Multiwall carbon nanotube absorber on a thin-film lithium niobate pyroelectric detector

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Received November 6, 2006; accepted November 26, 2006;
posted January 9, 2007 (Doc. ID 76783); published March 5, 2007

Multiwall carbon nanotubes (MWNTs) were applied in a bulk layer to a pyroelectric film to increase the detector sensitivity nearly fourfold without a substantial penalty to the low-frequency response (4–100 Hz). In addition, the spectral sensitivity over the wavelength range from 600 to 1800 nm was uniformly enhanced, with variations less than 1%. The results demonstrate the suitability of MWNTs as an efficient thermal absorber having low thermal mass. © 2007 Optical Society of America

OCIS codes: 040.0040, 160.2260, 160.1890, 310.1620, 310.6860, 120.3940.

Since first demonstrated by Levy *et al.*, single crystal lithium niobate ($LiNbO_3$) films prepared by crystal ion slicing (CIS) have been applied in several important areas of optoelectronics ranging from optical circuits to optical memory storage and nonlinear optics.[1,2] In the past, we also demonstrated that large-area pyroelectric detectors based on CIS films have an advantage over those prepared by conventional lapping and polishing, because it is possible to achieve higher sensitivity while maintaining the desirable pyroelectric properties of the bulk material. We recognized that the detector sensitivity could be further enhanced by a thermal absorber coating having a mass that would not dominate that of a detector and coating composite.[3] Since then, we have undertaken research related to high-efficiency detector coatings based on carbon nanotubes (CNTs). CNTs are known to have extremely high thermal conductivity and low thermal mass compared with other carbon-based coatings, metal blacks, and percolated metal structures, such as gold black.[4] Our application represents a simple and practical use of inexpensive and commercially available CNTs. We demonstrate improvements to the CIS pyroelectric detector by documenting spectral responsivity and frequency response measurements and comparing a nickel-(Ni-) coated detector (having only the essential metal electrode) with the same detector coated with multiwall carbon nanotubes (MWNTs).

The pyroelectric detector was fabricated as a 10 μm thick freestanding film with 250 nm thick nickel electrodes on each face as described elsewhere.[3] The film is fabricated by crystal ion slicing, whereby the face of a $LiNbO_3$ plate is bombarded with high-energy (~MeV) helium ions.[1] The average depth reached by the ions defines a sacrificial layer where the film may be separated from the parent material either by acid etch or thermal shock. It is possible to achieve uniform films from 5 to 10 μm thick with an aspect ratio (width:thickness, 400:1) far exceeding that practically possible with a conventional lapping and polishing process (100:1).

The CNT coating was prepared from commercially available MWNTs produced by chemical vapor deposition[5] (CVD). The purity of the bulk material is certified by the manufacturer to be greater than 96%. In addition, our own Raman spectroscopy (RS) measurements were performed in the backscattering configuration by use of 7 mW of an argon-ion laser providing 488 nm (2.54 eV) excitation. A 55 mm telephoto lens was employed to both focus the beam to ~0.25 mm^2 area and to collect the Raman scattered light. The scattered light was analyzed with a 0.27 m grating spectrometer equipped with a liquid-nitrogen-cooled charge-coupled detector and a holographic notch filter. Information derived from RS is important in terms of characterizing the relative quantities of carbon impurities and defective sites on the MWNTs. The "G band" at 1500–1650 cm^{-1} is a compilation of bands originating from the in-plane vibrational modes of carbon in the curved graphite lattice, while the "D band" at ~1350 cm^{-1} is generated by symmetry-lowering effects such as defects, tube ends, or the presence of nonnanotube carbon impurities.[6] Our own analysis of RS and the D/G peak height intensity ratio of the sample indicates

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the presence of a relatively large amount of graphitic material considered to be consistent with bulk material containing MWNTs. The D/G peak height intensity ratio of 0.600 indicates that these nanotubes are more completely graphitized and contain fewer carbon impurities than other CVD generated nanotubes we have studied, where $D/G \geq 1$ is common. The MWNTs were applied to the detector film by dispersing 0.33 g in 13.4 ml of chloroform (CCl_3) and sonicating the dispersion for 15 min in an ultrasound bath. The dispersion was then applied to the detector area by an airbrush technique documented previously.[4]

