Electrical Performance of Carbon Nanotube – Polymer Composites at Frequencies up to 220 GHz

Ali H. Alshehri*[†], Malgorzata Jakubowska[§], Marcin Sloma[§], Michal Horaczek[§],

Diana Rudka[§], Charles Free[†] and J. David Carey*[†]

[†] Advanced Technology Institute, University of Surrey, Guildford, GU2 7XH, United Kingdom

[§] Faculty of Mechatronics, Warsaw University of Technology, Warsaw, Poland

We have measured the sub-THz electrical response of screen printed carbon nanotube - poly(methyl methacrylate) polymer composites up to 220 GHz. The measured electrical losses using mm long coplanar waveguide geometries averaged as low as 0.15 dB/mm in the frequency range 40 GHz to 110 GHz and showed a reduction in signal loss with increasing frequency; a behaviour opposite to that found in conventional metallic conductors. Between 140 and 220 GHz the electrical losses averaged 0.28 dB/mm. We show that the low electrical losses are associated with the capacitive coupling between the nanotubes and discuss potential high frequency applications.

*Corresponding authors: A.Alshehri@surrey.ac.uk (Ali Alshehri) and David.Carey@surrey.ac.uk (J David Carey)

Carbon nanotube (CNT) electronics has firmly established itself as one of the most important areas of modern nanoelectronics.[1, 2] The suppression of carrier backscattering brought about by the nanotube's band structure results in long mean free paths leading to ballistic transport and opens up the possibility of GHz and sub-THz applications.[3] Tailoring the intrinsic electronic properties of the CNT by choosing semiconducting or metallic CNTs has already led to the fabrication of field effect transistors[3] and sensors[4] for the former type of nanotube and interconnects[5] and field emission materials[6] for the latter. Previous high frequency studies of CNTs have tended to concentrate on employing small (micron) electrode gaps, often making use of single or few singlewalled nanotube bundles as the active elements in a transistor architecture.[3] Chemical vapor deposited (CVD) carbon nanotubes bundles[7], vertically aligned arrays[8] or nanotube ropes[9] for possible applications as electrical interconnects have also been variously explored. However such measurements using short CNTs bundles are often affected by the presence of parasitic capacitances associated with the electrodes and the presence of large impedance mismatches.

Electrode architectures for transistors and interconnect applications imposes strict requirements for the environment that the nanotube can be found. Using a CNT composite frees up many of these constraints and at high frequency opens up the possibility of using large area, high bandwidth CNT electronics for communications, microwave and surface acoustic wave devices. In this Letter we have successfully characterised up to 25 mm long CNT - poly(methyl methacrylate) polymer composites up to 220 GHz. We show that the frequency response of the composites is significantly different from that of conventional metallic conductors and that capacitive coupling between the nanotubes plays an important role in the ac conduction.

The samples characterised consisted of CVD grown multiwalled CNTs (average length 1.5 μm, average diameter 9.5 nm, Nanocyl batch number NC3100) mixed with poly(methyl-methacrylate) (PMMA) to produce composites with 10 wt.% CNT loading. Apart from its ready availability and compatibility with high frequency electronics, PMMA was chosen to minimize any non-CNT conduction paths. Pure silver photoimageable contact pads were first printed, exposed to UV light for one second using an MA3 (Hibridas) exposure unit and fired at 850°C. The contact pads were then developed using 0.2% aqueous solution of ethanolamine and are 50 Ω matched with a 100 μm probe pitch size in a ground-signal-ground arrangement, Fig. 1(a). CNT-composites were screen printed (DeH 1202) unto 96% purity alumina substrate of 635 μm thickness to form coplanar waveguide (CPW) structures with lengths ranging from 5 mm to 25 mm and attached to the contact pads. After printing the pads, the CNT composites were printed and dried to remove volatile solvents and then cured at 120°C for one hour. The coplanar lines track widths were designed to be 400 μm and the tracks thicknesses (post firing) were approximately 20 μm, (Fig. 1b). The scattering or S-parameters of our CPW structures were measured using an HP 8510C vector network analyzer.

