Microwave characterization of vertically aligned multiwalled carbon nanotube arrays

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Vertically aligned multiwalled carbon nanotube (VACNT) films have been characterized by rectangular waveguide measurements. The complex scattering parameters (S-parameters) are measured by a vector network analyzer at X-band frequencies. The effective complex permittivity and permeability of the VACNT films have been extracted. The extracted parameters are verified by full wave simulations and very good agreement has been obtained. The results of the systematic error analysis are presented and the errors are within the acceptable range. The performance of VACNT films as an absorber is examined, and comparison with the conventional carbon loaded materials shows that a 90% size reduction is possible while maintaining the same absorption level. © *2011 American Institute of Physics*. [doi:10.1063/1.3592263]

Carbon nanotubes (CNTs) can be viewed as seamless cylinders rolled up from a piece of graphene sheet. CNTs can be single-walled (SWNTs) or multiwalled (MWNTs) depending on their constitution of one or multiple graphene sheets, respectively. These nanotubes can be considered as one-dimensional nanostructures due to their large aspect ratio (length/diameter); usually in the order of 10^4-10^7. This unique structure accounts for their extraordinary electrical and mechanical properties.

The scientific applications involving the use of CNTs have in theory made a range of solutions to problems possible. Examples are field emission displays, hydrogen-powered vehicles, artificial muscles, fuel cells, and batteries.[1–3] Recently, many microwave applications have been suggested, including nanosized antennas and nanointerconnects.[4,5]

SWNTs can be either metallic or semiconducting, depending on the geometry or the chirality of the specific nanotube. All armchair CNTs, for example, are metallic whereas zigzag and chiral can be either metallic or semiconducting.[5] In contrast to these SWNT, which may be metallic in only around 1/3 of cases, MWNTs are always metallic. For this reason MWNTs are appropriate candidates for microwave and terahertz applications as there is, as yet, no way to control the geometry of SWNTs during the growing period.

Although extensive studies have been done on CNTs at direct current (dc) and low frequencies, the electrical properties of CNTs, particularly of MWNTs have yet to be the subject of comprehensive study at microwave frequencies. Similar studies have been undertaken by this group in the terahertz frequency band.[6] In this current study, vertically aligned MWNT films (VACNT) are characterized at X-band by rectangular waveguide measurements. This method enables the accurate extraction of the effective material parameters from the measured S-parameters. The main difference of the current versus previous studies is the usage of highly vertically aligned nanotubes to the substrate (Fig. 1). In addition, all the S-parameters (amplitude and phase) are being measured, thus allowing both permittivity and permeability to be extracted. It is also shown that VACNT films are superior absorbers in the X-band frequency range, compared to conventional materials.

Plasma enhanced chemical vapor deposition (CVD) is an excellent method for depositing a variety of thin films at lower temperatures in comparison to those utilized in CVD reactors. For example, high quality silicon dioxide films can be deposited at 300 to 350 °C whereas CVD requires temperatures in the range of 650 to 850 °C to produce films of similar quality.

The vertically aligned multiwalled CNTs (VACNTs) samples have been fabricated in the Electrical Engineering Division, University of Cambridge. They are based on a silicon wafer, with dimensions of 42 mm × 50 mm. Fe catalyst was deposited onto an Al diffusion barrier thin film. Both

