A bottom-up engineered broadband optical nanoabsorber for radiometry and energy harnessing applications*

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***Abstract*—Optical absorbers based on vertically aligned multi-walled carbon nanotubes (MWCNTs), synthesized using electric-field assisted growth, are described here that show an ultra-low reflectance, 100X lower compared to Au-black from wavelength λ ~ 350 nm – 2.5 µm. A bi-metallic Co/Ti layer was shown to catalyze a high site density of MWCNTs on metallic substrates and the optical properties of the absorbers were engineered by controlling the bottom-up synthesis conditions using dc plasma-enhanced chemical vapor deposition (PECVD). Reflectance measurements on the MWCNT absorbers after heating them in air to 400ºC showed negligible changes in reflectance which was still low, ~0.022 % at λ ~ 2 µm. In contrast, the percolated structure of the reference Au-black samples collapsed completely after heating, causing the optical response to degrade at temperatures as low as 200ºC. The high optical absorption efficiency of the MWCNT absorbers, synthesized on metallic substrates, over a broad spectral range, coupled with their thermal ruggedness, suggests they have promise in solar energy harnessing applications, as well as thermal detectors for radiometry.**

I. Introduction

The ability of nanomaterials to trap light effectively has important implications for their use in energy harnessing, optical blacks for radiometry, as well as detectors. A survey of a host of nanomaterials, such as CdSe nanocrystals [1], graphene [2], graphene quantum dots [3], direct band gap one-dimensional (1D) Si nanowires (NWs) [4], and TiO_2 nanoparticles [5], reveals the promise such materials have in a wide range of optical applications. Nanomaterials are also actively being utilized for enhancing the optical absorption efficiency for energy harnessing applications or infrared (IR) detectors. For example, surface plasmon modes in 50-100 nm diameter spherical, metallic nanoparticles on amorphous Si, scatter light more effectively by coupling to incident electro-magnetic radiation, increasing the optical conversion efficiency of solar cells [6]. In this paper, we report on another type of nanomaterial which is exceptional at trapping incoming light as a result of its unique physical structure, a structure comprised of porous arrays of thin (10-15 nm diameter) vertically oriented multi-walled carbon nanotubes (MWCNTs). By virtue of the photo-thermal transduction mechanism, such CNT absorbers have promise in energy harnessing, high sensitivity thermal detectors, and in serving as a reference for quantifying absolute optical power in optoelectronics. Other potential applications include their use in radiative cooling, thermography, antireflection coatings, and optical baffles to reduce scattering.

Unlike earlier reports where the CNTs were synthesized directly on Si or SiO_2 [7,8], here we demonstrate high-efficiency MWCNT absorbers synthesized directly on metallic substrates. The ability to synthesize CNT ensembles that exhibit ultra-low reflectance on reflective metallic substrates is potentially useful for solar photo-thermal energy conversion applications within the λ ~ 300 nm – 2.5 µm spectral window. Typical solar selective coatings use cermets as the absorber of solar energy, which exhibit a reflectance that is 4-orders of magnitude higher[9] than those reported here. Furthermore, for these and other applications, absorbers which are thermally resilient are also highly desirable. We show here that the MWCNT absorbers exhibit a negligible change in optical absorption properties when exposed to temperatures as high as 400ºC in air, unlike the Au-black samples where degradation in performance occurred at temperatures as low as 200ºC.

In this paper, we present the techniques used to synthesize high-density arrays of CNTs using a plasma process, as described in Section II. Then in Section III, the optical characterization results are discussed which includes measurements that demonstrate the remarkable ruggedness of the CNT absorbers at high temperatures.

