# Metamaterial high pass filter based on periodic wire arrays of multiwalled carbon nanotubes

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(Received 5 June 2010; accepted 1 September 2010; published online 18 October 2010)

In this manuscript, we demonstrate metamaterials based on two-dimensional high density arrays of metallic multiwalled carbon nanotubes. They demonstrate a cutoff response toward electromagnetic waves and can be utilized for filtering applications. The plasma frequency, where the metamaterial displayed a sharp change in the reflection and transmission, depends on the geometry of their two-dimensional cubic lattice. A plasma frequency in the near infrared region of 1.5 μm was calculated numerically, for an array consisting of multiwalled nanotubes, having radius of 50 nm and lattice constant of 400 nm. Reflection experiments conducted on the nanoscale structures were in excellent agreement with numerical calculations. 
[doi:10.1063/1.3491840]

To obtain material properties not existing in nature, artificial materials such as metamaterials are used. These are composed of subwavelength structures fashioned together to exhibit the required values of permittivity and permeability in the desired frequency range. Metamaterials propose myriad interesting applications such as filtering in the terahertz range achieved by using two-dimensional (2D) periodic arrays of metallic cylinders.[1] It has been reported that periodic arrays of thin metal wire structures act as metamaterials and display a cutoff filtering response in the frequency domains depending on the array geometry.[2,3] These structures demonstrate plasma frequencies which are much lower than in the metal structures and can be utilized for filtering in microwave and terahertz frequency domains.[4] The objective of this letter is to present such plasmonic filters which operate in the optical regime. Such metamaterials are realized by using 2D periodic arrays of multiwalled carbon nanotubes (MWCNTs), as metallic nanowire structures.

Carbon nanotubes first discovered by Iijima in 1991 (Ref. 5) are very promising materials and have been the focus of enormous research. Two main types of carbon nanotube exist in stable states, single walled carbon nanotubes (SWCNTs) and MWCNTs.[6] SWCNTs are structurally similar to a single graphite sheet wrapped into a cylindrical tube and MWCNTs comprise an array of such tubes concentrically nested like the rings of a tree trunk. SWCNTs can be either metallic or semiconducting, depending on the direction about which the graphite sheet is rolled to form a nanotube cylinder. MWCNTs on the other hand are mostly metallic and are able to carry high current densities. 2D periodic arrays of vertically aligned MWCNTs can be grown at precisely determined locations by the process of plasma-enhanced chemical vapor deposition (PECVD).[7]

The optical properties of individual MWCNTs are defined by their dielectric function, which is anisotropic in nature[8] and matches very closely with that of bulk graphite.[9] However, the highly dense periodic arrays of MWCNTs display an artificial dielectric function, with a lower effective plasma frequency of order several hundred terahertz. Pendry *et al.*[1] demonstrated that the electromagnetic response of a metallic array composed of thin metallic wires, excited by an electric field parallel to the wires [transverse magnetic (TM) mode] is similar to that of a low-density plasma of very heavy charged particles, with a reduced plasma frequency $\omega_p$ providing a red-shifted plasmon wavelength:

$$\lambda_p = a\sqrt{2\pi \ln(a/r)}, \qquad (1)$$

where $a$ is the lattice constant of the 2D wire array, and $r$ is the radius of the wires. This concept can be used for lowering the plasma frequency in nanotube based applications and achieving negative dielectric constants for metamaterials. The lowering of the plasma frequency is due to the increase in the effective electronic mass within the nanotubes due to the induced current and corresponding magnetic field around them. According to Eq. (1), the effective plasma frequency strongly depends on the nanotube bundle radius and lattice constant. Their values can discretely be chosen to engineer MWCNT arrays of a desired plasma frequency. The resultant frequency dependent permittivity can be calculated using the Drude model for metals described as

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}. \qquad (2)$$

The effective permittivity $\varepsilon(\omega)$ is negative for frequencies less than $\omega_p$, therefore no wave propagation will take place inside the metamaterial. Electromagnetic waves propagation only occurs above $\omega_p$, due to which the structure acts as a nanophotonic high-pass filter. Here the structure was realized with square lattice array of MWCNTs having radius of 50 nm and lattice constant of 400 nm. The growth of high $a/r$ aspect ratio arrays of MWCNTs was a significantly difficult task overcome through e-beam lithography and an optimized growth recipe.