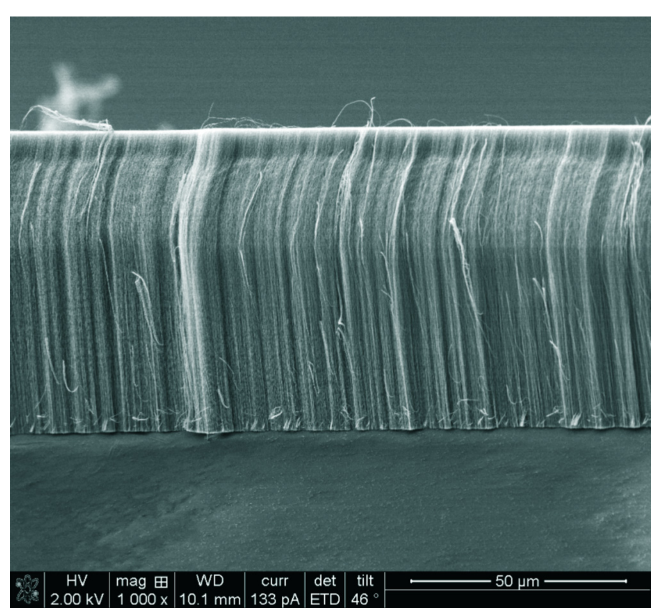

FIG. 1. (Color online) SEM image of the vertically aligned CNT film.

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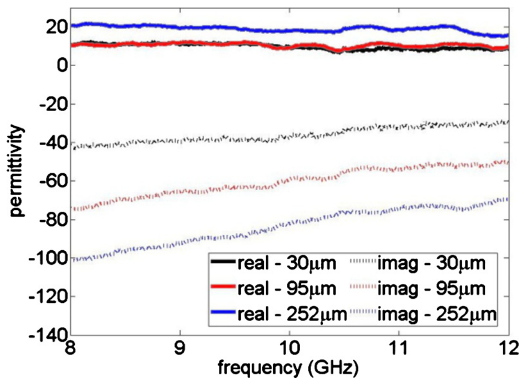

FIG. 2. (Color online) Effective medium extracted permittivity of the VACNT film.

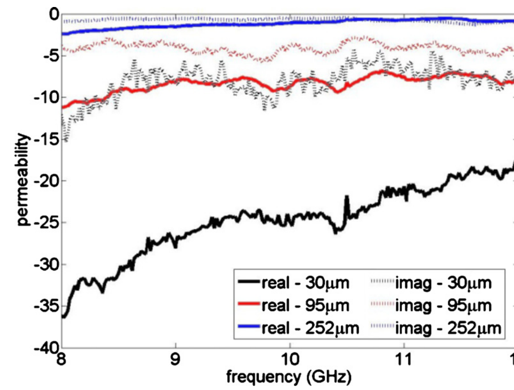

FIG. 3. (Color online) Effective medium extracted permeability of the VACNT film.

films were deposited onto the silicon substrate by sputter coating, to prevent the formation of $FeSi_x$. The thickness of the silicon wafer is 510 μm and the resistivity is 0.02 Ω cm. Upon annealing with H_2 for 3 min, the Fe thin film breaks up into nanoparticles which seed the growth of the nanotubes.

The nanotubes were grown in a bell jar vacuum chamber with a residual pressure of 10 mbar. The growth was initiated immediately by introducing C_2H_2 into the chamber and applying the dc glow discharge. After a growth time of 40 s, 2 mins, 5 mins, we obtained samples with nanotube lengths of 30 μm, 95 μm and 252 μm, respectively.

The transmission/reflection line technique was used to obtain the measurement used to describe the properties of the VACNT films. The samples, which are treated as an effective medium with a known thickness, are placed in a section of a waveguide following calibration. The vector network analyser (VNA) was used to measure both complex S-parameters, thus, allowing both ϵ and μ to be solved in terms of the S-parameters.

All three samples have been measured several times to demonstrate good repeatability. To extract the effective complex permittivity and permeability of the VACNT films, the Nicolson–Ross–Weir approach[7–9] was applied to the measured S-parameters for a given thickness. An algorithm has been developed based on that approach.