The S_{21} insertion loss is presented in both dB/mm and dB/λ; the latter quantity being a key design parameter since many dimensions in microwave devices are specified as a fraction of a wavelength e.g. a half - wavelength filter or quarter - wavelength coupler. Using different CPW lengths (5 - 25 mm with 5 mm increments) allows us to readily calculate from the measured data the losses per unit length between any two coplanar lines. This also allows us to avoid the need for a de-embedding procedure to remove the impedance mismatch at the probe – circuit interface. For two samples of different physical lengths l_1 and l_2 with measured insertion losses L_1 and L_2 the loss per unit length can be calculated as

$$loss(dB/mm) = \frac{L_2 - L_1}{l_2 - l_1} \tag{1}$$

Defining the signal loss in this way has the advantage of removing any system errors in the measurement. The insertion loss per wavelength was found by converting the physical length of the coplanar waveguide to its corresponding electrical length.[10] Figure 2(a) shows results of comparing the measured insertion losses of samples with lengths 5, 10, 15 and 20 mm with the loss in a 25 mm long sample. It can be seen that the S_{21} insertion loss initially decreases and in the frequency range of 40 - 110 GHz the insertion loss is largely constant at around 0.15 dB/mm (standard deviation 0.06 dB/mm, measured from 128 points). The observation of a reduction in the insertion loss as the frequency increases is a significant result since it is well known that in metallic conductors, for example in microstrip or CPW lines fabricated in Ag, that the losses are known to increase as the high frequency is increased (and usually attributed to the growing importance of surface roughness as the skin depth is reduced).[11] Our measured data show the opposite effect and this suggests that CNT loaded composites may offer improved device performance at the higher frequencies in the mm-wave frequency band.

Figure 2(b) shows the average insertion loss per wavelength (dB/λ) as a function of frequency; it can be observed that the loss tends to level off above 40 GHz with a mean value of 0.3 dB/λ (standard deviation 0.16 dB/λ, 128 points) and this indicates that the losses will become independent of the electrical size of a device at these high frequencies. Over the frequency range of 140 GHz to 220 GHz, the measured insertion loss for each sample was found to be similar and the average data from all the samples is plotted in Fig. 3 where the averaged loss is around 0.28 dB/mm (standard deviation 0.06 dB/mm, 201 points). Whilst there was an overall decrease in loss with increasing frequency, we see a slight increase in loss as we approach to 220 GHz due to the skin depth becoming much less than the rms surface roughness. Also plotted in Fig. 3 is the loss per wavelength which when averaged across all the samples came is 0.20 dB/λ (standard deviation 0.05 dB/λ, 201 points).

The different behaviour of the insertion loss with frequency, especially above 40 GHz found in the CNT - composites when compared to the more conventional metallic conductors is inextricably linked to the presence of CNTs embedded in a host matrix. At a 10 wt.% loading the samples will be in excess of the threshold for percolation controlled conduction which typically would be less than 1 wt.%.[12] The electrical description of these composites is to consider them as mm long dielectrics with randomly placed micro-long conductive elements acting as nano-dipoles. It is therefore immediately tempting to extract capacitance, inductances and resistances per unit length using the standard textbook analysis.[13] This discrete circuit component approach has been previously successfully applied to electrode geometries consisting of a number of single nanotube or small bundles of nanotubes.[14,15] However, the approach is not valid when the S-parameters are extracted from long conductors. It is known that for the conventional transmission line equations to be valid the electrical length of the conductor should be no more than about 1/20 of the signal wavelength. For our 25 mm long lines we calculate the electrical length to be 1.9λ at 10 GHz which is clearly much longer than 0.05λ. By contrast, in the study by Jun *et al.*[15] the CNT was 7 μm long and at 50 GHz, we calculate that the electrical length in that study to be 0.0027λ - safely well below the 0.05λ limit. Even with this limitation in mind it is still worth considering the composition of the composite from an electrical point of view.