Theoretical calculations of the plasma frequency and reflection coefficient of such a nanoscale brushlike array were conducted. For a square lattice of nanotube radius 50 nm and lattice constant 400 nm, the plasma frequency $f_p = \omega_p/2\pi$ of

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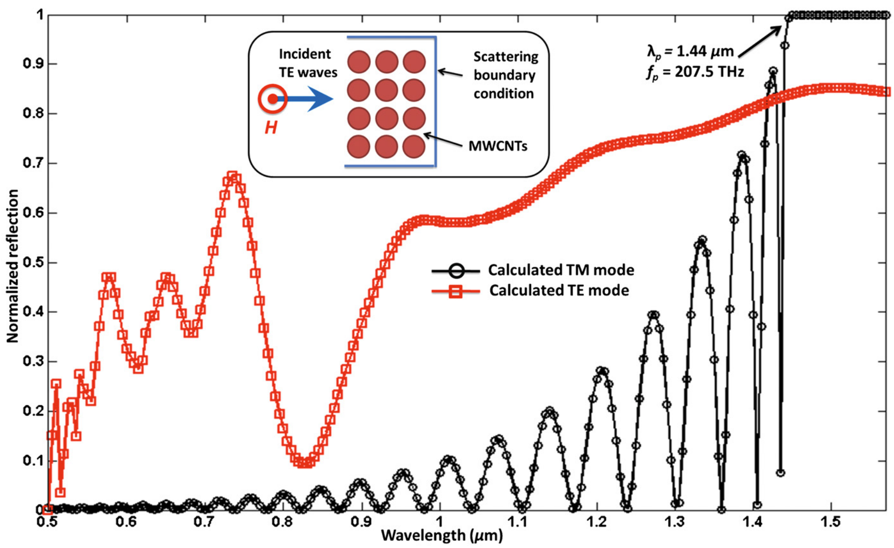


FIG. 1. (Color online) The calculated TM and TE reflection spectra for MWCNT based high pass filter. In TM-mode the incident light is polarized parallel to the wire structures and at the plasma frequency $f_p$ of 207.5 THz ($\lambda_p$=1.44 $\mu$m) a sharp drop in reflectivity is calculated. The inset shows the boundary conditions of the FEM model simulated to calculate the TE reflection spectrum.

207.5 THz with corresponding plasma wavelength of $\lambda_p$ =1.44 $\mu$m were calculated using Eq. (1). The value of the frequency dependent permittivity for the structure was calculated from Eq. (2). From Ref. 2, the reflection coefficient at normal incidence for such metamaterial can be calculated using Fresnel equations as

$$R=\left(\frac{Y^2[1-\exp(-2ik_1d)]}{1-Y^2\exp(-2ik_1d)}\right)^2, \tag{3}$$

where $Y=(Z_0-Z_1)/(Z_0+Z_1)$, with layer impedance $Z_i=\sqrt{\mu_0/\varepsilon_0\varepsilon_i}$ and $\varepsilon_0$ the permittivity in air. The frequency dependent permittivity and wave vector in the metamaterial are described by $\varepsilon_1=\varepsilon(\omega)$ and $k_1=\omega\times\sqrt{\varepsilon(\omega)}/c$, respectively. While the thickness of the metamaterial was of order 1 mm for our sample, diffraction out of the CNT layer restricts the propagation length to the confocal parameter of order $d$ =6 $\mu$m. The frequency dependent reflection coefficient was calculated as shown in Fig. 1. A sharp drop in the TM reflection is calculated at the plasma frequency, with high transmission of electromagnetic waves of larger frequencies. The small peaks in the plot arise from multiple reflections at the metamaterial interfaces.