For a VACNT film with a thickness d, the transmission, and reflection coefficients at the air-film interfaces can be obtained from the S-parameters. The S-parameters through the material, referenced to the air-film interfaces, are given by

$$S_{21} = \frac{(1-\Gamma^2)z}{1-\Gamma^2 z^2}, \tag{1}$$

$$S_{11} = \frac{(1-z^2)\Gamma}{1-\Gamma^2 z^2}, \tag{2}$$

where z and Γ are the transmission and reflection coefficients at the interface, respectively. According to the theory, the transmission coefficient inside the slab is given by $z=e^{-\gamma d}$ and the reflection coefficient $\Gamma=(\mu\cdot\gamma_o-\gamma)/(\mu\cdot\gamma_o+\gamma)$, where $\gamma_o=\sqrt{k_c^2-k_o^2}$ and $\gamma=\sqrt{k_c^2-\mu\varepsilon k_o^2}$ are the propagation constants in the two waveguides filled with free space and the sample respectively. The cut off wave number is given by $k_c=\pi/\alpha$ where $\alpha=22.86$ mm is the longer dimension of the rectangular waveguide cross-section at X-band.

There is an ambiguity that needs to be clarified once the propagation constant γ is solved in terms of the transmission coefficient. That ambiguity is caused by the function $\ln(1/z)$ which has an infinite number of solutions when z is complex. The propagation constant can be written as $\gamma=\ln|1/z|+j[arg(1/z)+2m\pi]/d$, where m is any integer. That equation is a continuous function, thus a different value of the branch index m may be required. Once γ is derived, then the permeability of the VACNT sample can be obtained and substituting that into the propagation constant, the permittivity of the sample is calculated

$$\mu = \frac{\gamma(1+\Gamma)}{\gamma_o(1-\Gamma)}, \tag{3}$$

$$\varepsilon = \frac{k_c^2-\gamma^2}{\mu k_o^2}. \tag{4}$$

The extracted complex permittivity ($\varepsilon=\varepsilon'-j\varepsilon''$) and permeability ($\mu=\mu'-j\mu''$) of all the samples are plotted in Figs. 2 and 3, respectively.

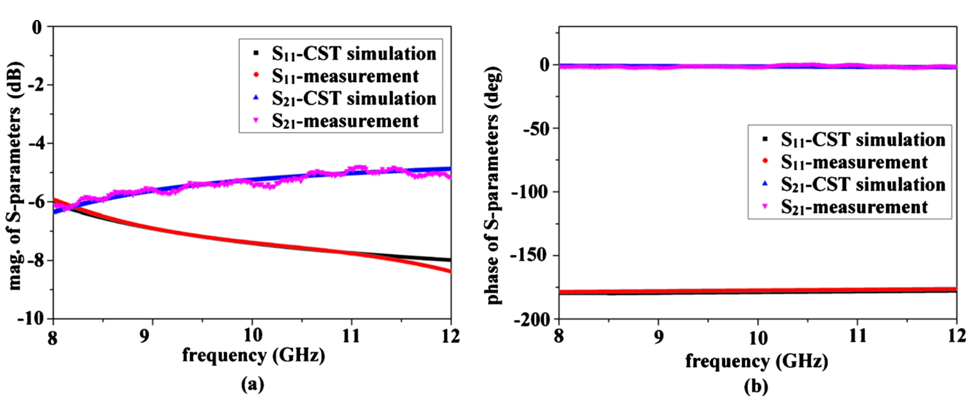

FIG. 4. (Color online) Simulated and measured reflection and transmitted coefficients of the VACNT film.

TABLE I. VNA uncertainties.

Thickness (μm)	S_{11}^{mag}	S_{11}^{ang} (deg)	S_{21}^{mag}	S_{21}^{ang} (deg)
30	0.037	0.49	0.012	0.08
95	0.035	0.45	0.015	0.09
252	0.026	0.29	0.028	0.14

It is expected that the corresponding permittivity and permeability of any homogeneous medium, such as the VACNT films, is independent of the thickness. The three different samples of VACNT films have been grown similarly but they are not identical to each other. It appears that they exhibit discrepancies arising from noncontrolled, geometrical uncertainties in parameters such as air-gaps with neighboring nanotubes, concentrations of CNTs and concentrations of the Fe catalyst, resulting in moderately distinct effective media in all three samples. It is also understood that lengthening nanotubes, create entanglements with adjacent ones, directly proportional to the resulting length. The aforementioned in addition to the measurement uncertainties of the S-parameters and thickness, lead to a much different value of effective permittivity and permeability in each sample as it is shown in Figs. 2 and 3.

