °C), as seen in Table 1, are used for the growth step. This is done to study the temperature effect on the properties of the grown CNTs. Annealing and growth for thermal CVD is done in the previously described manner at 750 °C. For PECVD process, annealing is done by flowing a 200 sccm of Amonia for 10 minutes at 650 °C. Then growth takes place by flowing C_2H_2 (precursor) along with Amonia (Annealing gas) at 100 sccm and 400 sccm, respectively for 30 minutes.

2.2 CNF Growth

For CNF fabrication, the process is similar to growing CNTs. Wafers are oxidized in a diffusion furnace to form insulation layer of 200-nm SiO_2 . The under layer in this case was chosen as SiO_2 . The difference in this process is that the catalyst layer is thicker. Twenty-nm Ni catalyst is deposited using E-Beam evaporator. After Ni deposition, PECVD is used for the CNF growth. Aixtron-Black Magic Pro is used for the PECVD process. The wafer is cleaned by 2 seconds of Ar flow at 500 sccm. Ni is then annealed by the flow of 200 sccm Amonia for 10 minutes at 650 °C. Then, plasma is turned on at 20 KHz alternating current and 150 W to start

the PECVD growth process. Growth takes place by flowing C₂H₂ (precursor) and Ammonia (annealing) at 100 sccm and 400 sccm for 30 minutes, respectively.

2.3 Copper Deposition

Three different processes are examined to deposit Cu; electroless plating, electroplating and sputtering. Prior to electroless plating, the surface of the CNT/CNF goes through activation process in order to enable uniform nucleation formation. Surface activation is conducted by several repeated rinsing of the nanostructure with a solution of 1 g/L of Tin Chloride (SnCl₂), 1 mg/L of Hydrochloric acid (HCl- 37%) and 1 g/L of Palladium Chloride (PdCl₂). The main purpose of this activation process is to seed the surface of CNT/CNF with Pd nuclei, which initiate the Cu electroless plating process. During the activation process, Pd ions on the surface of CNT/CNF are reduced by Sn⁺² according to $\text{Sn}^{2+} + \text{Pd}^{2+} \rightarrow \text{Pd}^0 + \text{Sn}^{4+}$ Eq. 1 to form Pd nuclei that will catalyze Cu plating.

Cu plating is then conducted using a solution of 16.67 g/L of Copper Sulfate Pentahydrate, 13.45 g/L of Ethylenediaminetetraacetic acid (EDTA) and 2Na 2H₂O and 1.28g/L of Hydrazine. The solution is maintained at 40 °C using a water bath, with continuous mixing of the solution. Cu deposition was performed after solution pH was increased above 11.0 using controlled addition of sodium hydroxide [31]. This pH restriction imposes the use of complexed Cu ions in the electroless solution in order to prevent precipitation of Cu (II) Hydroxide. A solution of ~4% hydrazine was then added slowly to make the hydrazine concentration 1.28 g/L. Hydrazine serves to reduce Cu ions to metallic Cu on the surface of the activated CNTs, as shown by the chemical reaction of

to three hours. Once the plating process was completed, the Cu coated CNTs were rinsed with deionized water and oven dried. A desired thickness of Cu can be achieved by plating several times.

For electroplating process, a CHI potentiostat workstation with a standard 3-electrode setup is used. At this workstation a pyrolytic graphite rod electrode was used as a counter electrode, and a saturated calomel electrode was used for a reference electrode in 1 M of CuSO_4 dissolved in 1 M of H_2SO_4 as electrolyte. A range of applied potential from -0.4 to -1.0 V was investigated. For calibration, the potential was applied for a certain time and investigated the deposition of Cu on the CNTs.

A physical Cu deposition technique was also tested. Plasma assisted sputtering system AJA was used as an alternative to deposit Cu on the CNT forest. A 7- μm layer of Cu is deposited at room temperature, under a pressure of 3 mTorr and at a growth rate of 10 Å/s.

