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# Skin effect mitigation in laser processed multi-walled carbon nanotube/copper conductors

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In this study, laser-processed multi-walled carbon nanotube (MWCNT)/Cu conductors are introduced as potential passive components to mitigate the skin effect of Cu at high frequencies (0–10 MHz). Suppressed skin effect is observed in the MWCNT/Cu conductors compared to primitive Cu. At an AC frequency of 10 MHz, a maximum AC resistance reduction of 94% was observed in a MWCNT/Cu conductor after being irradiated at a laser power density of 189 W/cm<sup>2</sup>. The reduced skin effect in the MWCNT/Cu conductors is ascribed to the presence of MWCNT channels which are insensitive to AC frequencies. The laser irradiation process is observed to play a crucial role in reducing contact resistance at the MWCNT-Cu interfaces, removing impurities in MWCNTs, and densifying MWCNT films. © 2015 AIP Publishing LLC.

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## I. INTRODUCTION

It is known that the AC conductivity in conventional copper (Cu) conductors is reduced at high operation frequencies due to current crowding at their surfaces known as the skin effect. This limitation leads to undesired introduction of a parasitic impedance and, therefore, energy loss and heat generation for extensive high frequency (HF) circuit applications such as contactless power transmittance.<sup>1</sup> So far several methods, such as using hollow copper tubes,<sup>2</sup> Litz wires,<sup>3</sup> and thin normal metal/ferromagnetic film composites,<sup>4–6</sup> have been proposed to suppress the skin effect. However, they add a considerable amount of complexity and cost to the realization of the circuits. Moreover, these approaches are not effective for a wide frequency range.<sup>2</sup> Therefore, attention has been turned towards using nanomaterials as alternative components for HF applications, due their extraordinary electrical properties.<sup>7–12</sup> Specifically, according to the superior electrical properties recently reported for multi-walled carbon nanotubes (MWCNTs) such as saturated skin depth and long mean free path, one potential solution to address this long standing limitation is to implement MWCNTs on Cu providing alternative conduction channels of lower resistance and frequency inertness.<sup>10–12</sup> Depositing MWCNTs on metallic surfaces using chemical vapor deposition (CVD) has been reported.<sup>13,14</sup> However, CVD of MWCNTs on metallic surfaces turned out to be a challenging task in terms of quality control (such as thickness and morphology) and reproducibility. Electrophoretic deposition (EPD) is considered a fast, simple, and cost-effective

approach to coat MWCNTs on metallic surfaces. Nevertheless, the yield and the resulting performance is usually affected by the poor adhesion, insufficient uniformity, and large MWCNT-Cu contact resistance originating from the high surface energy of the nanotubes and strong van der Waals attractive force among their graphitic shells.<sup>13,15–17</sup> Recently, laser irradiation techniques have been introduced for purifying<sup>18</sup> and modifying<sup>19</sup> carbon nanotubes in various composites. In contrast to conventional thermal annealing methods, laser irradiation offers numerous advantages such as intense and precise energy delivery.<sup>20</sup> The graphitic structure of the electrodeposited MWCNTs with a considerably low reflectance can be effective in absorbing incident irradiation projected onto a MWCNT film.<sup>21</sup>

Here, we report the fabrication of MWCNT coatings on Cu substrates by using the EPD technique followed by an infrared laser irradiation treatment. This laser-irradiation treatment was proved to be effective in improving the structural and electrical properties of the MWCNT/Cu conductors. Implementation of MWCNTs was demonstrated to be effective in mitigating the skin effect in Cu and reducing AC resistance at high frequencies up to 10 MHz.