In electrical measurements of composite materials it is often the effective (tunnel) junction resistance, R_T, and junction capacitance, C_J, that controls the electrical properties. In a previous study[16] one of us showed that for *in situ* electrical measurements made on a *single* multiwall carbon nanotube in polystyrene (PS) made in an electron microscope that it was possible to extract a value of C_J of about 2×10^{-19} F where the nm thick PS layer acted as a tunnel junction. To confirm the role of capacitive effects measurements of the phase shift over the entire frequency range on 5 mm and 25 mm long composite samples and on similar length Ag samples (silver conductive paste Heraeus C1075 S/SD) were made, see Ref. 21 for supplementary material (Fig. S1). At a representative frequency of 40 GHz we note that the phase difference between the composite and silver lines was 41° for the 5 mm line and 73° for the 25 mm line. The presence of this phase difference indicates capacitive coupling between the CNTs is present and plays an important role in the high frequency propagation through the composite material. The presence of this phase change could be of practical significant to the microwave circuit designer in that an alternative form of phase shifting element could be developed for use in the high frequency devices such as mixers and integrated phased arrays.[17]

Finally, it is worth commenting on the likely source of the capacitance and how it is related to conduction. Individual or bundles of CNTs are embedded in a matrix consist of long and thin conductors and separated from each other by a thin potential barrier. The barriers can be associated with the insulating PMMA between the nanotubes or the intrinsic barrier to conduction associated with direct nanotube – on – nanotube contact. Electrons will tunnel between the conducting regions taking the shortest electrical distance between the conductors. This results in tunnel junctions with small areas and small tunnel junction capacitance. Fluctuations in the local barrier heights and local barrier thickness gave rise to fluctuation induced tunnelling (FIT)[18] in which charge fluctuations induce voltage fluctuations across the tunnel junction. This can be modeled as a parallel plate capacitor with the capacitor area being effective area of tunnelling. This conduction mechanism has been reported in understanding the transport[19] and field emission characteristics[20] in other CNT composite systems. In the FIT mechanism the conducting elements are large (micron longer CNTs) and separated from the nm-size polymer tunnel junctions; this has profound implications for the treatment of the capacitance. Recalling that the reactance of capacitance associated with a capacitor scales as $1/\omega C$ then as one goes to higher frequencies then the reactance decreases for a given overall capacitance and this is reason why there is an overall decrease in insertion loss on going to higher frequencies.

In summary, we have characterized the high frequency behaviour of CNT - PMMA composite materials up to 220 GHz. Unlike the behaviour in conventional conductors the losses in lines fabricated using CNT composites were shown to decrease at higher frequencies giving a near constant value of 0.28 dB/mm between 140 and 220 GHz. The improved ac conduction is attributed to capacitive effects associated with the small nano-sized random junctions between nanotubes or small nanotube bundles. The results from this study potentially open up new avenues of exploitation based on high frequency CNT electronics.

Acknowledgement. AHA acknowledges funding for a PhD scholarship from the Ministry of Higher Education, Saudi Arabia.

References

[1] P. Avouris, Z.H. Chen and V. Perebeinos, Nature Nano. **2**, 605 (2007).

[2] C. Rutherglen, D. Jain and P. Burke, Nature Nano. **4**, 811 (2009).

[3] A. Bachtold, P. Hadley, T. Nakanishi and C. Dekker, Science **294**, 1317 (2001).

[4] P. Qi, O. Vermesh, M. Grecu, A. Javey, Q. Wang, H. Dai, S. Peng and K. J. Cho, Nano Lett. **3**, 347 (2003).

[5] J. Li, Q. Ye, A. Cassell, H.T. Ng, R. Stevens, J. Han and M Meyyappan, Appl. Phys. Lett. **82**, 2491 (2003). G.F. Close, S. Yasuda, B. Paul, S. Fujita and H-S Philip Wong, Nano Lett. **8**, 706 (2008).

[6] T. Connolly, R. C. Smith, Y. Hernandez, Y. Gun'ko, J.N. Coleman and J.D. Carey, Small **5**, 826 (2009).

[7] A. Tselev, M. Woodson, C. Qian, J. Liu, Nano Lett. **8**, 152 (2008); J.J. Plombon, K. P. O’Brien, F. Gstrein and V.M. Dubim, Appl. Phys. Lett. **90**, 063106 (2007).