3. Results

3.1 CVD Growth of CNTs on $\text{Fe}/\text{Al}_2\text{O}_3$ stack

The alignment and the density of CNTs are key qualities that dictate the electrical conductivity of CNTs [32]. More aligned and denser CNT bundles provide more paths for electrons and thus provide better ampacity. The following results are for the wafers subject to thermal CVD, using Al_2O_3 under-layer and Fe catalyst. This process was conducted at different growth temperatures (675, 700 725 and 750 °C). Growth temperature has a notable effect on the quality of grown CNTs as seen in Fig. 2. From observation, CNTs grown at 750 °C obtained the

highest quality; density and orientation. The growth rate are found to be 15 $\mu\text{m}/\text{min}$, 25 $\mu\text{m}/\text{min}$, 50 $\mu\text{m}/\text{min}$ and 80 $\mu\text{m}/\text{min}$ for the samples grown at 675 $^{\circ}\text{C}$, 700 $^{\circ}\text{C}$, 725 $^{\circ}\text{C}$ and 750 $^{\circ}\text{C}$, respectively. Thus, increasing the growth temperature increases the CNT growth rate. The temperature has shown to have a direct impact on the growth rate. It was shown previously that increase in temperature up to 900 $^{\circ}\text{C}$ in CVD process increased the growth rate by 4 times [30].

Fig. 2. CNT growth using CVD at different temperatures (a) 675 $^{\circ}\text{C}$, (b) 700 $^{\circ}\text{C}$, (c) 725 $^{\circ}\text{C}$, (d) 750 $^{\circ}\text{C}$. The scale shown in the SEM label is 5 Micron.

3.2 CVD Growth on Fe/Ti Stack

Previous studies have shown that using Ti as the under-layer promotes the adhesion between CNTs and the substrate [33,34]. Ti can also act as the seed layer for Cu electrodeposition in subsequent steps. Therefore, Ti is used as the under-layer. A 300-nm layer of Ti was deposited

using AJA sputtering system. A layer of 2.5-nm Fe was deposited as a catalyst using E-Beam evaporation. CNTs were then grown using the previously described thermal CVD recipe. As seen in Fig. 3, the quality of the CNTs is poor as they are tangled and short. Since the only difference between this step and previous step was the under-layer, Ti vs. Al_2O_3 , this indicates that Ti is not an appropriate under-layer material.

Fig. 3. SEM images of CNTs grown on Fe/Ti stack at (a) X2500 magnification, (b) X10,000 magnification

3.3 CVD and PECVD Growth on Fe/TiN and Ni/TiN Stacks

Since Ti layer did not produce satisfactory CNTs, a new conductive under-layer was examined. TiN is conductive and can act as a seed layer for subsequent electroplating. A layer of 300 nm thick TiN was deposited using the AJA sputtering system. Two kinds of catalysts were then deposited individually. Fe and Ni were deposited using E-Beam evaporation with their thicknesses of 2.5 nm and 7 nm, respectively. Both thermal CVD and PECVD growth of CNTs were carried out on each catalyst. Neither Fe nor Ni has yielded CNT growth using thermal CVD as depicted in Fig. 4.

Fig. 4. Results of using thermal CVD on (a) Fe/TiN and (b) Ni/TiN stacks

Using PECVD on both Fe and Ni catalysts has yielded CNT growth as seen in Fig. 5. Grown CNTs are self-aligned; however, they are significantly shorter ($\approx 3 \mu\text{m}$) and less dense than CNTs

grown using thermal CVD on Fe/AL₂O₃ stack. Moreover, growth rate is also low; it is almost 0.1 $\mu\text{m}/\text{min}$. Both CNTs grown on Fe/TiN and Ni/TiN have almost the same length range ($\approx 2 \mu\text{m}$), while CNTs grown on Ni/TiN are thicker than those grown on Fe/TiN. The measurements show an average diameter of 120 nm for Fe catalyst while it increases to 150 nm for Ni catalyst.

Fig. 5. SEM image of CNTs grown using PECVD on (a) Fe/TiN and (b) Ni/TiN stacks

3.4 Cu Deposition

Cu depositions were conducted on the grown CNTs that show promising properties such as growth rate, self-alignment and density.