To verify the algorithm that has been implemented based on the NRW approach, a computer simulation technology microwave studio (CST-MS) model is set up which comprises a slab with the thickness of the sample and the complex parameters that have been extracted from the above material. The slab is placed between two waveguides. The simulation results are plotted together with the experimental ones (Fig. 4).

A rigorous error analysis based on the uncertainties that have been introduced by the VNA is performed.[10] The uncertainties of the magnitudes and phases of both S_{11} and S_{21} are presented in Table I. Table II, shows the mean values of the errors for the four material parameters of all samples.

The average calculated error for the ε', ε'', and μ' is 22.7%, 10.3%, and 12.7%, respectively. The error introduced in the μ'' is relatively high, more than 70% and it is attributed to the sensitivity of the phase measurement. The uncertainties that have been introduced by the VNA (Table I) are well above the safe margin, thus the systematic error is the maximum possible.

Recently, has been reported that CNT films can highly absorb visible light[11] and apart from visible range, enhanced absorption can be observed over a broadband frequency.[12] The absorbing performance of the VACNT films in X-band is examined below. Figure 5 shows the absorption coefficient across the frequency band. The absorption of the VACNT films do not increase as the thickness increases, instead it appears a maximum of absorption at 95 μm. The number of samples presented in this letter is not sufficient enough to identify the optimum thickness of the VACNT film where the maximum absorption can be achieved but they reveal the trend of the absorption curve with the thickness.

TABLE II. Average systematic errors of material parameters.

Thickness (μm)	ε'	ε''	μ'	μ''
30	3.81	4.76	4.36	7.95
95	1.55	4.25	0.41	2.9
252	2.73	8.87	0.18	1.07

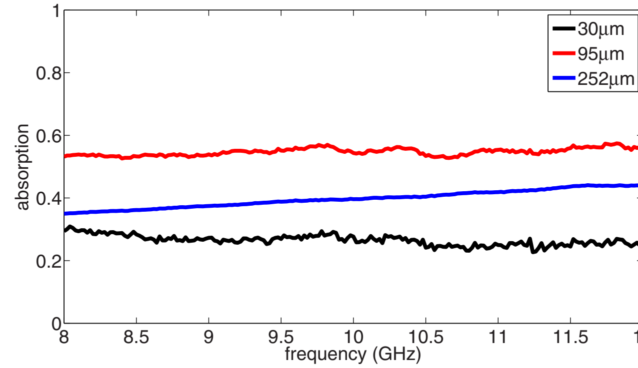

FIG. 5. (Color online) Measured absorption of the VACNT films.

Rozanov[13] has shown that if a metal-backed absorber is illuminated under normal incident, the thickness of that absorber in X-band frequencies has to be $d \geq (|\int_0^\infty \ln|R(\lambda)|d\lambda|/2\pi^2)$, where $R(\lambda)$ is the distribution of the reflection coefficient.

Solving the equation above for the frequencies over which the measurement has been performed and for the sample that maximum absorption has been measured, 95 μm, the minimum possible thickness of a conventional absorber is $d=1.1$ mm. Therefore, a 90% reduction in size has been achieved compared to conventional absorbers, maintaining the absorption shown in Fig. 5.

In summary, three films composed of VACNTs have been characterized at X-band frequencies. The relative permittivity and permeability of the VACNT films have been extracted from 8 GHz to 12 GHz using the Nicolson–Ross–Weir approach and good agreement with full wave simulations (CST-Microwave Studio) has been obtained. A systematic error analysis has been presented and the errors calculated were within the acceptable range of errors. The absorbing performance of VACNT films are examined and compared to conventional materials.

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