[8] A. Katsounaros, K.Z. Rajab, Y. Hao, M. Mann, W.I. Milne, Appl. Phys. Lett. **98**, 203105 (2011).

[9] L. Gomez-Rojas, S. Bhattacharyya, E. Mendoza, D.C. Cox, J.M. Rosolen and S.R.P. Silva, Nano Lett. **7**, 2672 (2007).

[10] T.C. Edwards and M.B. Steer, Fundamentals of interconnect and microstrip design, 2000, Wiley 3rd Edition, New York. p. 90.

[11] M. Jakubowska, Z. Tian, C. Free and K. Pitt, J Matter Sci: Matter Electron **17**, 127 (2006).

[12] B. Vigolo, C. Coulon, M. Maugey, C. Zakri and P. Poulin, Science **309**, 920 (2005).

[13] D.M. Pozar, Microwave Engineering, 2004, 3rd Edition, Wiley, New York.

[14] P.J. Burke, IEEE Trans. Nano. **2**, 55 (2003).

[15] S.C. Jun, J.H. Choi, S.N. Cha, C.W. Baik, S. Lee, H.J. Kim, J. Hone and J.M. Kim, Nanotechnology **18**, 255701 (2007).

[16] P. Smith, J. D. Carey, D.C. Cox, R.D. Forrest and S.R.P. Silva, Nanotechnology **20**, 145202 (2009).

[17] Hansen, R.C. Phased Array Antennas, **2009**, Volume 213, Wiley Series in Microwave and Optical Engineering, 2nd edition, Wiley-Interscience.

[18] P. Sheng, E. K. Sichel and J.I. Gittleman, Phys. Rev. Lett. **40**, 1197 (1978).

[19] B.R. Sankapal, K. Setyowati, J. Chen and H. Liu, Appl. Phys. Lett. **91**,173103 (2007).

[20] R.C. Smith, J.D. Carey, R.J. Murphy, W.J. Blau, J. N. Coleman, S.R.P. Silva, Appl. Phys. Lett. **87**, 263105 (2005).

[21] See supplementary material at http://dx.doi.org/10.1063/1.3651278 for Fig. S1. Measured phase from the CNT composite CPW (dashed - - -) and an Ag reference CPW (solid —) both of (a) 5 mm length and (b) 25 mm length.

Figure captions

Figure 1 (a) Schematic of the ground – signal – ground (GSG) electrode geometry. (b) Scanning electron microscope image of electrodes with the CNT composite. Here the silver photoimageable electrode pads can be seen on the left hand side of the image.

Figure 2 (Color online) Variation of the signal insertion loss (a) (dB/mm) and (b) calculated dB per wavelength as a function of frequency in the range up to 110 GHz. Comparison is made using equation 1 and the measured losses from the longest CPW (25 mm) for CPWs of length 20 mm (black —), 15 mm (blue □), 10 mm (red ●) and 5 mm (green ○) as indicated on the graph.

Figure 3 (Color online) Variation of the signal insertion loss (dB/mm) (—) and calculated dB per wavelength (---) as a function of frequency in the range of 140 – 220 GHz. The average loss per mm is 0.28 dB with a standard deviation of 0.06 dB. The average loss per wavelength is 0.20 dB with a standard deviation of 0.05 dB.

Figure S1 (Color online) Measured phase from the CNT composite CPW (dashed ---) and an Ag reference CPW (solid —) both of (a) 5 mm length and (b) 25 mm length.