The MWNT-coated detector is visibly black, due to the optical properties of the individual tubes, as well as the topology of the bulk. The refractive index of individual MWNTs has been modeled by Garcia-Vidal *et al.* and others.[7] Qualitatively, viewed by a scanning electron microscope, the topology has the appearance of a mat of bundled ropes with various clumps interspersed. The clumps are believed to be catalyst metals and nonnanotube carbons. The thickness of the coating is difficult to measure *in situ* due to the delicate nature of the 10 μm thick freestanding film. However, the thickness of similar films deposited on a glass slide has been estimated by optical microscopy to be between 5 and 10 μm thick. The robustness of the coating after the CCl_3 evaporates is comparable with that of enamel paint. It can be scratched with a rigid stylus, but it is not dislodged by forced air or water (~0.2 MPa). The mechanism of bundling and surface attachment is attributable to van der Waals forces and interaction of pi electrons occupying their orbital perpendicular to the axis of the tube.[5]

The spectral responsivity measurements shown in Fig. 1 were based on a lamp source, a grating monochromator, and a National Institute of Standards and Technology (NIST) transfer standard detector. The measurement procedure is that of direct substitution with a known NIST-calibrated transfer standard at 50 nm wavelength increments from 600 to 1800 nm. The NIST transfer standard was a pyroelectric wedge trap detector that was calibrated with the use of the

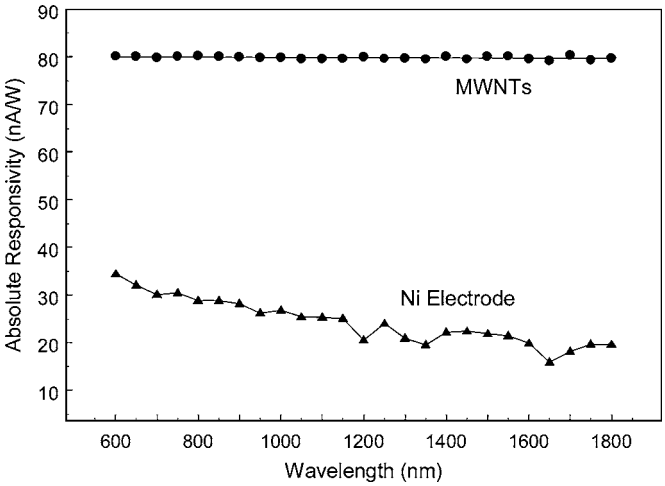

Fig. 1. Spectral responsivity measurements of the CIS pyroelectric detector compared with and without MWNT coating. The MWNT-coated detector data is indicated by solid circles, the Ni-coated data by solid triangles.

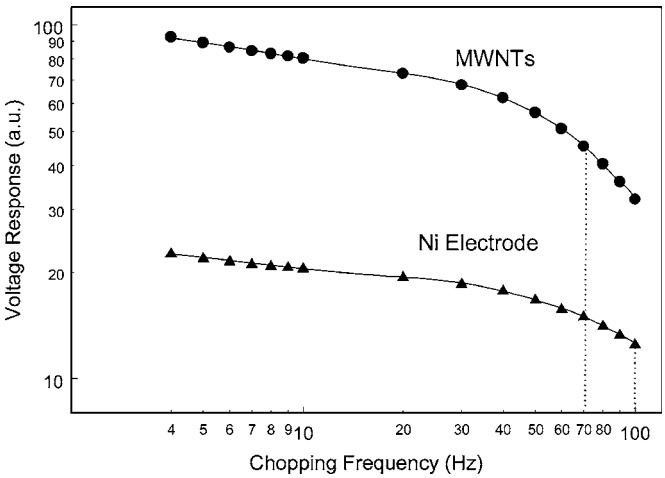

Fig. 2. Frequency-response measurements of CIS pyroelectric with and without MWNT coating.

NIST C-series standard calorimeter.[8] The output beam from the monochromator (transmitted through air) was directed alternately onto the CIS pyroelectric detector and the NIST transfer standard with a two-position mirror. The beam was focused to a 2 mm × 2 mm square spot, normal to the plane of the detector surface aperture. The monochromator slits were adjusted so that the bandpass of the monochromator was less than 6 nm. The chopping frequency of these measurements was 15 Hz. The total expanded uncertainty is 1.24% with a 96% confidence interval.[9]

The MWNT coating absorptivity can be deduced by comparing the relative responsivity of the Ni-coated detector with that of the MWNT-coated detector. The expected absorption efficiency of the Ni-coated detector was determined from the refractive index of nickel.[10] The calculated nickel absorptivity defines the relative responsivity of the detector at approximately 30%, where 100% would represent that of a perfect coating with no reflection, no transmission, and all photon energy is transferred to the detector as heat. The relative spectral responsivity at 15 Hz of the MWNT-coated and Ni-coated detector is 85%. The absorptivity is comparable with that which we have reported previously for MWNTs grown on the detector substrate and SWNTs applied by airbrush, and approximately that of amorphous carbon or graphite alone.[7,11] It is immediately apparent from our spectral responsivity measurement results that the MWNT coating increases the detector responsivity about four times compared with the Ni-coated detector, and that variations of spectral uniformity are small compared to the measurement uncertainty.