3.4.1 *Electroless Plating*

Electroless plating was conducted on the CVD grown CNTs on Fe/Al₂O₃ stack because these CNTs had shown the highest growth rate (80 $\mu\text{m}/\text{min}$) and the most self-aligned densest structure. The advantage of electroless plating is that it does not need a seed layer. This process was conducted by United Technology Research Center. It was unsuccessful because CNTs detached from the surface of the substrate when it was left in the plating solution. The reason is believed to be the weak adhesion between the CNTs and the catalyst-coated substrate.

3.4.2 *Electroplating*

Electroplating Cu was conducted on the CVD grown CNTs on Fe/Al₂O₃ stack. Electroplating of the samples was done by immersing them in the electroplating solution for 30 hours. However, Cu was deposited discretely only on the top of the CNTs as seen in the SEM image and the associated Dispersive Energy Spectroscopy (EDX) results (Fig. 6). Cu was found deposited **only** on the CNTs that are located around to the clips that are used to connect the sample to the potentiostat. **This may have been due to the close proximity of the CNTs to the potential sources that allowed some electricity to conduct through. The reason that the Cu only deposited on the tips could be attributed to several reasons. CNTs bond with other material at the end rather than the sides, because the atomic bonds at the end contacts usually are not complete in an open CNT. This could be the reason that Cu only was deposited on the tips of CNTs.** Furthermore, most CNTs detached from the surface because of the weak adhesion between CNTs and the substrate. Discrete Cu deposition of the top part of CNTs is believed to be a result

of the lack of a conductive layer—seed layer—beneath CNTs and interlocked CNTs located at the top and near the potentiostat clips. These clips are slightly conductive so that it could attract few Cu ions. Another possibility for the Cu deposition on the top of the CNTs is that tip-growth mode of CNTs took place such that CNTs grow beneath the catalyst nuclei located on the top of the CNTs that would act as seed layer for the Cu deposition. However, Fe peaks were not found in the EDX spectrum in Fig. 6 and that makes this possibility invalid.

Fig. 6. Electroplated CNTs (a) SEM images of the CNTs covered with Cu on vicinity of the potentiostat, (b) EDX spectrum showing the existence of copper.

Cu Electroplating of PECVD grown CNTs on Fe/TiN and Ni/TiN stacks was also attempted. However, Cu could not be deposited as electricity did not pass through. The measured resistance was found to be 1 MΩ. However, CNTs were stable and did not detach from the substrate during the electroplating process. Thus, a different dry way of Cu deposition is required.

3.4.3 Cu Sputtering

Cu deposition by sputtering was attempted on the CVD grown CNTs on Fe/Al₂O₃ stack. However, as seen in Fig. 7-b, Cu could not infiltrate CNTs due to fact that CNTs are very packed and dense and there is little space in between for the copper to infiltrate. This method can probably be used successfully on a lower density CNTs. As seen in Figure 7-c, the copper nicely covers the CNTs at the edge of the wafer. This indicates that this method has potential to be used to develop these composite. However, as sputtering is typically a slow process and requires much energy, it may not be an ideal technique for scale up of the fabrication.

Fig. 7. SEM images of (a) Cu deposited CNTs using e-beam evaporation in the middle of the wafer, (b) a close up view of the CNTs indicating no copper infiltration in between CNTs (c) CNTs covered with copper at the edge of the wafer

3.5 CNF/Cu-composite

PECVD growth of CNFs is successful as shown in Fig. 8-a. The nanostructure is clearly CNFs since conical basal planes could be observed from the Transmission Electron Microscope (TEM) images (Fig. 8-b). CNFs are around 4 μm long and diameters' range is 100-300 nm as shown in Fig. 8-a and are well aligned.

Fig. 8. Illustration of the grown CNFs using (a) SEM imaging and (b) TEM imaging

Cu was successfully deposited by using electroless plating as shown in Fig. 9. CNFs are strongly anchored to the substrate and they did not detach from the surface during the plating process. Cu successfully infiltrates CNFs so that the CNF/Cu-composite is created.