Furthermore, the reflection spectrum of the metamaterial for the light polarized perpendicular to the nanotubes [labeled here as the transverse electric (TE) mode] was studied using finite element method (FEM) simulation. A 2D lattice of MWCNTs was modeled as thin rods of infinite length in air, with incident polarized across their diameters. The lattice consisted of eight rows of 15 MWCNTs with radius of 50 nm and lattice constant of 400 nm. The modeled geometry and calculated spectra for TE polarization is also shown in Fig. 1. Unlike the TM mode no cutoff filtering effect was observed and the results are in good agreement with the measured experimental spectra for TE polarization. A dip was observed near 800 nm corresponding to the transmission band of metallic wire arrays,[10] associated with Bragg diffraction.

To achieve this metamaterial high pass filter in the optical domain, metallic cylinders of nanoscale dimensions and interspacing are required. MWCNTs are promising materials to establish such metamaterials structures and the advancement in nanotechnology facilitates the fabrication of high $a/r$ aspect ratio nanotube arrays. Square lattice arrays of vertically aligned MWCNTs were grown on silicon substrates. Each nanotube array was grown directly on a silicon wafer by PECVD after employing e-beam lithography to pattern a 5 nm thick nickel catalyst layer into an array, with each dot being 100 nm in diameter. This allowed the growth of a single MWCNT of 50 nm radius on each dot. The substrate was heated by dc current under vacuum of $10^{-2}$ mbar to 650 °C at a ramping rate of 100 °C per minute. This mild heating process is preferred to protect the catalyst dots from cracking. Ammonia gas was then introduced to etch the surface of the nickel catalyst islands. Acetylene was chosen to be the carbon source, and was imported into the deposition chamber after the temperature reached 690 °C, followed by a dc voltage of 640 V between the gas shower head and the heating stage to create plasma of 40 W in power. The growth process lasted for 10–15 min at 725 °C, which gives MWCNTs of nearly 1–2 $\mu$m in height. An array of individual nanotubes is shown in the electron microscopy image of Fig. 2(a) and with a higher magnification view in Fig. 2(b).

Due to the small lattice constant the nanotubes were tangled at various regions of the substrate. Additionally, some array defects were produced due to inhomogeneous depth of the nickel catalyst layer, affecting the decomposition of the carbon source, and hence, producing shorter MWCNTs. However, a steady periodicity required for a 2D square lattice was common throughout. Achieving longer MWNCTs also remains a difficult task. Beyond heights of

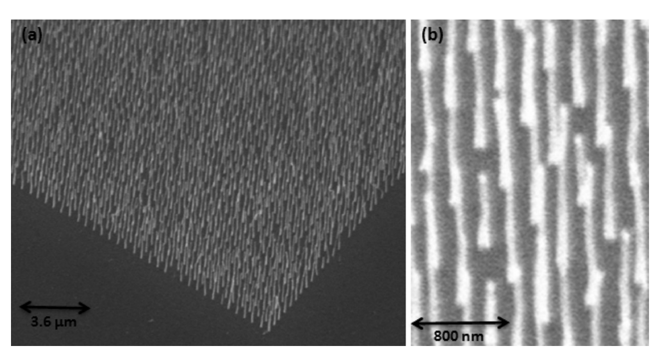


FIG. 2. (a) Electron microscopy image of a 2D square lattice array of MWCNTs having radius of 50 nm and lattice constant of 400 nm, grown on silicon substrate using PECVD. (b) The same in higher resolution.

