CARBON letters

Note

Carbon Letters Vol. 18, 67-70 (2016)

Enhancement of reflectance of densified vertically aligned carbon nanotube forests

Masud Rana, MAsyraf MRazib, T. Saleh♠ and Asan G.A. Muthalif

Smart Structures, Systems and Control Research Laboratory (S3CRL), Department of Mechatronics Engineering, Faculty of Engineering, International Islamic University Malaysia, Kuala Lumpur 50728, Malaysia

Key words: carbon nanotubes forest, densification, polarization, reflectance

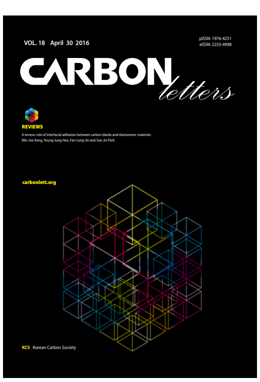
Article Info

Received 2 November 2015
Accepted 24 February 2016

***Corresponding Author**
E-mail: tanveers@iium.edu.my
Tel: +603-61965709

Open Access

DOI: http://dx.doi.org/10.5714/CL.2016.18.067



http://carbonlett.org

pISSN: 1976-4251
eISSN: 2233-4998

Vertically aligned carbon nanotubes (VACNTs), also known as a carbon nanotube (CNT) forest, are a porous material that is well known for its exceptional optical absorbance property. The reflectance from a VACNT forest has been reported to be as low as 0.045% [1,2]. It is known as the darkest material on Earth. Because of its remarkable material properties, it has various other applications as gas sensors [3], pressure sensors [4], temperature sensors [5], and strain sensors [6]. Recently, various efforts have been made to mechanically manipulate the vertical structure of the nanotubes in the CNT forest and to conduct their optical characterization [7,8]. Optical reflection from bare VACNTs has also been investigated at different wavelengths by Wąsik et al. [9]. Controlled densification by wetting of the CNT forest is another post processing technique that has been reported by other researchers [10]. A densification process is necessary to make the CNT forest useful as a future electronics interconnect [10]. However, no study has been done so far on the optical behavior of CNT forests densified by a wetting process. In this letter, for the first time, we investigate and explain the nature of the optical reflectance of densified VACNTs.

Fig. 1 illustrates how the CNT forest is able to absorb most incident light. It was reported elsewhere that VACNT arrays are highly porous [11]. As a result, when incident light enters the bare CNT forest, it goes through several internal reflection-absorption cycles *via* individual nanotubes and finally makes its way out of the CNT forest as shown in Fig. 1b. Hence, a very low amount of light bounces back (approximately 0.045%) [1,2].

Mathematically, a simple model can be developed to estimate the final amount of light coming out of a CNT forest after several internal reflections; this process is explained by eq (1):

$$\alpha = ar^{n} \tag{1}$$

where α is the total amount of reflected light coming out of the CNT forest, a is the total power of incident light, r is the optical reflectance of an individual nanotube, which has a value of ~15% [12], and n denotes the total number of reflections inside the void space of the VACNTs. The graphical presentation of model eq (1), above, can be visualized in Fig. 1b, which shows that the final reflection from the CNT forest drops drastically as the number of internal reflections increases.

In line with the above hypothesis, reflection from VACNTs is expected to be enhanced if the nanotubes of the CNT forest can be squeezed and densified so that incident light beams cannot penetrate into the forest due to the reduced porosity. To verify this, we carried out simple water assisted densification of VACNTs to reduce the porosity. Subsequently, the optical reflectance was investigated.

The vertically aligned CNT samples were synthesized using a typical chemical vapor deposition method on a highly doped silicon substrate (<100> n-type, resistivity 0.008–0.015 Ωcm). Then, as a catalyst, Al and Fe in thin layers of 10 and 2 nm, respectively, were deposited on the silicon substrate using an e-beam evaporator. After that, the production of VACNTs was carried out by balancing the flow of different gases such as ethylene (C_2H_4),

