Nanostructural Characterization of Carbon Nanofibers for On-chip Interconnect Applications with Scanning Transmission Electron Microscopy

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Abstract — Recent studies in the nanostructural characterization for on-chip interconnect using carbon nanofibers (CNFs) is presented. In this paper, we compare the resistance and structure between Ni and Pd-catalyzed CNFs, which show differing electrical properties. These samples are characterized with scanning transmission electron microscopy (STEM). Our analysis reveals the nanostructure of CNFs in detail. We also discuss the growth mechanisms of CNFs and the choice of catalyst materials used for interconnects development.

Index Terms — Carbon nanofiber, on-chip interconnect, scanning transmission electron microscopy

I. INTRODUCTION

There has been an abundance of research in application development for CNTs and carbon nanofibers (CNFs) due to their unique electronic and physical properties. Nanoelectronic devices fabricated using these carbon-based nanostructures have been introduced for both transistor and interconnect applications [1,2]. For interconnect applications, the resistance of carbon nanostructures must be minimized. Resistance is closely tied to the CNF structure as determined by different growth processes [3-6]. Therefore low-resistance interconnect development using CNFs requires understanding of the structure and critical feedback to the manufacturing process from high-resolution microscopy.

We have proposed a bottom-up approach for CNF interconnects [7]. The CNFs are vertically grown on a metal substrate by plasma-enhanced chemical vapor deposition (PECVD)[8]. Subsequently, SiO\textsubscript{2} is deposited using tetraethoxysilane (TEOS) chemical vapor deposition (CVD) and the sample is treated with chemical mechanical polishing (CMP). Current sensing atomic force microscopy (CSAFM) and wafer probe station electrical measurements are used to characterize the resistance of the CNF [9,10].

In this paper, we report the resistance of Ni-catalyzed and Pd-catalyzed CNF. Characterization of these CNFs with scanning transmission electron microscope (STEM) is presented to elucidate the electrical properties.

II. EXPERIMENTAL

The as-grown vertically aligned CNF array and CNFs embedded in SiO\textsubscript{2} after CMP are shown in Fig. 1. The current-voltage (I-V) measurements using CSAFM are used to obtain the resistances of Ni-catalyzed and Pd-catalyzed CNFs. The CNFs embedded in SiO\textsubscript{2} after CMP (Fig. 1 (b)) are used for I-V measurement. In this I-V measurement, CNFs with similar length (approximately 4um) and diameter (approximately 50nm) are used. In order to prepare a STEM sample for the characterization of the CNF-body, CNFs without SiO\textsubscript{2} (Fig. 1(a)) are dispersed in isopropyl alcohol and then placed onto a copper grid coated with a lacy carbon film. The samples are characterized using a STEM with point-to-point resolution of 0.204nm. The cross-sectional STEM sample for the characterization of the CNF-metal interface is prepared using focused ion beam (FIB) thinning. The CNFs embedded in SiO\textsubscript{2} (Fig. 1(b)) are used as the sample for FIB thinning because SiO\textsubscript{2} can protect the CNF-metal interface from damage during FIB thinning. In addition, in order to maintain the integrity of CNFs after sample preparation, a micro-sampling technique and sputtering...
using a 10kV focused ion beam are used to prepare the STEM sample.

III. CHARACTERIZATION BY ELECTRICAL MEASUREMENT

The three major components of resistance when measuring single CNF resistance with CSAFM are AFM-to-CNF contact resistance, intrinsic CNF resistance owing to nanofiber morphology, and the CNF-metal interface at the base of the nanofiber. The two-terminal measurement data presented in this work includes all three resistive components. An AFM probe tip coated with Pt and attached to a conductive cantilever was used as one electrode and the second electrode was contacted by directly probing the 30 nm thick Ti seed layer connected to the CNF base.

Fig. 2 shows a typical I-V curve of single CNF catalyzed by Ni and Pd. The resistance of a typical single Ni-catalyzed CNF is about 13kΩ. The resistance of a typical single Pd-catalyzed CNF is about 9kΩ. Because the length and diameter of these CNFs are similar, this difference in resistance is attributed to structural difference between the two. The CNFs studied here do not show a resistance dependence on diameter ranging from 30-100 nm. However, different morphologies may result in differing resistance values.