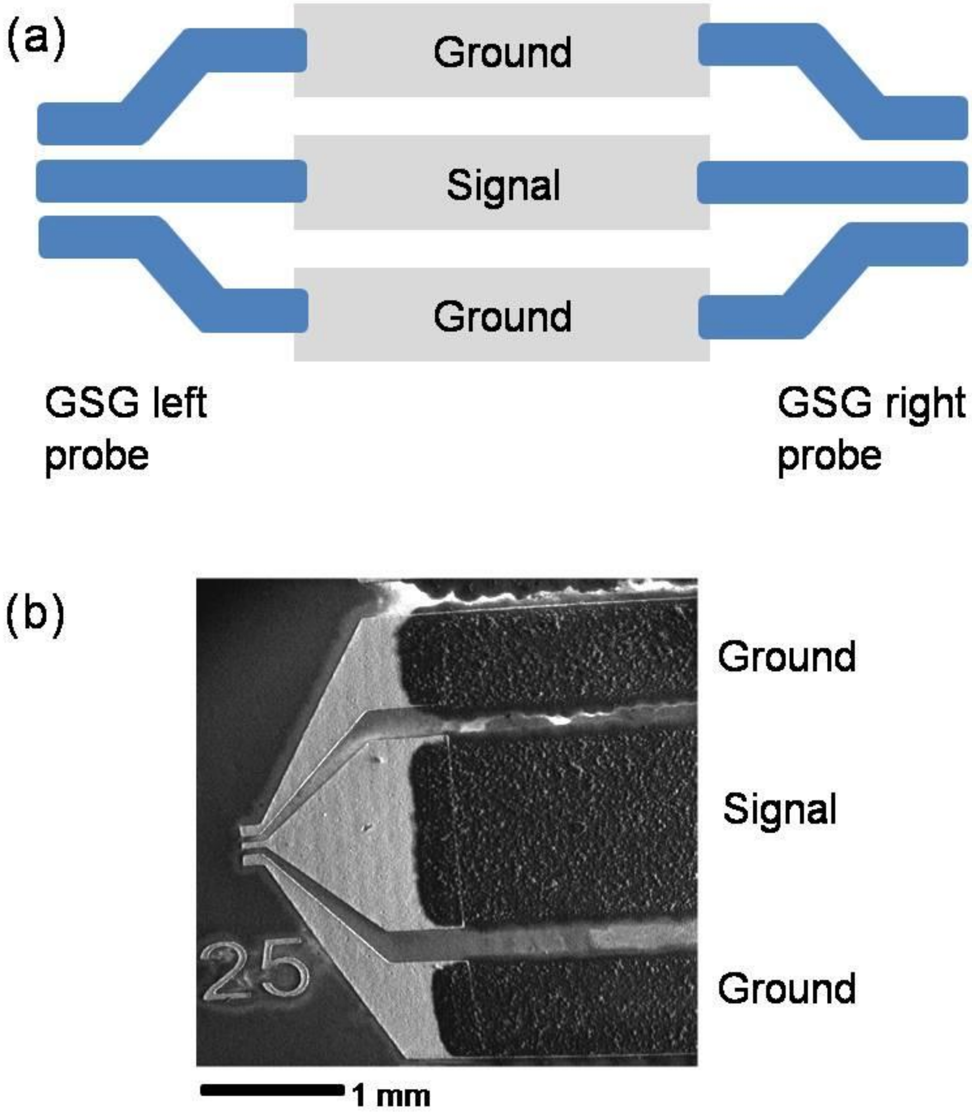

Figure 1 (a) Schematic of the ground – signal – ground (GSG) electrode geometry. (b) Scanning electron microscope image of electrodes with the CNT composite. Here the silver photoimageable electrode pads can be seen on the left hand side of the image.