II. Synthesis

A. Choice of Substrate

The starting substrate for the synthesis of our MWCNTs was a <100> Si wafer on which a layer of 100 – 200 nm thick NbTiN was deposited reactively in a N_2 and Ar ambient using dc magnetron sputtering at a power of ~ 220 W and 5 mTorr. Bi-metallic layers of Co (thickness range 0.6 nm - 6 nm) and 2.5 nm thick Ti were e-beam evaporated and served as the catalyst. Beside the Co/Ti/NbTiN/Si templates, control samples of Co/Ti/Si, Co/NbTiN/Si and Co/Si were also prepared. Multiple samples (area ~ 4 cm^2) were placed on a carrier wafer during PECVD growth so that a comparative analysis could be performed for different combinations of starting templates at the same synthesis conditions. At the desired temperature, which ranged from 550 - 750ºC, H_2 was flowed into the chamber for several minutes, and the growth gases acetylene (C_2H_2) and ammonia (NH_3) were then introduced. The discharge was ignited for a fixed duration,

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and depending on the growth conditions, the growth rate ranged from 500 nm - 1 μm/min.

The choice of the starting template for the PECVD synthesis of our MWCNTs was vital in synthesizing CNTs with a high areal or site density, which impacts the optical absorption characteristics of the samples. For example, the SEM image in Fig. 1a shows amorphous carbon deposits when Co/Ti was placed directly on Si at 750ºC; the optical image on the right of Fig. 1a shows a largely reflective surface. On the other hand, the bi-metallic Co/Ti/NbTiN sample appeared visually black (inset of Fig. 1b). Inspection of this sample in the scanning-electron-microscope (SEM) revealed a high areal density of CNTs (Fig. 1b), suggesting that under identical synthesis conditions, the bi-metallic Co/Ti catalyst on the NbTiN is favorable for synthesizing MWCNTs which trap incoming light and suppress reflection, causing the sample to appear visually black. The lack of growth of MWCNTs on Co/Ti/Si templates (Fig. 1a) suggests that the presence of a refractory metallic nitride, such as NbTiN, is important in preventing diffusion and alloying of the catalyst with the underlying Si at the high temperatures. In addition, the density of MWCNTs in the absence of the Ti layer on the Co/NbTiN templates was low, which points to the importance of Ti in the Co-Ti bi-metallic catalyst system.

(a)

(b)

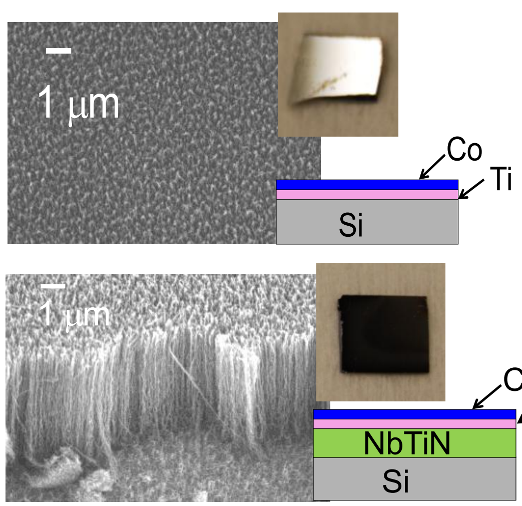

Figure 1. a) SEM micrograph of a Co/Ti/Si sample (bottom right inset) after dc PECVD growth. Top right inset shows an optical image of the sample depicting a reflective surface. (b) SEM micrograph of a Co/Ti/NbTiN sample (bottom right inset) after growth, depicting a high areal density of MWCNTs. Top right inset shows an optical image of the sample depicting a visually black sample. The spatial uniformity of the MWCNT ensembles is high over large length scales. Growth conditions were: 750ºC, 170 W of plasma power, 30 % C_2H_2, 5 Torr; Co/Ti thickness in (a) and (b) was 0.9 nm/2.5 nm. SEMs taken at 30º viewing angle.

With other catalysts such as Ni,[10] PECVD is also well-known to yield carbon nanofibers. In general, while achieving a high yield of CNTs on metallic substrates has been more challenging with thermal CVD, a high site density of MWCNTs is achieved here with PECVD and engineering the catalyst appropriately using the Co-Ti catalyst system. Besides being of interest as absorbers in solar photo-thermal applications, the high areal density of MWCNTs on reflective metallic substrates with resistivity ρ ~ 110 μΩ-cm, could be beneficial in other electronic applications, since contact resistance is potentially lower compared to CNTs grown directly on high ρ Si substrates. The high magnification image in Fig. 1c shows the surface of the MWCNTs arrays is rough and not continuous, a factor which also contributes to scattering the incoming light diffusively.