## II. EXPERIMENTAL PROCEDURES

MWCNTs (Cheap Tubes, Inc.) with an average diameter of 25 nm and length of 20 μm were used. The EPD solution was prepared by dispersing 40 mg MWCNTs into 20 ml 1, 2-dichloroethane. The mixture was then ultrasonicated for 3 h. 2 pieces of rectangular Cu plates were used as the electrodes for MWCNT deposition (Fig. 1(a)). The dimension of the as-prepared MWCNT/Cu conductors was 2 × 0.8 cm<sup>2</sup> each. The EPD of MWCNTs was carried out at

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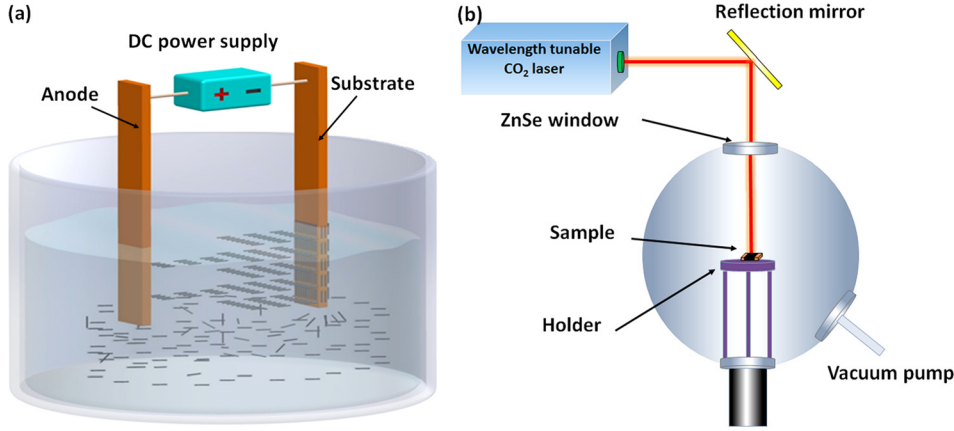


FIG. 1. Schematic experimental setups for (a) EPD and (b) laser irradiation.

an applied voltage of 40 V for 3 min. This process was repeated three times in order to maintain a constant MWCNT concentration in the solution during the process. The average thickness of the MWCNT coating was 30  $\mu\text{m}$ . Laser irradiation of the samples was carried out at a wavelength of 9.219  $\mu\text{m}$  using a wavelength-tunable continuous wave CO<sub>2</sub> laser (PRC, Inc., 9.2–10.9  $\mu\text{m}$ ). As shown in Fig. 1(b), the laser beam with a Gaussian shape was projected onto the MWCNT/Cu surface in a vacuum chamber with a background pressure of  $5 \times 10^{-3}$  Torr for 3 min. This irradiation time was fixed to achieve optimum MWCNT-Cu resistance reduction while avoiding Cu surface damages and MWCNT film delamination resulting from excessive laser irradiation. The chamber pressure and irradiation time were kept the same for each experiment in order to achieve comparable results, and the laser power densities were tuned in the range of 49–189 W/cm<sup>2</sup>. The absorption depth of the laser irradiation in MWCNT films is reported between 20 and 40  $\mu\text{m}$  independent of the incident wavelength in the mid-infrared range.<sup>21</sup> Thus, with respect to the thickness of the fabricated MWCNT coating, a wavelength of 9.219  $\mu\text{m}$  was chosen for the irradiation process in order to realize the beam absorption in depths close to the MWCNT-Cu interface without damaging Cu. Table I summarizes the power densities applied for the laser irradiation. Laser irradiations with a power density higher than 189 W/cm<sup>2</sup> led to partial separation and rupture of the MWCNT film, therefore were not investigated.

Surface morphologies of the MWCNT/Cu conductors were characterized using a field-emission scanning electron microscope (FESEM; Hitachi S4700). Raman spectra of the samples were acquired using a Renishaw in Via Raman microscope equipped with a 514 nm laser as the irradiation source and a  $\times 50$  objective. The AC resistance of the

samples was measured using an impedance Analyzer (HP, 4192 A). The probe-sample contact resistance and the parasitic impedance were de-embedded.

### III. RESULTS AND DISCUSSION

The measured AC resistance and inductive reactance of the MWCNT/Cu conductors before and after laser irradiation are shown in Fig. 2(a). Due to the skin effect, the monotonic increase in the magnitude of resistance/reactance with the increase of frequency is typical for the Cu conductors. In the laser-processed MWCNT/Cu conductors, the resistance/reactance increase at high frequencies is obviously suppressed.