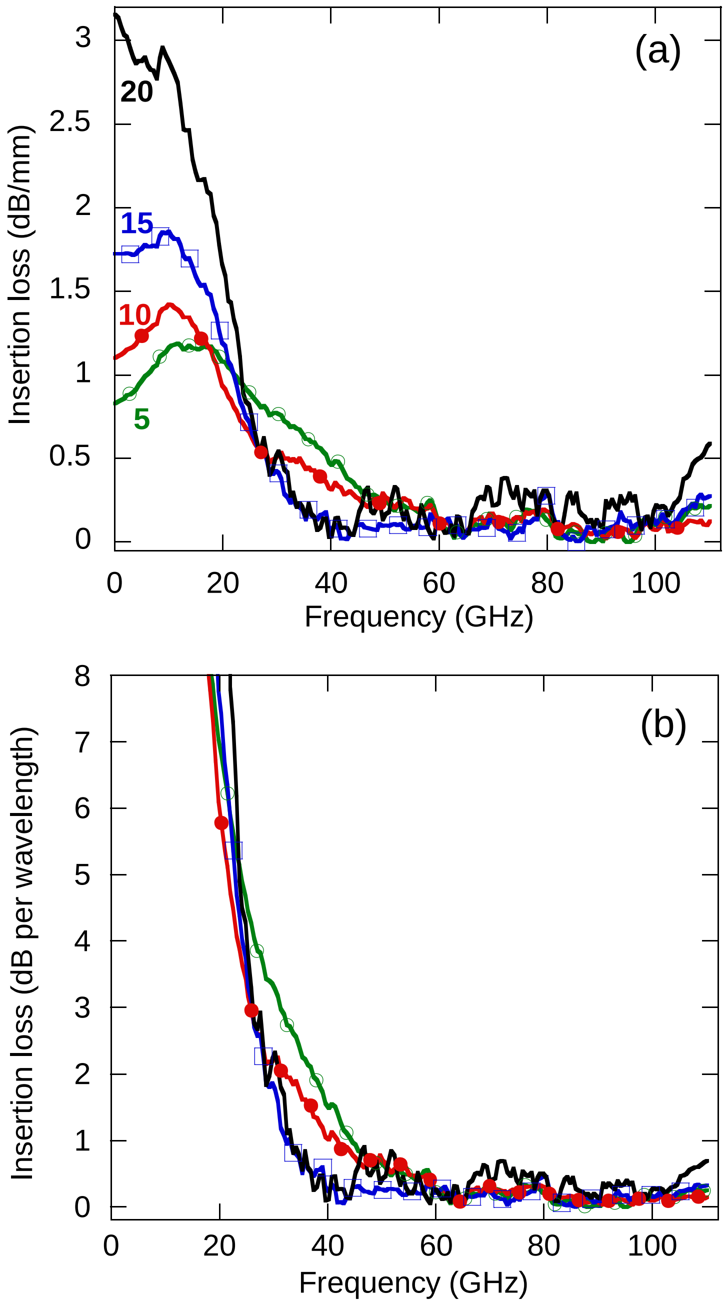

Figure 2 (Color online) Variation of the signal insertion loss (a) (dB/mm) and (b) calculated dB per wavelength as a function of frequency in the range up to 110 GHz. Comparison is made using equation 1 and the measured losses from the longest CPW (25 mm) for CPWs of length 20 mm (black —), 15 mm (blue □), 10 mm (red ●) and 5 mm (green ○) as indicated on the graph.