B. Catalyst Engineering

Through our experiments, we have also noted the importance of optimizing the catalyst thickness for maximizing the optical response. A detailed analysis of the impact of catalyst thickness on the optical reflectance properties of the MWCNT absorbers was conducted for a wide range of catalyst thicknesses (Fig. 2). This data (at λ ~ 1.5 μm) shows that the minimum reflectance decreases as the thickness of the catalyst decreases. However, the reflectance increases when ultra-thin catalysts ~ 0.6 nm are used due to the inability to nucleate a high enough areal density of MWCNTs. This behavior was consistent for two different acetylene gas concentrations, as shown. The ability to engineer optical absorption efficiency by controlling the bottom-up synthesis conditions of our MWCNT arrays, such as catalyst thickness, is an attractive feature in tuning the optical absorption properties of the MWCNT absorbers.

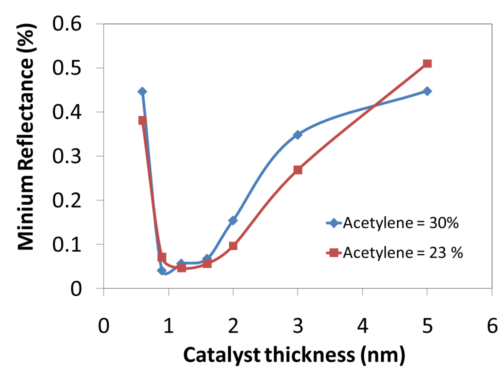

Figure 2. The reflectance measurement as a function of the catalyst thickness (taken at λ ~ 1.5 μm) for two acetylene gas ratios (30 % and 23 %). The increase in reflectance with the ultra-thin catalyst thickness of ~0.6 nm is due to the inability to synthesize a high yield of the CNTs. Growth conditions were: 750ºC, 170 W of plasma power, 5 Torr, 12 min. growth time.

III. OPTICAL PROPERTIES

A. Broad-band Optical Response from UV to SWIR

The optical measurements on the samples were conducted from λ ~ 350 nm to 2500 nm using a high resolution, fiber coupled, spectroradiometer (ASD inc, Fieldspec Pro) where a standard halogen light beam was aimed at normal incidence to the sample, as shown by the inset of Fig. 3. The bare fiber connector of the spectroradiometer was oriented at ~ 40º from the normal. Relative reflectance spectra were obtained by first white referencing the spectroradiometer to a 99 % reflective spectralon panel. The reflected light intensity from the sample under test was then measured and the spectra were compared for samples synthesized at different growth conditions. The optical reflectance response for the CNT absorber film is shown in Fig. 3, where the spectra are also compared to a standard optical black, Au-black absorber sample, which was synthesized using approaches similar to prior reports.[11] The SEM micrograph in the inset of Fig. 2 reveals the percolated structure comprising of random networks in the porous Au-black sample, quite unlike the highly aligned MWCNTs in our absorber arrays (Fig. 1b). The reflectance of the CNT absorber is nearly 100 X lower than that of the Au-black absorber sample, ~ 0.02 % at λ ~ 2 μm, compared to 1.1 % for Au-black. Other families of absorbers, such as NiP with micro-scale surface asperities, have higher reflectance ~ 0.5 – 1 % for λ ~ 320 – 2140 nm,[12] while ultra-black NiP alloy has a reflectance ~ 0.16 - 0.18 % from λ ~ 488 – 1500 nm;[13] black paint has a reflectance > 2.5 % from λ ~ 600 – 1600 nm. A mechanism by which porous objects suppress reflection *R* is through a reduction in the effective refractive index *n* of the object, where according to Fresnel's law (for normally incident light), $R = \left(\frac{n - n_o}{n + n_o}\right)^2$, with $n_0(air) \sim 1$. It is clear from this that reflection will be minimized when $n \rightarrow n_0$, implying that porosity is a desirable feature for minimizing reflection, a characteristic that is also present in our largely porous Au-black absorber samples (SEM in the inset of Fig. 3). However, our data in Fig. 3 shows that the preferential vertical alignment in the porous MWCNT arrays appears to be more effective at trapping light. This could arise from the fact that the coupling of electrons in the vertically oriented CNTs to the incoming, normally-incident radiation is very weak, which minimizes back-scattering and enables light to propagate into the long pores within the arrays until it is finally absorbed.