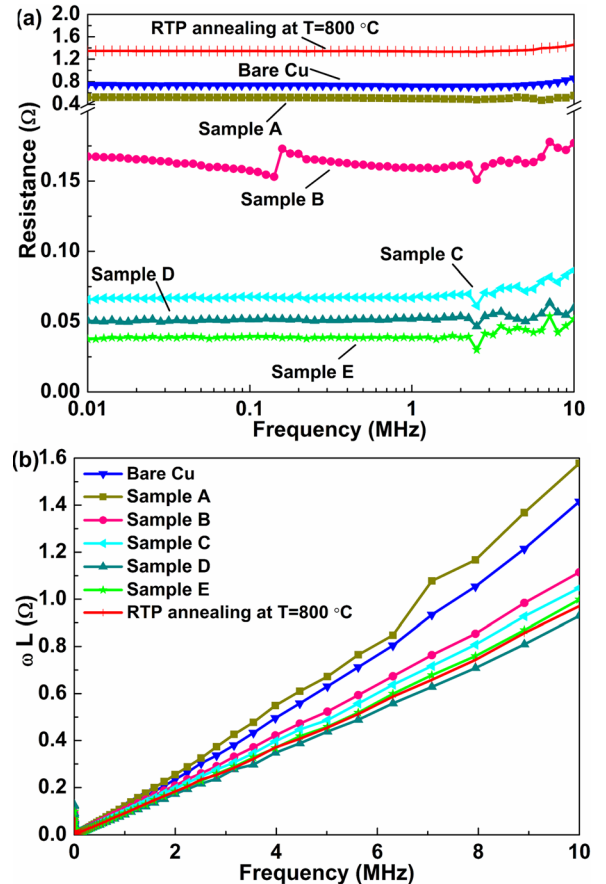


FIG. 2. (a) AC resistance and (b) reactance of MWCNT/Cu conductors as the function of frequency and laser power density.

TABLE I. Laser power densities used for irradiating MWCNT coatings.

Sample	Laser power density (W/cm <sup>2</sup> )
A	49
B	97
C	143
D	164
E	189

TABLE II. Comparison of electrical characteristics among the fabricated MWCNT/Cu conductors and ordinary Cu.

	6 MHz			10 MHz		
	R ( $\Omega$ )	$\omega L$ ( $\Omega$ )	Resistance reduction rate $\left(\Delta\% = \frac{R_{Cu} - R_{Sample}}{R_{Cu}} \times 100\right)$	R ( $\Omega$ )	$\omega L$ ( $\Omega$ )	Resistance reduction rate $\left(\Delta\% = \frac{R_{Cu} - R_{Sample}}{R_{Cu}} \times 100\right)$
Cu	0.75	0.76	...	0.85	1.40	...
Sample A	0.48	0.81	36	0.55	1.58	35
Sample B	0.17	0.64	77	0.17	1.11	80
Sample C	0.08	0.60	90	0.08	1.04	91
Sample D	0.05	0.52	93	0.06	0.92	93
Sample E	0.04	0.56	95	0.05	0.99	94

The most significant reduction is observed in sample-E which was irradiated at the highest power density of  $189/\text{cm}^2$ . Different from the results obtained from the samples after laser irradiation, the AC resistance obtained from thermally annealed sample at  $800^\circ\text{C}$  increases even more than bare Cu. This phenomenon is ascribed to the increased Cu surface roughness after thermal treatments which is a well-known limitation for furnace annealing techniques.<sup>22</sup>

The overall resistance reduction rate for each sample was calculated by

$$\Delta\% = \frac{R_{Cu} - R_{Sample}}{R_{Cu}} \times 100, \quad (1)$$

where  $R_{Cu}$  and  $R_{sample}$  are the measured AC resistance values for bare Cu and laser-irradiated MWCNT/Cu conductors, respectively. As shown in Fig. 2(b), the reactance of the laser-irradiated MWCNT/Cu conductors is close to that of bare Cu. The slightly decreased reactance at laser power densities higher than  $49 \text{ W}/\text{cm}^2$  is ascribed to the large momentum relaxation time of MWCNTs.<sup>10,23</sup> A summary of the resistance reduction rates relative to bare Cu, along with the AC resistance and reactance of the samples at  $f = 6 \text{ MHz}$  and  $10 \text{ MHz}$ , is presented in Table II. The resistance reduction rate is in direct relation with the laser power density, and therefore, the reduction in the magnitude of the resistance can be modified and controlled by tuning laser power density.