Fig. 9. CNF/Cu-composite (the inset is a picture of the deposited sample in centimeter-scale)

Resistivity of the CNF/Cu-composite was measured by using 4-Probe resistivity measurement technique. It is important to note that this measurement indicates in-plane resistivity and not through the thickness. The advantages of CNTs and CNFs in increasing conductivity is due to the tunneling effect within the hollow space of CNTs and using the basal plains of the CNFs as explained in the introduction. Therefore, these structures are meant to increase the conductivity through the thickness and in the direction of the CNTs and CNFs orientation. Therefore, the in plane measurements are not hypothesized to provide higher conductivity as compared to copper. Measurements were taken at seven different locations and the average obtained resistivity is found to be $1.88 \times 10^{-5} \Omega \cdot \text{cm}$, which is one order of magnitude lower than the reported CNF resistivity ($4.4 \times 10^{-4} \Omega \cdot \text{cm}$) [6,12] and one order of magnitude higher than known Cu's resistivity ($1.7 \times 10^{-6} \Omega \cdot \text{cm}$) [35] used for interconnects (Fig. 10). These results intuitively make sense. The in-plane conductivity of the CNF-Cu composite could not be higher than copper alone due to the fact that the CNFs are actually create disturbance to the

current as the current travels perpendicular to the axial orientation of the CNFs. It is also intuitive to have higher conductivity than CNFs alone in the in-plane direction, because in the case of CNFs alone, there is no continuous side connections in between the CNFs to allow the current to travel laterally in between these CNFs. The major improvements are expected to occur in the orientation of CNTs CNFs.

Additionally, Cu is incapable of maintaining its physical integrity at miniaturized scales due to low reliability and electro-migration issues that have not been observed in CNF structure [6,12]. Therefore, Cu addition to CNF enhanced the conductivity of CNF, and CNF/Cu-composite has a great promise to replace Cu in the next-generation interconnect.

Fig. 10. Comparison of the obtained resistivity of CNF, CNF/Cu-composite and Cu

4. Discussion

The summary of the CNT growth results obtained during the course of this study is presented in Table 2. As indicated in this table, thermal CVD with Fe/Al₂O₃ has yielded self-aligned, long and dense CNTs. Moreover, the best alignment and densest CNTs have been obtained at growth

temperature 750 °C. CNTs grown on Fe/Ti stack using thermal CVD are tangled and very short. CVD was also conducted on Fe/TiN and Ni/TiN but CNTs were not obtained. However, CNTs have been obtained when PECVD was used for the growth process instead of thermal CVD. Moreover, the obtained CNTs are self-aligned but neither dense nor long. The growth rate is very low (0.1 $\mu\text{m}/\text{min}$)

Table 2. Summary of CNT growth results

Process	Under-layer	Catalyst	Temp (C°)	CNTs?	Key Properties	Attempted etching TSVs?	Observed CNTs inside TSVs?
CVD	Al_2O_3	Fe	675	Yes	Dense and aligned	Yes	No
			700	Yes	Dense and aligned	Yes	No
			725	Yes	Dense and aligned	Yes	No
			750	Yes	aligned, dense and fast growth (80 $\mu\text{m}/\text{min}$)	Yes	Yes
	Ti	Fe	750	Yes	Tangled and very short	No	
	TiN	Fe	750	No		No	
		Ni	750	No		No	
PECVD	TiN	Fe	650	Yes	aligned, not dense and slow growth (0.1 $\mu\text{m}/\text{min}$)	No	
		Ni	650	Yes		No	

Table 23 shows a summary of the attempts made to create the composite materials by depositing copper using different approaches. Table summarized the copper deposition technique in the first column and the catalyst/under layer (method used for growing CNTs) in the top row. The dposition process results show limited success in some areas. For example, the electroplating of CNTs without any conductive underlayer as seed layer, only showed the deposition on top of the CNTs and in the areas closed to the electrode connected to the wafer. This could be attributed to high electric potential field in those regions and connectivity of the CNTs tangled on top that allowed the electric current to flow and copper deposition to occur. For

the CNTs grown on Fe/Al₂O₃ using thermal CVD, CNTs detached from the substrate during both the electroplating and the electroless plating techniques. However, Cu was found on the top of CNTs from the electroplating process, since the CNTs are interlocked at the top and it allowed current to pass through them in some parts. Cu deposited by sputtering could not infiltrate CNTs because of the high density of the CNTs. It is hypothesized that a lower CNT density could result in infiltration of copper in between the CNT strands and creation of the Cu-CNT composites. Electroplating of CNTs grown on Fe/TiN and Ni/TiN could not be accomplished because of the high resistance of the wafers although conductive TiN layer was deposited to perform as a seed layer. The hypothesis is that the interface resistance between the CNTs and the TiN layer is so high that it is very likely that the current could not pass through the CNTs to attract the copper ions.