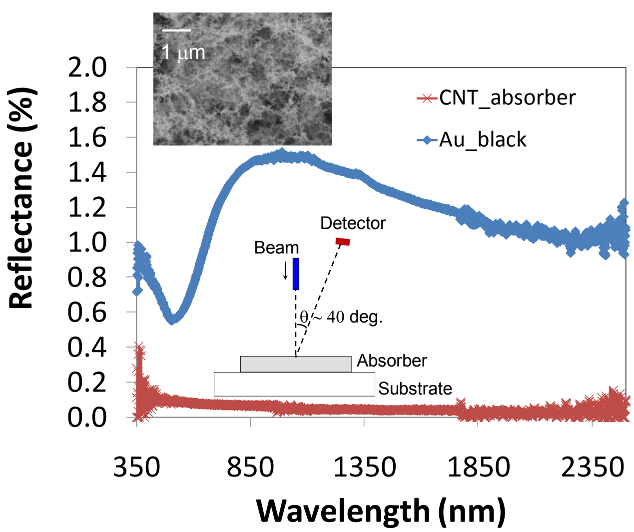

Figure 3. Reflectance measurement from λ ~ 350 nm - 2500 nm for the MWCNT absorber synthesized using dc PECVD and a Au-black absorber sample. An SEM micrograph of the Au-black absorber sample (taken at 30º viewing angle) is shown in the top inset which depicts a percolated, randomly aligned network of fibers, unlike the vertically aligned MWCNT arrays. The measurement set-up is illustrated in the bottom inset. The Au-black reference sample has a reflectance that is nearly ~100 X larger than our CNT absorbers, ~ 0.02 % at λ ~ 2 μm compared to 1.1 % for Au-black.

Our MWCNT absorbers also show a much lower reflectance compared to top-down synthesized Si nanotips that have a reflectance of ~ 0.09 % at λ ~ 1 μm [14]. Shown in Fig. 3a are reflectance spectra taken for two samples synthesized at Co catalyst thicknesses of ~ 5 nm and 0.9 nm. The sample with 0.9 nm thick Co has a wavelength independent response from λ ~ 350 nm - 2.5 μm with a reflectance in the 0.02 – 0.03 % range. The sample with the ~ 5 nm thick Co, synthesized at identical conditions, has a wavelength dependent reflectance which decreased from 0.94 % at λ ~ 400 nm to ~ 0.33 % at λ ~ 2.0 μm.

B. Thermal Ruggedness

Here we also present empirical data which demonstrates for the first time, the exceptionally low optical reflectance properties of the MWCNT absorber arrays after they were exposed to temperatures as high as 400ºC in air. The Au-black absorber samples, which served as our reference, are shown in the SEM images at 25ºC (Fig. 4a), and when they were heated to temperatures as high as 400ºC (Fig. 4b). At 400ºC, the percolated structure of the Au black sample fragments and collapses. At the same time, the structural characteristics of the MWCNT absorber samples are largely unchanged from 25ºC (Fig. 4c) and when they were heated to 400ºC (Fig. 4d) in air. From the corresponding optical spectra (Fig. 5) it is apparent that the reflectance of the Au-black absorber sample increases after it is heated from 25ºC to 200ºC (2 %) and reaches ~ 23 % at 400ºC (at λ ~ 2.0 μm). This dramatic change in optical properties appears consistent with the change in morphology seen in the Au-black absorber sample with increasing temperature (Fig. 6a – (b)). On the other hand, the spectral reflectance of the CNT absorbers is still very low, exhibiting a slight increase to ~ 0.022% after heating to 200ºC (inset of Fig. 7), and remains remarkably unchanged after exposure to temperatures as high as 400ºC; this can be correlated to the structural integrity of the CNT absorbers from 25ºC (Fig. 4c and (d)) to 400ºC. These tests on the MWCNT absorbers suggest they have exceptional promise to serve as an efficient and rugged absorber, potentially for solar photo-thermal applications as well as with thermal detectors for radiometry.