The frequency-response measurements were acquired by means of modulating a mechanical chopper referenced to a dual-phase lock-in amplifier. A temperature-stabilized 850 nm diode laser having a Gaussian beam distribution was spatially filtered and imaged on the detector surface with a beam diameter less than 2 mm (that is, having greater than 99% of the beam power within 2 mm diameter). The frequency was incrementally varied from 4 to 10 Hz at 1 Hz steps and 10 to 100 Hz at 10 Hz steps. Frequency measurement results are shown in Fig. 2.

When we consider the lumped thermal model for the voltage generated by a pyroelectric detector, the frequency response is a function of both thermal and electrical time constants. The thermal mass of the detector limits the low-frequency response, while the electrical capacitance limits the high-frequency response. This frequency-response relationship is somewhat intuitive and well known. However, according to Muralt in a review of pyroelectric thin films, the dominance of the thermal over the electrical time constant is not the same for thin films as for "bulk" devices.[12] The frequency responses shown in Fig. 2 of the Ni-coated and MWNT-coated detectors decrease with increasing frequency. This is consistent with Muralt and thin-film pyroelectric detectors in general. In addition, the frequency response of the MWNT-coated detector, which we expect to be more massive, is decreased at higher frequencies at a greater rate than the Ni-coated detector. This is quantified at the frequency where the responsivity is 50% of the maximum (indicated by a dashed line in Fig. 2). For the Ni-coated detector this is at approximately 100 Hz, and is 70 Hz for the MWNT-coated detector. The frequency-response measurements indicate that there is a penalty for increased mass at higher chopping frequency. However at lower frequencies, particularly at 15 Hz where the spectral responsivity measurements were acquired, the improvement is attributable to the higher optical absorption efficiency of the MWNT coating. The 3 dB point is shown by the vertical dashed line. The MWNT-coated detector data are indicated by solid circles, and the Ni-coated detector data are indicated by solid triangles.

The importance of spectral uniformity and low thermal mass generally applies to other thermal detector platforms such as thermopiles and calorimeters, just as it does to pyroelectric detectors. One of the advantages of a thermal detector is that, in principle, the spectral responsivity is inherently uniform. In practice, however, the spectral responsivity will vary if the thermalization is wavelength dependent. Therefore, a thermal detector coating both having a low thermal mass and that is spectrally uniform is valuable for applications such as building optical power meters and other tools for radiometry. MWNTs were chosen over single-wall carbon nanotubes (SWNTs) for the present investigation because a detector coating made of high-purity nanotubes will exhibit spectral features that are characteristic of interband transitions of metallic and semiconducting material as shown by Gilbert *et al.*[13] Recently we demonstrated that CNTs, or at least submicrometer diameter carbon fibers, can be grown on a freestanding $LiNbO_3$ pyroelectric by CVD.[14] Although a CVD-grown coating holds promise for optimized topology and maximum heat transfer, the process of merely spraying MWNTs in suspension is desirable from the standpoint of convenience, cost, and detector yield. The MWNTs used in this Letter are among the cheapest CNT material that is commercially available (~U.S.$8/g). Therefore, our results indicate that large-area detectors or detector arrays could be coated economically.

We have shown that applying bulk MWNTs to a thin-film pyroelectric detector increases the detector responsivity substantially. The spectral responsivity from 600 to 1800 nm was uniform to within the stated uncertainty. The unique nature of the frequency response was investigated and indicates that the MWNT coating does not contribute significantly to the mass of the film-coating composite, while the detector maintains its advantage over a bulk device. The enhanced performance, along with the facile and inexpensive application of the coating, is promising for applications such as radiometric detectors and thermal detector arrays. Our goal for this early work was to demonstrate the viability of a relatively low-cost coating material available "off the shelf," having the desirable thermal properties of CNTs as reported in the literature. Further investigation into the thermal properties and topology of the coating are warranted to further enhance the absorption efficiency and extend uniform spectral responsivity into the ultraviolet as the well as the infrared.

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