The overall behavior of the MWCNT/Cu conductors was further studied by analyzing the real part of the resistance ( $R_{\text{MWCNT-Cu}}$ ) at the MWCNT-Cu interfaces in order to investigate the mechanism behind the electrical behavior of the laser irradiated MWCNT/Cu conductors. Fig. 3 shows the  $R_{\text{MWCNT-Cu}}$  plot versus frequency for sample E irradiated with the power density of  $189 \text{ W}/\text{cm}^2$ . For a MWCNT/Cu sample without laser irradiation, the  $R_{\text{MWCNT-Cu}}$  decreases as the frequency increases, indicating a capacitive behavior at the MWCNT-Cu interface. The  $R_{\text{MWCNT-Cu}}$  decrease is ascribed to the porous MWCNT coating and considerable amount of unfilled voids which introduce an equivalent dielectric effect at the MWCNT-Cu interface. However, after laser irradiation, the interfacial resistance exhibits a resistive behavior with minor magnitude changes indicating densification of the MWCNT coating, reduced amount of voids, and therefore, neutralized dielectric behavior. In addition,

$R_{\text{MWCNT-Cu}}$  remains constant at frequencies lower than  $3 \text{ MHz}$  (see the inset in Fig. 3). These transitions, which were observed for all of the investigated MWCNT/Cu conductors, are ascribed to the successful implantation of the MWCNT channels, which are less sensitive to frequency changes, and therefore, contribute to the suppression of the skin effect in Cu conductors.

Fig. 4(a) shows the Raman spectra of the MWCNT films before and after laser irradiation. Both D- and G-band are observed in all samples. D-band to G-band ratio ( $I_D/I_G$ ) and Full Width Half Maximum (FWHM) of the D-band are depicted in Fig. 4(b) as a function of laser power density.  $I_D/I_G$  reflects the ratio of structural defects and degree of disorder in the graphitic walls of nanotubes.<sup>24</sup> As the irradiated power density increases, the  $I_D/I_G$  ratio decreases from 1.01 to 0.86, indicating the reduction of dangling bonds and improvement of crystallinity in graphitic shells of the MWCNTs. Moreover, the FWHM of the D-band decreases as the laser power density increases, indicating improved structural integrity and reduced impurities in the MWCNT coatings. The crystallinity improvement and impurity reduction are reported to be beneficial in suppressing skin effect.<sup>10</sup>

The effect of the laser irradiation in structural modification of the MWCNTs is noticeable in FESEM images. Fig. 5 compares the morphology of a MWCNT coating before and after laser irradiation. A dense MWCNT film is

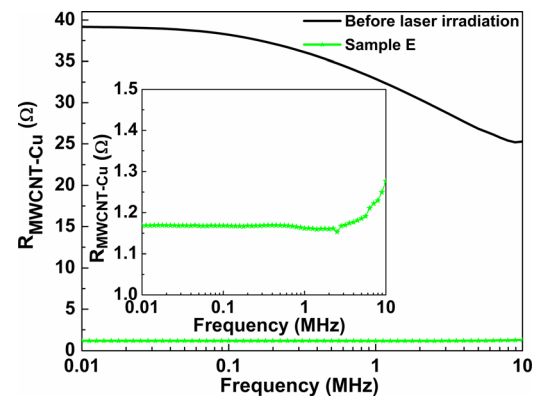


FIG. 3.  $R_{\text{MWCNT-Cu}}$  of a MWCNT/Cu conductor as the function of frequency before and after the laser irradiation (sample-E, laser power density of  $189 \text{ W}/\text{cm}^2$ ). The inset is a zoomed view of sample-E showing slightly increased  $R_{\text{MWCNT-Cu}}$  above  $3 \text{ MHz}$ .