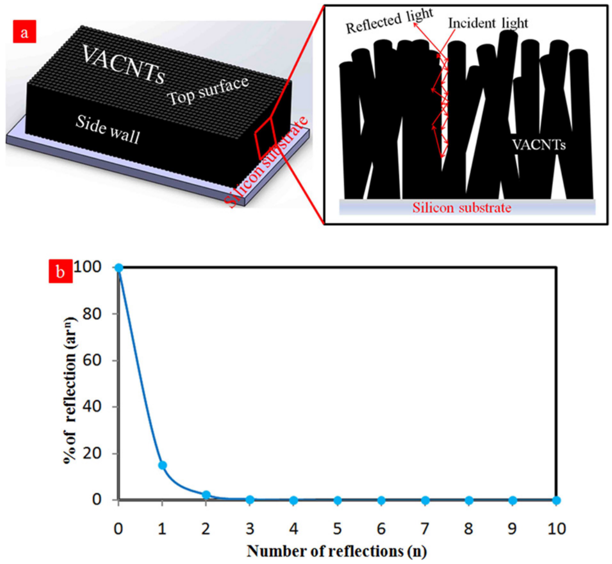


Fig. 1. (a) Multiple reflections of incident light inside void space of vertically aligned carbon nanotubes (VACNTs). (b) Variation of final output light from the carbon nanotube forest after several internal reflections, as described in Fig. 1a.

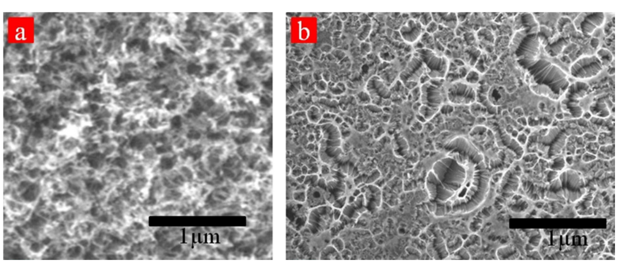


Fig. 2. Field emission scanning electron microscope images of top views of original (a) and densified (b) vertically aligned carbon nanotubes (scale bar, 1 μm).

hydrogen (H_2) and argon (Ar) with different ratios at various temperatures. Through this process, the vertically aligned CNTs grew to several 100s of μm in length, with diameters in a range of 10 to 50 nm. The detailed process of VACNT sample preparation has been demonstrated by Khalid et al. [13].

Vertically aligned CNTs are known as the darkest materials on earth due to their significant absorption of incident light, which results from their intrinsic porosity [11]. To minimize this porosity among adjacent VACNTs, we have attempted a simple method known as water assisted densification of VACNTs. To this effect, a bare VACNT forest (as grown and attached to the Si substrate) was sunk in water for 12 h. After that, it was dried at ambient temperature for 6 h. Wetting followed by evaporation is a proven technique for densifying a CNT forest [10]. Moreover, the field emission scanning electron microscope image (Fig. 2) shows the topography of the original CNT forest and the densified CNT forest. As water evaporates, the individual CNTs become closer due to capillary action [10], as can be seen in Fig. 2b.

To investigate the polarized reflectance from densified VACNTs, we used the experimental arrangement shown in Fig.

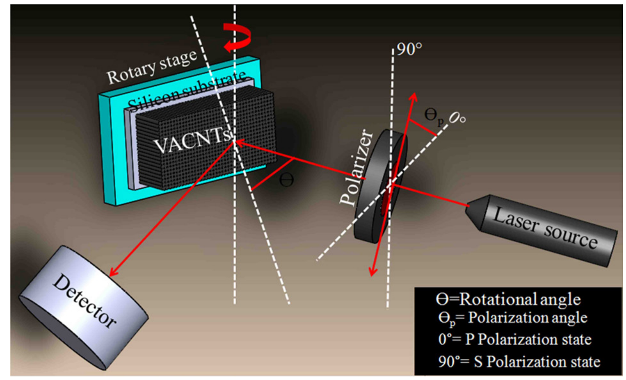


Fig. 3. Experimental arrangement to investigate polarized reflectance for original and densified vertically aligned carbon nanotubes (VACNTs).

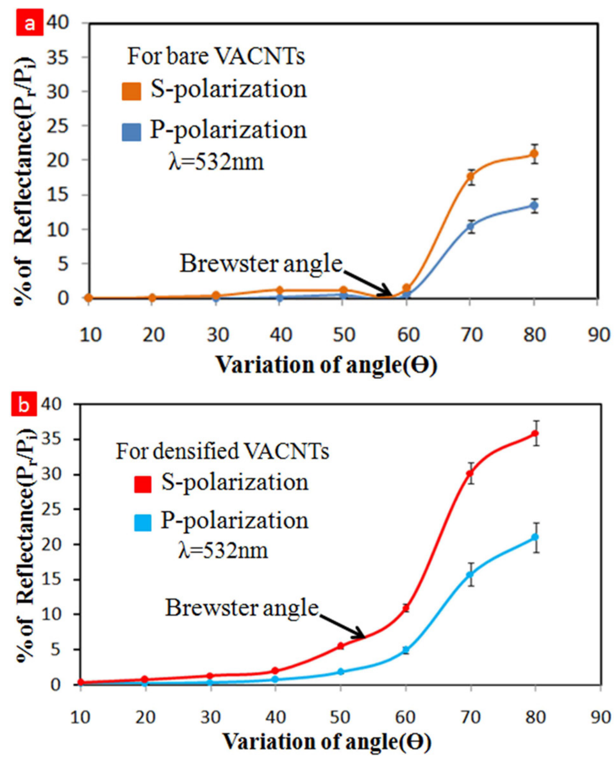


Fig. 4. Polarized reflectance of original vertically aligned carbon nanotubes (VACNTs) (a) and water densified VACNTS (b), respectively, at various incident angles (θ) for S- and P-polarized light.