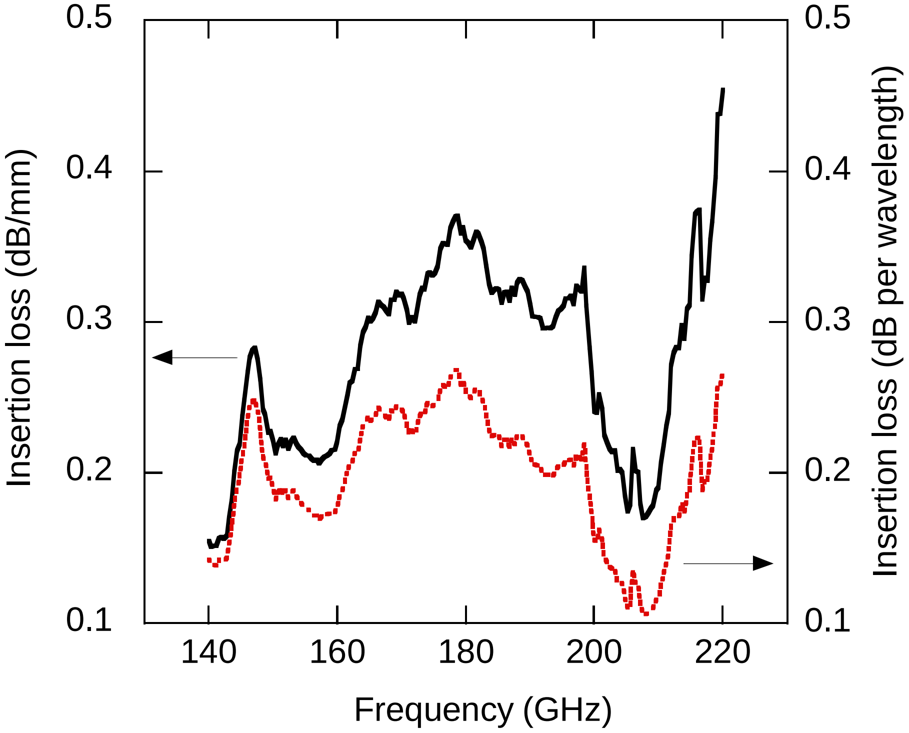

Figure 3 (Color online) Variation of the signal insertion loss (dB/mm) (—) and calculated dB per wavelength (---) as a function of frequency in the range of 140 – 220 GHz. The average loss per mm is 0.28 dB with a standard deviation of 0.06 dB. The average loss per wavelength is 0.20 dB with a standard deviation of 0.05 dB.

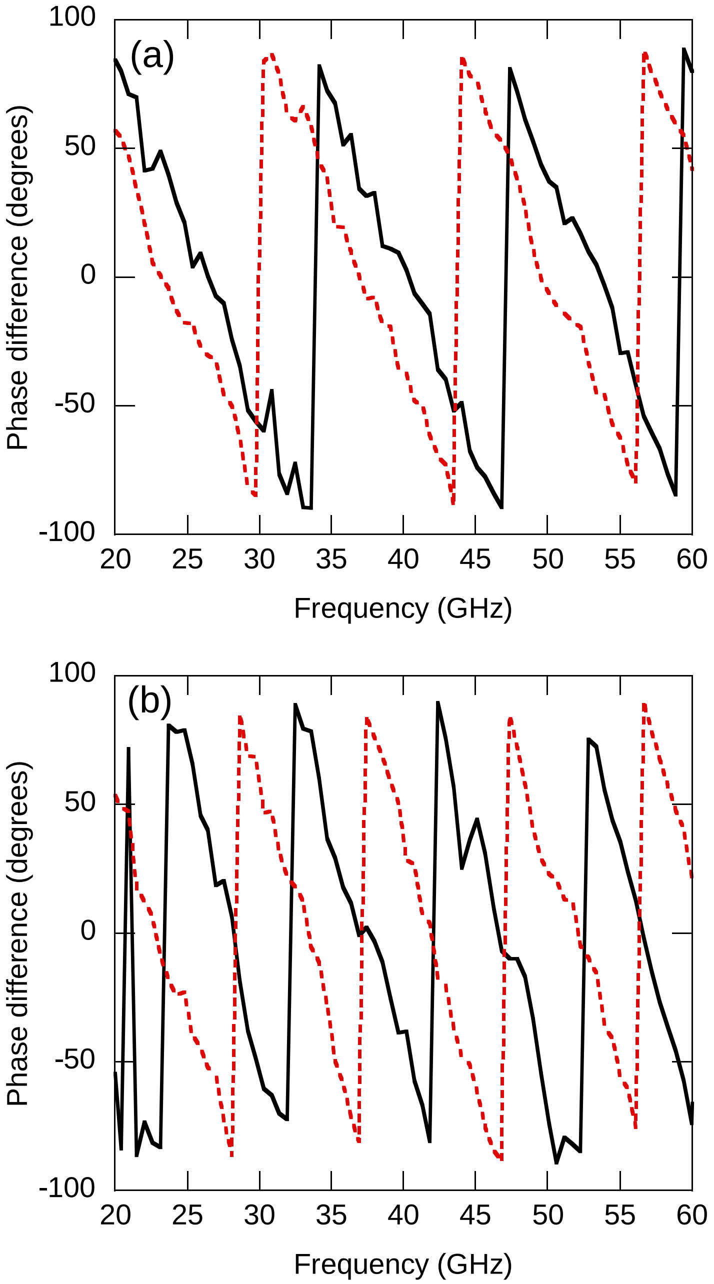

Figure S1 (Color online) Measured phase from the CNT composite CPW (dashed ---) and an Ag reference CPW (solid —) both of (a) 5 mm length and (b) 25 mm length.