Lightweight Cu/Carbon Nanotube Composite Electric Conductors

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Abstract

We present our progress in developing copper-matrix carbon nanotube (Cu/CNT) composites as realistic nextgen electric conductors substituting copper. There is a rising demand for lighter Cu-substitutes with superior electrical, thermal, and mechanical performances. To address this demand, we report homogeneous Cu/CNT at least 2/3rd as light as Cu in a variety of structures (macroscale wires, microscale pillars, etc.) with competitive electrical conductivities, heat-/current-stabilities and tensile strengths. Our composite room temperature electrical conductivities are $1-3 \times 10^5$ S/cm (vs. 5.9 × 10⁵ S/cm for Cu) with temperature coefficients of resistivity (TCR) 10% of Cu-TCR, and current carrying capacities (CCC) rivalling Cu. Our Cu/CNT is heat-stable with coefficients of thermal expansion (CTE) ~4 ppm/°C, closer to Si-CTE (~3 ppm/°C) and much lower than Cu-CTE (~17 ppm/°C). We observe Cu/CNT performances to depend on Cu spatial distribution and CNT attributes, indicating possibilities for performance-tuning.

1. Introduction

Electric conductors outdoing Cu are necessary for nextgeneration macro and microscale electrical and electronic devices that aim for higher functionality, efficiency, and sustainability [1]. Alternatives to Cu wires in aviation and automobile industries are urgently needed to achieve fuel savings and CO_2 emission cuts. The electronics industry requires interconnects with better current and heat stabilities than Cu to enable smaller and more complex devices with higher power consumption.

Neat carbon nanotubes (CNTs) and CNT assemblies have been explored as potential lightweight Cu-alternatives, albeit with limited success. Individual CNTs ballistically transport electrons and exhibit superior current and heat-stabilities than copper. However, while individual CNTs are too small in size for practical application, the best CNT assemblies show conductivities 10 times < Cu [2]. Also, integrability of CNTbased materials into existing electrical and electronics systems remains a roadblock to practical application.

We believe deficiencies of neat CNT materials can be overcome by combining nanotubes and Cu into composites. In Cu/CNT, nanotubes can act as weight reducers and transfer their exceptional performances to Cu, improving performances. In this paper, we present our research progress [3-6] with developing Cu/CNT with competitive electrical performances as well as mechanical and thermal robustness as promising lightweight Cu-alternatives.

2. Experimental and results

Materials and Methods

For Cu/CNT fabrication, we used 2-step Cu electrodeposition of CNT templates (Fig. 1). Cu is first seeded from an organic electrolyte (copper acetate/acetonitrile) capable of infiltrating hydrophobic CNT templates. Cu seeds are then grown using conventional acidified aqueous $CuSO_4$ electrodeposition.

We used various kinds of CNT templates to obtain a variety of Cu/CNT structures – macroscale wires, microscale CNT pillars, etc. (Fig. 1). For wires, we used multiwall(MW) CNT wire (CNTW) templates twist-spun from substrategrown vertical MWCNT arrays (Muratec, Murata Machinery Ltd., Japan) as well as singlewall (SW) CNTWs directly spun from a chemical vapor deposition (CVD) furnace. The CNT wall number and diameter were confirmed by transmission electron microscopy (TEM). For micropillars, our templates were SWCNT pillar arrays (100, 20, and 10 micron in diameter, 500 micron in height) on Si/SiO₂ substrates obtained by supergrowth CVD.

Three vital Cu/CNT electrical properties necessary for practical application were measured: (1) Room-temperature electric conductivity (4-probe), (2) Temperature stability of electrical resistance (4-probe) as temperature coefficient of resistivity (TCR), (3) Stability against current failure as current carrying capacity (CCC) (2-point). In addition to electrical performances, stability against thermal expansion (coefficient of thermal expansion, CTE) and tensile robustness were tested. We also checked the effect of CNT-Cu mixing (spatial distribution) on composite performances. Samples with various levels of mixing were obtained by tuning electrodeposition parameters. The mixing levels were confirmed by cross section scanning electron microscopy (SEM).



