



# Carbon multi-walled nanotubes grown by HWCVD on a pyroelectric detector <sup>☆</sup>

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## Abstract

Carbon multi-wall nanotubes (MWNTs) were grown on a lithium niobate (LiNbO<sub>3</sub>) pyroelectric detector with a nickel film as the catalyst by hot-wire chemical vapor deposition (HWCVD). Two detectors are documented, each with slightly different deposition conditions. The absolute spectral responsivity of each device was measured from 600 nm to 1800 nm and indicates that the MWNT-coating absorptance is spectrally uniform, with variations of only a few percent. We also discuss growth of MWNTs on LiTaO<sub>3</sub> by CVD and the limitations presented by the Curie temperature of the pyroelectric material.

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## 1. Introduction

There has been a great deal of research related to the development and understanding of carbon

nanotubes in their various forms. Practical applications for this material remain somewhat elusive and therefore justification of the pursuit of scientific understanding has been challenging for some researchers. We have recently demonstrated a pyroelectric detector with an absorber coating consisting of purified single-wall nanotubes (SWNTs) [1,2]. Carbon SWNTs and multi-wall nanotubes (MWNTs) may form the basis of the next generation of absorber coatings for thermal detectors for high accuracy optical and thermal

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radiometry, particularly for high-energy infrared (IR) and ultraviolet (UV) laser measurements. Thus we have a practical and immediate application of carbon nanotubes, with scientific and engineering challenges.

All of the primary measurement standards in the US and elsewhere for establishing traceability to fundamental units for radiometry are with few exceptions based on thermal detectors. These devices employ some form of thermal-absorber coating such as carbon-based paint or a diffuse metal such as gold black [3,4]. Carbon nanotube coatings present an alternative to the present technologies. The high thermal conductivity [5], damage resistance [6], and optical absorption efficiency indicated by our present measurements as well as those reported in the literature, along with the necessity of establishing and maintaining radiometric standards, is the basis of this work. To the best of our knowledge, this is the first report of an optical detector employing MWNTs as the thermal absorber.

The thermal coating based on carbon nanotubes is similar to other percolated structures in the sense that incident light is converted to heat and conducted to the substrate on which the coating is deposited. The carbon nanotubes may be any of the several forms: for example, SWNTs in bulk form [2] or MWNTs grown onto a substrate as we describe in this paper. The optical properties and absorption efficiency depends on the size, depth, distribution, and topology of the nanotubes. The preferred topology has been objectively analyzed by an effective medium approximation (EMA), which is based on percolation theory [7,8].

## 2. Coating

The MWNT-coated detectors were fabricated from lithium niobate ( $\text{LiNbO}_3$ ) crystals 250  $\mu\text{m}$  thick with nickel (Ni) electrodes 20 nm thick. The detectors were nominally identical with the exception of the coating variations. For comparison, a pyroelectric detector coated with a 2.6 Torr gold-black was fabricated [4].

The HWCVD was performed in a quartz tube reactor enclosed in a clamshell furnace. A single

0.5 mm diameter tungsten filament 23 cm in length was operated at  $\sim 20$  A, 25 V and at 1700  $^\circ\text{C}$  as determined by an optical pyrometer. Graphitic MWNTs with a modest amount of non-nanotube carbon impurities were produced in 1:5  $\text{CH}_4$ :Ar at 150 Torr with the furnace at 600  $^\circ\text{C}$ . This was repeated on a separate detector, but with a deposition pressure of 80 Torr. Similar growth conditions were employed for MWNT growth on nickel-coated quartz and crystalline silicon substrates. The various substrates were placed on a boron nitride sample holder at a distance of 5 mm from the filament. Transmission electron microscopy and Raman spectroscopy were employed to show that the MWNTs on the  $\text{LiNbO}_3$ , quartz, and silicon substrates were highly graphitic and that a modest amount of non-nanotube carbon was present [9]. The two detectors coated with MWNTs deposited by HWCVD are referred to as HW80 (for the 80 Torr HWCVD deposition) and HW150 (for the 150 Torr HWCVD deposition).