IV. CHARACTERIZATION BY STEM

STEM images at low magnification of Ni-catalyzed CNFs near the base reveal a conventional fiber-like structure [6,11-12] as shown in Fig. 3(a). The structural transition of cup-shape angle from tip to bottom of the CNF is observed as Cui et al. has recently reported [13]. High-resolution STEM observations show that the carbon structures comprising the cup-shape are graphitic layers with 0.34nm spacing (Fig. 3(b)-(d)). Although multiwall (MW)-like layers parallel to the nanofiber axis are observed, many graphitic layers have separated to form a cup-shape structure (Fig. 3(b)). Toward the base of the nanofiber, all MW-like layers turn into cup-shape (Fig. 3(c)) with the base of the cup almost perpendicular to the nanofiber axis (Fig. 3(d)). A cross-section of the CNF/substrate interface is shown in Fig. 4. The structure of the CNF/substrate interface embedded in SiO₂ consists of many graphitic layers that are almost parallel to the substrate as observed in Fig. 3(d). This interfacial region has a thickness approaching 100 nm. For interconnect applications, this structure gives rise to significant contact resistance, as electrons must flow across the basal planes of the graphitic layers.

STEM images of Pd-catalyzed CNFs at low magnification are shown in Fig. 5(a). Pd-catalyzed CNFs have both cup-shape and MW-like structures similar to...
Ni-catalyzed CNFs. One of the striking characteristics of this Pd-catalyzed CNF is that the MW-like structures do not separate into cup-shape layers (Fig. 5(b)). Although the cup-shape structure joins with the MW-like layers, the structure terminates approximately every 50 nm as shown in Fig. 5(b),(c). This MW-like structure is observed not only at the tip section but also near the base of the nanofiber (Fig. 5(d)). Also, the cup-shape structure is not observed at the bottom section. The cross-sectional image is shown in Fig. 6. The interfacial structure of Pd-catalyzed CNFs shows MW-like morphology approaching the CNF interface that is nearly perpendicular to the substrate. The cup-shape structure of the Pd-catalyzed CNF near the interface (Fig. 4(b)) is not observed as in the case of Ni-catalyzed fibers. Thus, as electrons flow parallel to the nanofiber axis, the resulting resistance of a Pd-catalyzed CNF-metal interface is lower than its Ni-catalyzed counterpart.
V. THE GROWTH MECHANISM OF CNF

From our STEM results, a CNF growth model is suggested as shown in Fig. 6. In the case of Ni-catalyzed CNF (Fig.6(a)), after some graphitic layers are formed under the Ni catalyst particle, the cup-shape structure is produced as the growth continued, as Cui et al. has reported [13]. In contrast, Pd-catalyzed growth initially forms MW-like graphite layers parallel with CNF axis on the side of the Pd particle (Fig.6(b)). After the particle is separated from the substrate, the interior structure under the Pd catalyst is produced, while MW-like structures continue to grow on the sidewall of the Pd particle. The initial growth mechanism of our Pd-catalyzed CNF is probably similar to that of Helveg [14]. For our interconnect development, Pd-catalyzed CNFs creates a better interface structure and CNF-body morphology than Ni-catalyzed CNFs due to having a MW-like structure near the CNF-metal interface.

![Fig.6 The growth mechanism of (a) Ni-catalyzed CNF (b) Pd-catalyzed CNF](image)

VI. CONCLUSION

In summary, the resistances of Ni-catalyzed and Pd-catalyzed CNFs have been obtained from I-V measurements using CSAFM. These results show that the resistance of a Ni-catalyzed CNF is higher than that of a Pd-catalyzed CNF. The interface and body structures of Ni-catalyzed and Pd-catalyzed CNFs revealed using STEM are analyzed to account for the difference in resistance. While Ni-catalyzed CNFs have stacked graphitic layers near the CNF-metal interface, Pd-catalyzed CNFs have MW-like structure spanning the entire CNF, which leads to low resistance for on-chip interconnect applications. Pd seems to be a more suitable catalyst for our interconnect development than Ni.

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REFERENCES