Fig. 1 Cu/CNT fabrication by 2-step Cu electrodeposition of CNT templates.

Results

We fabricated Cu/CNT in various structures (Fig. 2A). Our Cu/CNT are at least 2/3rd as light as Cu with a high CNT volume% (\geq 40%) homogeneously mixed in a Cu matrix. With ~40-45 vol% CNTs, the Cu/MWCNT wire and Cu/SWCNT pillar densities are ~5.2 g/cm³, while that of Cu/SWCNT wires are ~2.0 g/cm³. The low density of the Cu/SWCNT wires is ascribed to the presence of voids.

Cu/CNT electrical performances are shown in Fig. 2(B-D). All composites show high room temperature electrical conductivities - typically 100-fold higher than neat CNT templates, and lower conductance decrease with temperature (lower TCR) vs. Cu. The heat-stable high electrical conductivity makes Cu/CNT more reliable electrical conductors than Cu for high-temperature operation e.g., in motor windings. In addition to conductivity and its temperature stability, Cu/CNT current stabilities (CCC) rival that of pure copper.

Cu/CNT electrical performances seem to depend on CNT structure (Fig. 2B-D). Among wires (with many CNT ends and junctions), Cu/MWCNT conductivity and TCR are 10% and 50% of Cu, respectively. In comparison, Cu/SWCNT wires perform better with conductivity 30% and TCR 10% of Cu despite the presence of CNT ends and voids. Cu/SWCNT pillars with nanotubes running end-to-end show conductivities of the same order of magnitude as Cu and better temperature stability than Cu/MWCNT wires. From our preliminary data, SWCNTs ($\phi \sim 1-2$ nm) seem to lead to better Cu/CNT electric performances than MWCNTs ($\phi \sim 20$ nm).

In addition to electrical performances, we measured Cu/CNT robustness against thermal expansion (CTE) and mechanical strain (Fig. 3A-B). Both properties are dependent on CNT-Cu mixing. Samples with three CNT-Cu mixing levels were tested – *full mix, partial mix,* and *no mix* (Fig. 3C). Cu/CNT with highest stability to thermal expansion and mechanical strength are obtained when CNTs are uniformly distributed in a solid Cu matrix (*full mix*).



Fig. 2 (A) Cu/CNT wires and pillars with SEM cross sections. Cu/CNT electrical performances: (B) room temperature 4-probe conductivity, (C) conductance vs. temperature, and (D) CCC.



Fig. 3 (A) CTE and (B) stress vs. strain for composites with three types of CNT-Cu mixing. (C) Cu/CNT cross section schematics depicting three types of mixing.

Full mix Cu/CNT tensile strengths are at least equal to commercial (annealed) copper. In terms of CTE, *full mix* Cu/CNT show values ~4 ppm/°C, which matches with Si-CTE (~3 ppm/°C) and is much lower than Cu-CTE (~17 ppm/°C). In comparison, samples with partial or no CNT-Cu mixing show poorer mechanical strengths and CTE values closer to copper.

As shown earlier, Cu/CNT shows CCC (current stability) competitive to Cu. The CTE values show that Cu/CNT heatstability is superior to Cu. This combination of thermal and current stability makes Cu/CNT a promising interconnect material. Cu/CNT interconnects can carry higher currents without failure and the CTE match with Si minimizes thermal expansion-driven delamination from substrates.

3. Conclusions

We have developed Cu/CNT electric conductors as promising Cu-substitutes for next-generation electrical and electronic devices. Our Cu/CNT fabricated in various structures is lighter than and rivals copper in terms of electrical conductivity as well as thermal, electrical, mechanical, and current stabilities.

Acknowledgements

We thank Muratec, Murata Machinery Ltd. for providing the MWCNT wire spools used in this work. The authors are grateful to M. Nishimura, H. Oosako, S. Nemoto and R. Shiina for technical assistance.

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