We also attempted to produce MWNTs on lithium tantalate ( $\text{LiTaO}_3$ ) by both HWCVD and CVD. These attempts failed in two ways. Our first samples fragmented, due presumably to strain from heating. Later samples, which remained intact and were packaged as a detector, failed to produce a measurable electrical signal. We estimate that the temperature of the furnace during the CVD process was 750  $^\circ\text{C}$ , which exceeds the Curie temperature of  $\text{LiTaO}_3$  (665  $^\circ\text{C}$ ) [10]. Therefore we suspect that the strict orientation of the  $z$ -axis spontaneous polarization (perpendicular to the detector electrodes) was destroyed during heating.  $\text{LiTaO}_3$  is our first choice of pyroelectric material because the pyroelectric coefficient of  $\text{LiTaO}_3$  (0.018  $\mu\text{C}/(\text{cm}^2\text{K})$ ) [11] is more than twice that of  $\text{LiNbO}_3$  (0.0083  $\mu\text{C}/(\text{cm}^2\text{K})$ ) [12]. It is possible that the orientation of the spontaneous polarization could be biased during heating with an externally applied electric field. Thus our future attempts may include applying an external electric field or modifying our processing parameters to accommodate a lower growth temperature (below the Curie temperature).

Our initial interest in carbon nanotubes as a thermal detector coating began with the simple observation that carbon nanotube coatings are

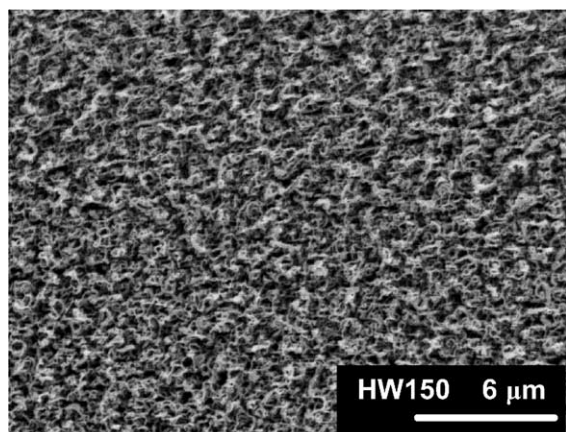


Fig. 1. STEM image of the MWNT coating deposited on the  $\text{LiNbO}_3$  pyroelectric detector designated as HW150.

visibly black. Upon further examination, by means of a scanning electron microscope (SEM), we observed that carbon nanotube coatings are topologically similar to other percolated structures that are efficient infrared absorbers [4,7]. In the present case, we imaged the HWCVD-deposited MWNTs by means of a field emission scanning tunneling electron microscope (STEM) operating at 2 keV, and a working distance of 5 mm with 1.5 s exposure. The image of the coating is shown in Fig. 1 and reveals that the MWNT size and coverage is uniform.

### 3. Experimental results

The measurement system for the spectral responsivity results was based on a lamp source, a grating monochromator, and a NIST transfer-standard detector [13]. The calibration procedure provided absolute spectral responsivity relative to a known NIST-calibrated transfer standard at 50 nm wavelength increments from 600 nm to 1800 nm. The NIST transfer standard was a pyroelectric wedge trap detector that was calibrated using the NIST C-series calorimeter [14]. The output beam from the monochromator (transmitted through air) was directed alternately onto the NIST standard detector and the test detector with a two-position mirror. The beam was focused to a beam size of approximately  $2 \text{ mm} \times 2 \text{ mm}$ , normal

to the plane of the detector surface, with a bandwidth of 6 nm or less. The relative response for each pyroelectric detector was measured by use of a lock-in detection scheme. The amplitude of the input beam from the monochromator was modulated at 15 Hz by means of a mechanical chopper. The detector signal was amplified in current mode at  $10^{-10} \text{ A/V}$  with a transimpedance amplifier. The absolute responsivities of the MWNT-coated detectors are shown in Fig. 2. The relative responsivities of the MWNT-coated detectors compared to a gold-black coated pyroelectric detector is shown in Fig. 3. The relative

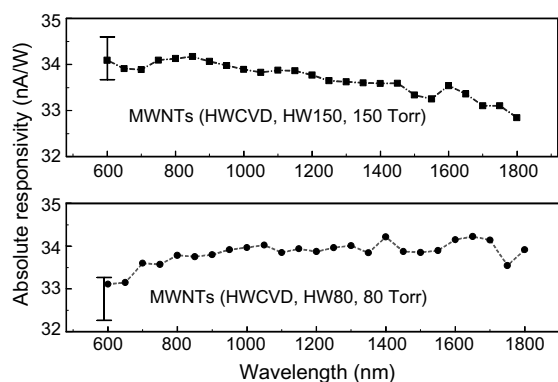


Fig. 2. Absolute spectral responsivities of two pyroelectric detectors with MWNT coatings. The error bar shown is representative for each data point with a relative expanded uncertainty of 1.24%.