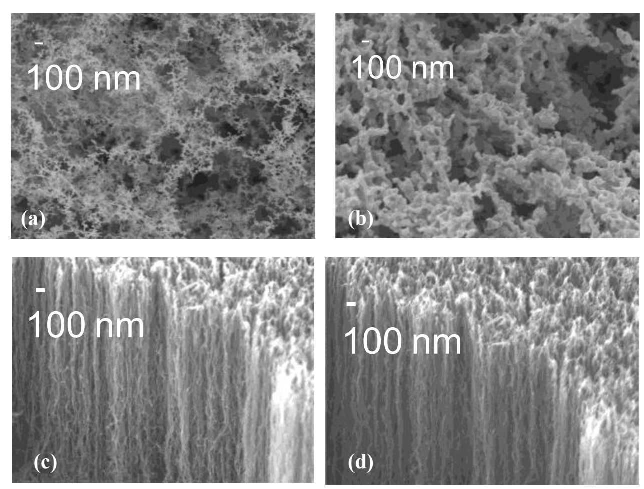

Figure 4. SEM images in (a) – (d) correspond to thermal tests conducted on Au-black absorber samples and CNT absorber samples. The Au-black absorber sample at a) 25ºC and after heating to b) 400ºC for 1 hour in air. The CNT absorber sample at c) 25ºC and after heating to d) 400ºC. The MWCNT absorbers have a high structural integrity since no change in morphology is detected after heating to 400ºC in air in an oxidizing environment. All SEMs taken at 30º viewing angle.

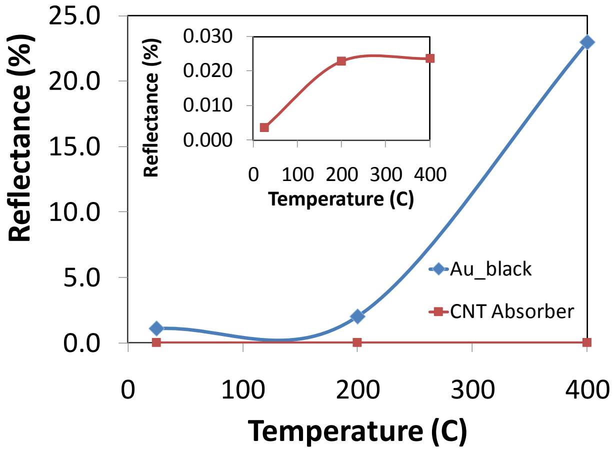

Figure 5. Optical reflectance measurements were made in the λ ~ 350 nm – 2500 nm range for the Au-black and CNT absorber samples at 25ºC and after subjecting them to temperatures up to 400ºC. Shown is the reflectance of the Au-black and CNT absorber samples as a function of temperature. The Au-black absorber shows a reflectance up to 23% after heating to 400ºC. The inset shows the reflectance of the CNT sample increases slightly after exposure to 200ºC but it is still very low, ~ 0.022% at λ ~ 2 μm and remains unchanged after exposure to temperatures as high as ~ 400ºC.

IV. CONCLUSION

In conclusion, we have successfully shown that dc PECVD synthesized MWCNTs on metallic substrates exhibit ultra-low reflectance properties over a wide spectral range from UV-to-IR for relatively thin (< 10 μm) absorber ensembles. The structural characteristics of the MWCNT absorbers was engineered by controlling the bottom-up synthesis parameters during PECVD, such as catalyst thickness, pressure and plasma power which enabled optimization of the optical properties of the absorbers. The structural characteristics and optical reflectance of the CNT absorbers remained remarkably unchanged up to 400ºC. The ultra-low reflectance of the MWCNT absorbers synthesized on metallic substrates over a broad-spectral range coupled with their high temperature ruggedness suggests they have promise in solar photo-thermal applications and thermal detectors for radiometry applications.

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