Table 3. Summary of Cu depositions results

Sample Cu Deposition	Fe/Al ₂ O ₃ (CVD)	Fe/TiN (PECVD)	Ni/TiN (PECVD)
Electroplating	<ul style="list-style-type: none"> Only at the top of CNTs CNTs detached 	<ul style="list-style-type: none"> No Cu deposition Very high resistance Strong adhesion 	<ul style="list-style-type: none"> No Cu deposition Very high resistance Strong adhesion
Electroless Plating	No (detachment)	Not attempted	Not attempted
Sputtering	Only on the top	Not attempted	Not attempted

Cu-CNF composites were fabricated successfully and the approach seems to be promising. The in-plane measure conductivity, as hypothesized was higher than the CNFs alone and lower than copper. However, it is noted that the advantages of CNTs and CNFs are their ability to transport electrons in axial directions and therefor, a through thickness measurements deemed to be more appropriate technique.

5. Conclusion

Fabrication of CNT/ and CNF/Cu composites for interconnects has been investigated in this paper. For CNT/Cu-composite, CVD growth of CNTs on Fe/Al₂O₃ results in high quality CNTs which are convenient for vertical interconnect. More investigation, however, is recommended in order to enhance the adhesion between CNTs and substrate. PECVD growth on Ni/ and Fe/TiN also resulted in CNTs that are strongly anchored to the substrate but more investigation has to be done in order to increase the growth rate and the density. These issues associated with both CVD- and PECVD-grown CNTs processes can be addressed by conducting a systematic optimization technique considering different catalyst layers, different cooling conditions (post-growth) and Cu deposition techniques. A successful fabrication technique of CNF/Cu-composite is proposed, and CNF/Cu-interconnect (for lateral connections) has shown an improved electrical performance with respect to CNF-interconnect. However, resistivity is still higher than that of Cu-interconnects. More investigation of Cu deposition techniques and the surface roughness of the composite can lead to improved electrical performance.

Acknowledgement

This paper is based upon research funded by the National Science Foundation under CMMI grant number 1415165. The authors would like to express their profound gratitude to the support from NSF. We are also very thankful for the facilities provided by the Microsystems Technology Laboratories at the Massachusetts Institute of Technology.

References

- [1] H. Li, C. Xu, N. Srivastava, K. Banerjee, Carbon Nanomaterials for Next-Generation Interconnects and Passives: Physics, Status, and Prospects, *IEEE Trans. Electron Devices*. 56 (2009) 1799–1821. doi:10.1109/TED.2009.2026524.
- [2] R. Martel, T. Schmidt, H. Shea, Single- and multi-wall carbon nanotube field-effect transistors, *Appl. Phys.* (1998).
- [3] S. Tans, A. Verschueren, C. Dekker, Room-temperature transistor based on a single