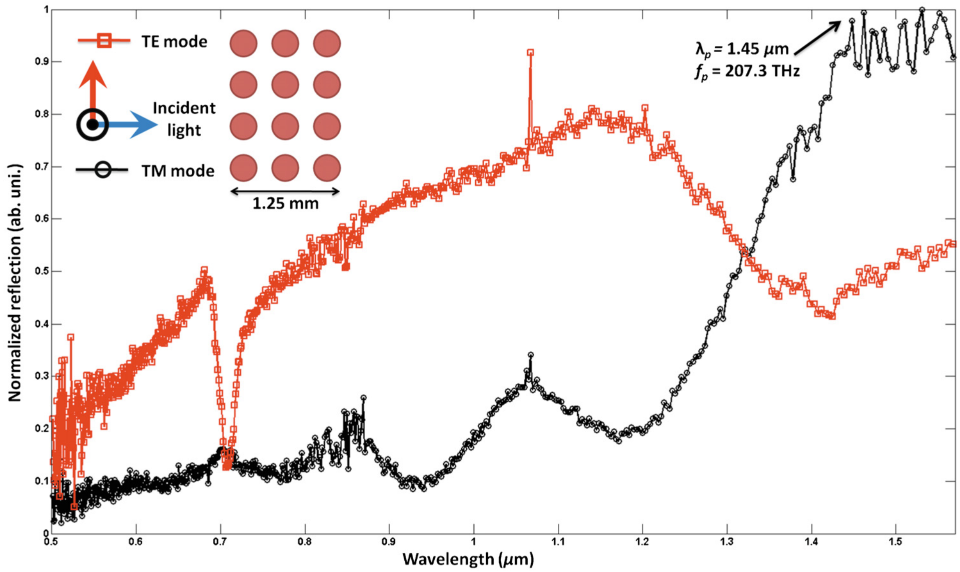


FIG. 3. (Color online) The reflection measurement from the sample for light polarized parallel (TM) and perpendicular (TE) to the MWCNTs. A sharp drop in the reflected TE-mode is observed at plasma frequency ($\lambda_p$=1.45 μm) which matches well the theoretical result. No such cutoff effect is observed for the TE-mode.

4 μm the nanotubes become fairly thin leading to their tips collapsing onto the neighboring tubes. Growth of longer tubes will require further optimization of the plasma generation technique and stronger electric fields for the vertical alignment of the tubes. According to metamaterial theory[1] it is crucial that the wire structures are thin and their height longer than the operating wavelengths. Without the effect of thin wires the plasmon wavelength $\lambda_p$ is of the same order as the lattice constant producing diffraction effects. Using thin wires increases the plasma wavelength and reduces the diffraction effects. Therefore, a MWCNT radius of 50 nm and height of 2 μm was sufficient for this study as it established an aspect ratio (height to radius) of 40. The radius was thus considerably smaller than the plasma wavelength $\lambda_p$=1.44 μm of the metamaterial.

The CNT sample was characterized using a goniometer setup to obtain the reflection spectra. A white-light laser based on holey-fiber continuum generation was utilized for illumination,[11] with light well collimated and having an optical spectrum from 480 nm up to 2 μm. The polarization of the white-light laser beam could be selected before the beam was guided onto the sample. The sample size of 1.25 mm was significant for these experiments and much larger than the incident beam's spot size. An Ocean Optics USB2000 spectrometer was utilized to capture the reflected signal for the spectral range of almost 450–1600 nm, with resolution 0.2 nm.

The measured reflection spectrum at 60° incidence angle for light polarized parallel (TM) and perpendicular (TE) to the nanotubes is shown in Fig. 3. It shows a rapid change in reflection at the frequency of 207 THz ($\lambda$=1.45 μm) and closely matches the calculated plasma frequency of the sample. Additionally small peaks were observed which can be explained by the defects in the periodic array of MWCNTs. The spectrum with light polarized perpendicular (TE) to the nanotubes did not show any significant cutoff effect, showing that most of the light was not reflected. However, a rapid drop in reflection at $f_p$ for parallel polarized light shows that the periodic array of MWCNTs acts as high pass filter for near optical frequencies. The plasma frequency for the metamaterial can be further increased into the optical regime by increasing the material density of the sample, i.e., by increasing the radius of the tubes and decreasing the lattice constant as presented in Eq. (1). Growth of well aligned MWCNTs at interspacing of less than 500 nm can be achieved by optimizing the catalyst layer and growth time in the PECVD process.[12]

In conclusion, we have demonstrated a near optical high pass filter, based on 2D square lattice array of MWCNTs. Arrays of nanotubes act as metamaterials displaying reduced plasma cutoff frequency of about 207 THz. A rapid drop in reflection spectrum was calculated at the plasma frequency. The measured filtering response is in good agreement with theory of these materials. Their property can be utilized for optical wave filtering in the nanoscale applications. The plasma frequency of the structure can be modified by varying the geometrical parameters. Plasmonic characteristics of nanotubes arrays also have great potential in nanoscale optical wave guiding and photonics crystals.

This work was supported by EPSRC EP/G060649/1. Haider Butt specially thanks Professor Gehan Amaratunga for his research grant toward this work.

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