3. In this case, we used a partially polarized laser source (having a visible wavelength of 532 nm) and a polarizer to change the state of polarization of the incident light by rotating directly from P ($\theta_i = 0°$) to S ($\theta_i = 90°$). The incident light was directed towards the sample (VACNTs) at the angle θ, which can be varied by rotating the sample (VACNTs), which is attached to a rotary stage. The reflection from the VACNTs was captured by a photo-detector at 10º intervals until θ = 80º. In this study, the incident optical power (P_i) was measured behind the polarizer and the power reflected (P_r) from the CNT forest was also measured. Then, reflectance was calculated using the ratio of P_r/P_i. Using a green laser light (λ = 532 nm), we studied the reflectance from

DOI: http://dx.doi.org/10.5714/CL.2016.18.067

both the bare CNT forest and the densified CNT forest for comparison.

Fig. 4 reveals the reflectance characteristics for both the densified (Fig. 4a) and bare VACNTs (Fig. 4b) only at the P- and S-polarization states for different angles of incidence. It can be seen that there is an increasing trend over the entire incident angle, although the S-polarized reflectance is always significantly higher than the P-polarized reflectance, which is consistent with the reflection characteristics (i.e., Fresnel reflection) for a smooth interface [14]. According to Fresnel's theory, the reflectance values of S- and P-polarized light will follow the relationship explained in eqs (2) and (3). The P-polarized light will reach a minimum value at a particular angle of incidence, which is known as the Brewster angle, due to the full transmittance of light through the sample. The Brewster angle is more prominent in the bare CNT forest than it is in the densified CNT forest, in which the Brewster angle is in the range of 58°.

$$R_S = \left|\frac{n_1 \cos\theta_i - n_2 \cos\theta_t}{n_1 \cos\theta_i + n_2 \cos\theta_t}\right|^2 = \left|\frac{n_1 \cos\theta_i - n_2\sqrt{1-\left(\frac{n_1}{n_2}\sin\theta_i\right)^2}}{n_1 \cos\theta_i + n_2\sqrt{1-\left(\frac{n_1}{n_2}\sin\theta_i\right)^2}}\right|^2 \tag{2}$$

$$R_p = \left|\frac{n_1 \cos\theta_t - n_2 \cos\theta_i}{n_1 \cos\theta_t + n_2 \cos\theta_i}\right|^2 = \left|\frac{n_1\sqrt{1-\left(\frac{n_1}{n_2}\sin\theta_i\right)^2} - n_2 \cos\theta_i}{n_1\sqrt{1-\left(\frac{n_1}{n_2}\sin\theta_i\right)^2} + n_2 \cos\theta_i}\right|^2 \tag{3}$$

R_s = reflection of S-polarized light
R_p = reflection of P-polarized light
n_1 = refractive index for first medium, air
n_2 = refractive index for second medium, densified CNT forest
θ_i= incident angle
θ_t = transmittance angle

The reflectance of P-polarized light for bare VACNTs varied from 0.03% to 13.53%; for S-polarized light, the variation was from 0.05% to 21% (as shown in Fig. 4a). These values of obtained reflectance are in a range similar to that found in a previous study [9] that investigated the specular reflectance of a bare CNT forest with a 514 nm laser source. Interestingly, when we used the densified CNT forest, the maximum reflectance increased to ~7.5% for P-polarized light and to ~14.5% for S-polarized light at an incident angle of 80°. Because the CNT forest is densified, individual nanotubes come closer and seal the opening of the top surface of the original VACNT, which retards the penetration ability of the incident laser beam into the CNT forest. Hence, the optical reflectance from the densified CNT forest is higher than that from the bare VACNTs.