- carbon nanotube, *Nature*. (1998).
- [4] Q. Cao, S.-J. Han, J. Tersoff, A.D. Franklin, Y. Zhu, Z. Zhang, G.S. Tulevski, J. Tang, W. Haensch, End-bonded contacts for carbon nanotube transistors with low, size-independent resistance, *Science* (80-.). 350 (2015) 68–72. doi:10.1126/science.aac8006.
 - [5] V. Desmaris, A.M. Saleem, S. Shafiee, J. Berg, M.S. Kabir, A. Johansson, Carbon Nanofibers (CNF) for enhanced solder-based nano-scale integration and on-chip interconnect solutions, in: 2014 IEEE 64th Electron. Components Technol. Conf., IEEE, 2014: pp. 1071–1076. doi:10.1109/ECTC.2014.6897421.
 - [6] Q. Ngo, T. Yamada, M. Suzuki, Y. Ominami, A.M. Cassell, J. Li, Structural and electrical characterization of carbon nanofibers for interconnect via applications, *IEEE Trans. Nanotechnol.* 6 (2007) 688–695.
 - [7] M. Nihei, A. Kawabata, D. Kondo, M. Horibe, S. Sato, Y. Awano, Electrical Properties of Carbon Nanotube Bundles for Future Via Interconnects, *Jpn. J. Appl. Phys.* 44 (2005) 1626–1628. doi:10.1143/JJAP.44.1626.
 - [8] Y. Ominami, Q. Ngo, M. Suzuki, A.J. Austin, C.Y. Yang, A.M. Cassell, J. Li, Interface characteristics of vertically aligned carbon nanofibers for interconnect applications, *Appl. Phys. Lett.* 89 (2006) 263114. doi:10.1063/1.2423241.
 - [9] International Technology Working Groups. International Technology Roadmap for Semiconductors, 2011.
 - [10] J.R. Black, Electromigration-A Brief Survey and Some Recent Results, *IEEE Trans. Electron Devices.* 16 (1969) 338–347.
 - [11] B.Q. Wei, R. Vajtai, P.M. Ajayan, Reliability and current carrying capacity of carbon nanotubes, *Appl. Phys. Lett.* 79 (2001) 1172. doi:10.1063/1.1396632.
 - [12] A.M. Cassell, A.J. Austin, S. Krishnan, M. Meyyappan, C.Y. Yang, Characteristics of aligned carbon nanofibers for interconnect via applications, *IEEE Electron Device Lett.* 27 (2006) 221–224. doi:10.1109/LED.2006.870865.
 - [13] K. Kannan, S. Kannan, B. Kim, Development of hybrid electrical model for CNT based Through Silicon Vias, in: 2013 IEEE Int. Symp. Circuits Syst., IEEE, 2013: pp. 1022–1026. doi:10.1109/ISCAS.2013.6572023.
 - [14] T. Wang, S. Chen, D. Jiang, Y. Fu, K. Jeppson, L. Ye, J. Liu, Through-Silicon Vias Filled With Densified and Transferred Carbon Nanotube Forests, *IEEE Electron Device Lett.* 33 (2012) 420–422. doi:10.1109/LED.2011.2177804.
 - [15] R. Xie, C. Zhang, M.H. van der Veen, K. Arstila, T. Hantschel, B. Chen, G. Zhong, J. Robertson, Carbon nanotube growth for through silicon via application., *Nanotechnology.* 24 (2013) 125603. doi:10.1088/0957-4484/24/12/125603.
 - [16] S. Vollebregt, R. Ishihara, The direct growth of carbon nanotubes as vertical interconnects in 3D integrated circuits, *Carbon N. Y.* 96 (2016) 332–338. doi:10.1016/j.carbon.2015.09.071.
 - [17] C. Subramaniam, T. Yamada, K. Kobashi, A. Sekiguchi, D.N. Futaba, M. Yumura, K. Hata, One hundred fold increase in current carrying capacity in a carbon nanotube-copper composite., *Nat. Commun.* 4 (2013) 2202. doi:10.1038/ncomms3202.