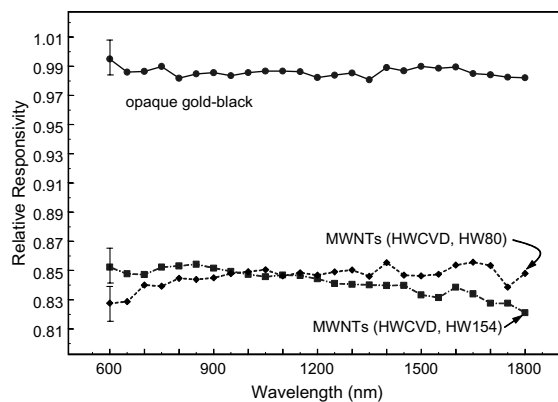


Fig. 3. Relative spectral responsivities of pyroelectric detectors with MWNT coatings compared to a similar detector with a gold black coating. The error bar shown is representative for each data point with a relative expanded uncertainty of 1.24%.

expanded uncertainty for the spectral responsivity measurement is 1.24%. The level of confidence for the relative expanded uncertainty is approximately 95%.

#### 4. Discussion

Variations of the spectral responsivity measurements are relatively small compared to our measurement uncertainty. Repeated measurements of the response as a function of wavelength indicate that the responsivity increase for detector HW80 and responsivity decrease for HW150 is slight (less than 3%) but definite. The absolute responsivity for each detector is approximately 33 nA/W at the chopping frequency of 15 Hz. The spectral responsivity measurements indicate that the MWNT coatings are spectrally uniform and have an absorption efficiency of approximately 85%. This was confirmed by comparing similar responsivity measurements for a 250  $\mu\text{m}$  thick, freestanding  $\text{LiNbO}_3$  pyroelectric detector with a gold-black coating having greater than 99% absorption efficiency [15]. The present results indicate that the MWNT coating is inferior to gold black in terms of absorption efficiency. We are nonetheless encouraged by this early result because the spectral responsivity of the MWNT-coated pyroelectric is reasonably uniform. We expect to improve the absorption efficiency as we gain a greater understanding of the process parameters of the HWCVD that will change the coating properties such as tube alignment and length. Furthermore, the promise of high damage resistance of the MWNT coating compared to gold black justifies further experiments to enhance the MWNT absorptivity.

In the past we demonstrated a pyroelectric detector coating of SWNTs with responsivity variations as large as 15% in the 1500 nm region [2]. The synthesis of the SWNTs was accomplished by use of a laser vaporization method similar to that of Guo et al. [16,17]. The purified SWNTs were dispersed in chloroform and applied with an airbrush and dried under a steady stream of nitrogen [2]. The airbrush technique for depositing SWNTs obtained by laser vaporization is arguably

simpler and does not require heating the detector substrate. However the spectral uniformity of the HWCVD-deposited MWNTs may justify the added risk. A summary of the spectral properties of a SWNT-coated pyroelectric detector and MWNTs grown on a pyroelectric detector, compared to a gold-black coated pyroelectric detector, is being published elsewhere [18].

#### 5. Conclusion

We presented experimental growth and characterization of carbon multi-wall nanotubes (MWNTs) directly on the detector material by the process of chemical vapor deposition (CVD) and hot wire CVD (HWCVD). Based on our measurements and imaging, we conclude that it is possible to grow MWNTs on a pyroelectric detector and that the coating will enhance the detector responsivity. We note however that the high temperature necessary for CVD is potentially damaging. Based on information by Berber et al. [5]. We believe that it is necessary to grow the MWNTs directly on the detector surface, as we describe here, if we are to achieve the highest thermal diffusivity and damage resistance. In the future, by varying growth conditions such as the catalyst metal, growth temperature and duration, we can vary the topology and therefore optimize the optical properties of the MWNT coating without compromising the detector properties and yet enhancing the spectral uniformity. We will continue to investigate both SWNTs and MWNTs as the next generation of thermal coatings for our thermal detectors for laser power and energy measurements.