In this letter, we have explained the underlying reason for the exceptional optical absorption characteristics of the CNT forest and also showed for the first time the optical characterization of densified VACNTs. It was observed that the densification process reduces the porosity of the bare CNT forest. Therefore, incident light was unable to penetrate into the forest and bounced back from the top surface. This eventually increases the reflectance of the densified VACNTs compared to that of the bare CNT forest by ~14.5% for S-polarized light and ~7.5% for P-polarized light. These findings could be useful in exploring the use of a densified CNT forest as an angle sensor because of the change of reflectance (for both S- and P-polarized light) with the rotational angle; this angle changes more for the densified CNT forest than it does for the bare CNT forest. Moreover, with the obtained understanding of the optical behavior of the densified CNT forest, we can now use this device as an on/off sensor to detect water vapor.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

This work was supported by research grants provided by Ministry of Higher Education, Malaysia (FRGS13-083-0324) and the Ministry of Science Technology and Innovation (SF14-008-0058). The authors would like to acknowledge Dr. Alireza Nojeh from the University of British Columbia for providing us with the CNT forest samples.

References

[1] Yang ZP, Ci L, Bur JA, Lin SY, Ajayan PM. Experimental observation of an extremely dark material made by a low-density nanotube array. Nano Lett, **8**, 446 (2008). http://dx.doi.org/10.1021/nl072369t.
[2] Hsieh KC, Tsai TY, Wan D, Chen HL, Tai NH. Iridescence of patterned carbon nanotube forests on flexible substrates: from darkest materials to colorful films. ACS Nano, **4**, 1327 (2010). http://dx.doi.org/10.1021/nn901910h.
[3] Modi A, Koratkar N, Lass E, Wei B, Ajayan PM. Miniaturized gas ionization sensors using carbon nanotubes. Nature, **424**, 171 (2003). http://dx.doi.org/10.1038/nature01777.
[4] Bsoul A, Ali MSM, Takahata K. Piezoresistive pressure sensor using vertically aligned carbon-nanotube forests. Electron Lett, **47**, 807 (2011). http://dx.doi.org/10.1049/el.2011.1498.
[5] Karimov KS, Chani MTS, Khalid FA. Carbon nanotubes film based temperature sensors. Physica E: Low Dimens Syst Nanostruct, **43**, 1701 (2011). http://dx.doi.org/10.1016/j.physe.2011.05.025.
[6] Kanoun O, Müller C, Benchirouf A, Sanli A, Dinh TN, Al-Hamry A, Bu L, Gerlach C, Bouhamed A. Flexible carbon nanotube films for high performance strain sensors. Sensors, **14**, 10042 (2014). http://dx.doi.org/10.3390/s140610042.
[7] Saleh T, Moghaddam MV, Ali MSM, Dahmardeh M, Foell CA, Nojeh A, Takahata K. Transforming carbon nanotube forest from darkest absorber to reflective mirror. Appl Phys Lett, **101**, 061913 (2012). http://dx.doi.org/10.1063/1.4744429.
[8] Mukherjee S, Misra A. Broadband wavelength-selective reflectance and selective polarization by a tip-bent vertically aligned multi-walled carbon nanotube forest. J Phys D: Appl Phys, **47**, 235501 (2014). http://dx.doi.org/10.1088/0022-3727/47/23/235501.
[9] Wąsik M, Judek J, Zdrojek M. Polarization-dependent optical reflection from vertically aligned multiwalled carbon nanotube arrays. Carbon, **64**, 550 (2013). http://dx.doi.org/10.1016/j.carbon.2013.07.068.

[10] Jiang D, Wang T, Chen S, Ye L, Liu J. Paper-mediated controlled densification and low temperature transfer of carbon nanotube forests for electronic interconnect application. Microelectron Eng, **103**, 177 (2013). http://dx.doi.org/10.1016/j.mee.2012.11.007.

[11] Puretzky AA, Geohegan DB, Jesse S, Ivanov IN, Eres G. In situ measurements and modeling of carbon nanotube array growth kinetics during chemical vapor deposition. Appl Phys A, **81**, 223 (2005). http://dx.doi.org/10.1007/s00339-005-3256-7.

[12] Zeng H, Jiao L, Xian X, Qin X, Liu Z, Cui X. Reflectance spectra of individual single-walled carbon nanotubes. Nanotechnology, **19**, 045708 (2008). http://dx.doi.org/10.1088/0957-4484/19/04/045708.

[13] Khalid W, Ali MSM, Dahmardeh M, Choi Y, Yaghoobi P, Nojeh A, Takahata K. High-aspect-ratio, free-form patterning of carbon nanotube forests using micro-electro-discharge machining. Diam Relat Mater, **19**, 1405 (2010). http://dx.doi.org/10.1016/j.diamond.2010.08.007.

[14] Wang XJ, Wang LP, Adewuyi OS, Cola BA, Zhang ZM. Highly specular carbon nanotube absorbers. Appl Phys Lett, **97**, 163116 (2010). http://dx.doi.org/10.1063/1.3502597.