- [18] Q. Ngo, B. Cruden, A. Cassell, Thermal interface properties of Cu-filled vertically aligned carbon nanofiber arrays, *Nano Lett.* (2004).
- [19] X. Chen, J. Xia, J. Peng, W. Li, S. Xie, Carbon-nanotube metal-matrix composites prepared by electroless plating, *Compos. Sci. Technol.* 60 (2000) 301–306. doi:10.1016/S0266-3538(99)00127-X.
- [20] and K.T. E. Dujardin, T. W. Ebbesen, H. Hiura, Capillarity and wetting of carbon nanotubes, *Science* (80-.). 265 (1989) 1850–1852.
- [21] F. Wang, S. Arai, M. Endo, Metallization of multi-walled carbon nanotubes with copper by an electroless deposition process, *Electrochem. Commun.* 6 (2004) 1042–1044. doi:10.1016/j.elecom.2004.08.007.
- [22] L.M. Ang, T.S. a Hor, G.Q. Xu, C.H. Tung, S.P. Zhao, J.L.S. Wang, Decoration of activated carbon nanotubes with copper and nickel, *Carbon N. Y.* 38 (2000) 363–372. doi:10.1016/S0008-6223(99)00112-8.
- [23] S. Suárez, L. Reinert, F. Mücklich, Carbon Nanotube (CNT) -Reinforced Metal Matrix Bulk Composites: Manufacturing and Evaluation, in: *Diam. Carbon Compos. Nanocomposites*, 2016: pp. 130–180. doi:10.5772/61410.
- [24] C.L.P. Pavithra, B. V Sarada, K. V Rajulapati, T.N. Rao, G. Sundararajan, A new electrochemical approach for the synthesis of copper-graphene nanocomposite foils with high hardness., *Sci. Rep.* 4 (2014) 4049. doi:10.1038/srep04049.
- [25] S. Arai, T. Osaki, Fabrication of Copper/Multiwalled Carbon Nanotube Composites Containing Different Sized Nanotubes by Electroless Deposition, *J. Electrochem. Soc.* 162 (2014) D68–D73. doi:10.1149/2.0971501jes.
- [26] K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, W.I. Milne, G. Pirio, P. Legagneux, F. Wyczisk, J. Olivier, D. Pribat, Characterization of plasma-enhanced chemical vapor deposition carbon nanotubes by Auger electron spectroscopy, *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.* 20 (2002) 116. doi:10.1116/1.1428281.
- [27] V.I. Merkulov, A. V. Melechko, M.A. Guillorn, D.H. Lowndes, M.L. Simpson, Effects of spatial separation on the growth of vertically aligned carbon nanofibers produced by plasma-enhanced chemical vapor deposition, *Appl. Phys. Lett.* 80 (2002) 476. doi:10.1063/1.1433905.
- [28] T. de los Arcos, M. Gunnar Garnier, P. Oelhafen, D. Mathys, J. Won Seo, C. Domingo, J. Vicente García-Ramos, S. Sánchez-Cortés, Strong influence of buffer layer type on carbon nanotube characteristics, *Carbon N. Y.* 42 (2004) 187–190. doi:10.1016/j.carbon.2003.10.020.
- [29] P.B. Amama, C.L. Pint, S.M. Kim, L. McJilton, K.G. Eyink, E.A. Stach, R.H. Hauge, B. Maruyama, Influence of alumina type on the evolution and activity of alumina-supported Fe catalysts in single-walled carbon nanotube carpet growth., *ACS Nano.* 4 (2010) 895–904. doi:10.1021/nn901700u.
- [30] C.J. Lee, J. Park, Y. Huh, J. Yong Lee, Temperature effect on the growth of carbon nanotubes using thermal chemical vapor deposition, *Chem. Phys. Lett.* 343 (2001) 33–38. doi:10.1016/S0009-2614(01)00680-7.
- [31] J. DUFFY, L. PEARSON, M. PAUNOVIC, The effect of pH on electroless copper

- deposition, *J. Electrochem. Soc.* 130 (n.d.) 876–880.
- [32] N. Behabtu, C.C. Young, D.E. Tsentalovich, O. Kleiner, X. Wang, A.W.K. Ma, E.A. Bengio, R.F. ter Waarbeek, J.J. de Jong, R.E. Hoogerwerf, S.B. Fairchild, J.B. Ferguson, B. Maruyama, J. Kono, Y. Talmon, Y. Cohen, M.J. Otto, M. Pasquali, Strong, light, multifunctional fibers of carbon nanotubes with ultrahigh conductivity., *Science*. 339 (2013) 182–6. doi:10.1126/science.1228061.
 - [33] Y. Chai, K. Zhang, M. Zhang, P.C.H. Chan, M.M.F. Yuen, Carbon Nanotube/Copper Composites for Via Filling and Thermal Management, in: 2007 Proc. 57th Electron. Components Technol. Conf., IEEE, 2007: pp. 1224–1229. doi:10.1109/ECTC.2007.373950.
 - [34] Q. Chen, Carbon nanotube reinforced metal composites, US Pat. 7,651,766. (2010).
 - [35] S.P. Murarka, S.W. Hymes, Copper metallization for ULSL and beyond, *Crit. Rev. Solid State Mater. Sci.* 20 (1995) 87–124. doi:10.1080/10408439508243732.