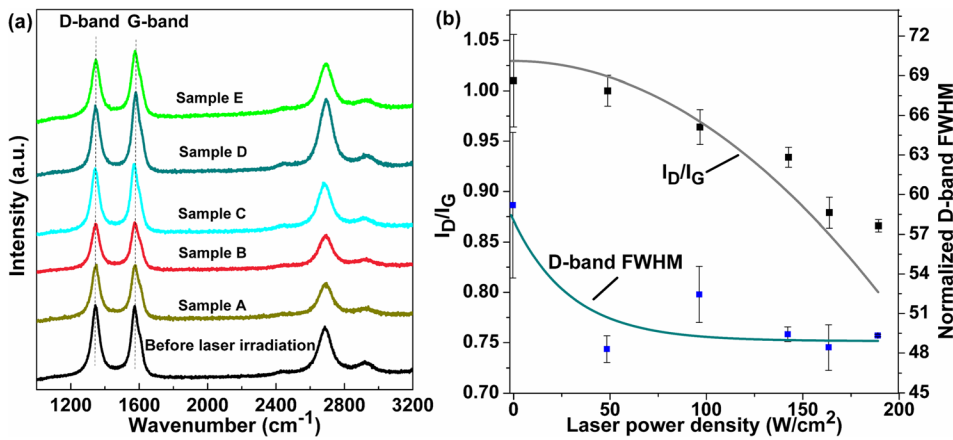


FIG. 4. (a) Raman spectra of MWCNT/Cu conductors before and after the laser irradiation. (b)  $I_D/I_G$  ratio and FWHM of D-band as the functions of the laser power density along with their fitting curve. (The error bars represent the standard deviation.)

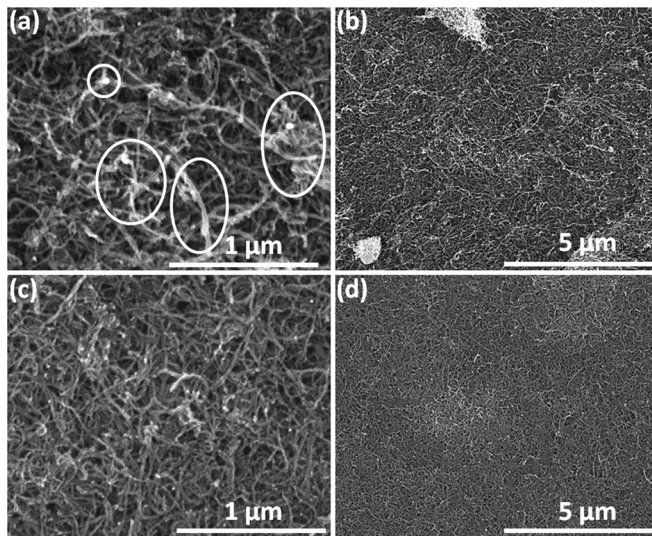


FIG. 5. FESEM images of a MWCNT coating before ((a) and (b)) and after ((c) and (d)) laser irradiation at a power density of  $189 \text{ W/cm}^2$ .

observed after the laser irradiation, as shown in Figs. 5(c) and 5(d), compared to the primitive film before laser irradiation, Figs. 5(a) and 5(b). A dense MWCNT film with reduced amount of voids indicates improved tube-tube contacts, therefore reduced tube-tube resistance. This modification is attributed to removal of the impurities such as amorphous carbon and disruption of solvent induced bubbles as evidenced in the Raman spectra in Fig. 4, which causes the MWCNT film to undergo a structure reconstruction after the laser irradiation and therefore, become denser, smoother, and more intertwined than it appears before laser irradiation.

#### IV. CONCLUSION

In summary, laser-processed MWCNT coatings are developed to suppress skin effect in Cu. Obviously, reduced AC resistance is observed in the laser-processed MWCNT/Cu conductors compared to bare Cu. The resistance reduction is observed to be proportional to laser irradiation power density below the MWCNT film breakdown threshold. At 10 MHz, a maximum AC resistance reduction of 94% was observed in a MWCNT/Cu conductor after being irradiated at a laser power density of  $189 \text{ W/cm}^2$ . The AC resistance

reduction and skin effect suppression are ascribed to the implementation of MWCNTs, which provide low-resistance current channels insensitive to frequency changes. Additional roles of the laser irradiation are found to be vital in densifying MWCNTs, reducing tube-tube contact resistance, and removing impurities in MWCNTs, which are beneficial in forming densely packed MWCNT films and reducing resistance.

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