#### References

- [1] J.H. Lehman, A.C. Dillon, C. Engtrakul, Carbon nanotubes based coatings for laser power and energy measurements using thermal detectors, Conference on Lasers and Electro-Optics, OSA Technical Digest (Optical Society of America, Washington DC, 2004).
- [2] J.H. Lehman, C. Engtrakul, T. Gennett, A.C. Dillon, Single-wall carbon nanotube coating on a pyroelectric detector, *Appl. Opt.* 44 (2005).

- [3] W.R. Blevin, W.J. Brown, Black coatings for absolute radiometers, *Metrologia* 2 (1966) 139–143.
- [4] J.H. Lehman, E. Theocharous, G. Eppeldauer, C. Pannell, Gold-black coatings for freestanding pyroelectric detectors, *Meas. Sci. Technol.* 14 (2003) 916–922.
- [5] S. Berber, Y. Kwon, D. Tománek, Unusually High Thermal Conductivity of Carbon Nanotubes, *Phys. Rev. Lett.* 84 (2000) 4613–4616.
- [6] J.S. Kim, K.S. Ahn, C.O. Kim, J.P. Honga, Ultraviolet laser treatment of multiwall carbon nanotubes grown at low temperature, *Appl. Phys. Lett.* 82 (2003) 1607–1609.
- [7] W. Becker, R. Fettiĝ, A. Gaymann, W. Ruppel, Optical and electrical properties of black gold layers in the far infrared, *Infrared Phys. Technol.* 40 (1999) 431–445.
- [8] F.J. Garca-Vidal, J.M. Pitarke, J.B. Pendry, Effective Medium Theory of the Optical Properties of Aligned Carbon Nanotubes, *Phys. Rev. Lett.* 78 (1997) 4289–4292.
- [9] A.C. Dillon, A.H. Mahan, P.A. Parilla, J.L. Alleman, M.J. Heben, K.M. Jones, K.E.H. Gilbert, Continuous Hot Wire Chemical Vapor Deposition of High-Density Carbon Multiwall Nanotubes, *Nanolett.* 3 (2003) 1425–1429.
- [10] K. Nassau, H.J. Levinstein, G.M. Loiacono, Ferroelectric lithium niobate. 2. Preparation of single domain crystals, *J. Phys. Chem. Solids* 27 (1966) 989–996.
- [11] M.E. Lines, A.M. Glass, Primary Pyroelectric Effect in  $\text{LiTaO}_3$ , *Phys. Rev. Lett.* 39 (1977) 1362–1365.
- [12] R.L. Byer, C.B. Roundy, Pyroelectric coefficient direct measurement technique and application to a nsec response time detector, *Ferroelectrics* 3 (1972) 333–338.
- [13] J.H. Lehman, Calibration Service for Spectral Responsivity of Laser and Optical-Fiber Power Meters at Wavelengths Between 0.4  $\mu\text{m}$  and 1.8  $\mu\text{m}$ , *NIST Spec. Publ.* 250–253 (1999) 1–39.
- [14] J.H. Lehman, Pyroelectric trap detector for spectral responsivity measurements, *Appl. Opt.* 36 (1997) 9117–9118.
- [15] J.H. Lehman, G. Eppeldauer, J.A. Aust, M. Racz, Domain engineered pyroelectric radiometer, *Appl. Opt.* 38 (1999) 7047–7055.
- [16] T. Guo, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, Catalytic growth of Single-walled Nanotubes by Laser Vaporization, *Chem. Phys. Lett.* 243 (1995) 49–54.
- [17] A.C. Dillon, T. Gennett, K.M. Jones, J.L. Alleman, P.A. Parilla, M.J. Heben, A simple and complete purification of single-walled carbon nanotube materials, *Adv. Mater.* 11 (1999) 1354–1358.
- [18] A.C. Dillon, A.H. Mahan, R. Deshpande, C. Engtrakul, J.L. Alleman, J.L. Blackburn, K.E.H. Gilbert, M.J. Heben, P.A. Parillia, K.M. Jones, R. To, S.-H. Lee, J.H. Lehman, Hot-wire Chemical Vapor Synthesis for a Variety of Nanomaterials with Novel Applications, *Thin Solid Films*, in press.