CARBON NANOTUBE-BASED COATINGS FOR LASER POWER AND ENERGY MEASUREMENTS*

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Abstract

We describe carbon nanotube (CNT) based coatings for thermal detectors for laser power and energy measurements. The value of thermal properties of CNTs obtained from the literature indicates that such coatings have desirable properties such as low thermal mass and high thermal conductivity. We describe the process by which we produce CNTs and apply them to thermal detectors, including laser vaporization and chemical vapour deposition on detector materials such as $LiTaO_3$, $LiNbO_3$ and copper. We describe additional novel processing steps that include surface preparation, the deposition of a barrier layer and annealing in air. We present spectral responsivity measurements over the wavelength range from 0.8 μm to 14 μm for carbon single wall nanotubes (SWNTs) as well as carbon multiwall nantotubes (MWNTs) compared to gold black.

Introduction

Nearly all of the primary radiometric standards for laser power and energy measurements in the world are based on thermal detectors such as pyroelectric detectors, thermopiles, or calorimeters. In most cases, thermal detectors employ some form of thermal absorber coating, and the thermal detector responsivity is proportional to the spectral absorptivity of the thermal coating. Desirable thermal detectors for high accuracy laser measurements have broad and uniform spectral responsivity as well as relative variations in spatial uniformity less than 1 %. In principle, the response as a function of wavelength (the spectral responsivity) of thermal detectors depends on the variation of reflectance of the detector coating as a function of wavelength. For our application, a thermal absorber must be resistant to damage and aging while maintaining high absorption efficiency and high thermal conductivity over the range of laser power and energy served by our calibration services (0.157 μm to 10.6 μm). Theoretical and experimental investigations reported in the literature indicate that desirable properties may be achieved while maintaining properties that have a significant advantage over present alternatives such as carbon based paints or metal blacks.

Thermal Properties

The combination of high thermal conductivity and low specific heat are important considerations for thermal detector coatings in general and coatings used in electrical substitution or other schemes where the electrical inequivalence would compromise the accuracy of the device to which it is applied, such as the electrically calibrated pyroelectric[1], cryogenic radiometer[2], or isoperibol calorimeter.[3] For SWNTs, the thermal conductivity ranging from 100 to 1000 W/m·K as reported by Berber[4] is exceptional and distinguishes carbon nanotubes from present alternatives. The specific heat of 600 mJ/g·K reported for SWNTs is not exceptional, but combined with the high thermal conductivity provides a material having a thermal diffusivity that is many times greater than alternatives such as gold black or carbon black.[1]

Fabrication

Bulk production of carbon single- and multi-wall nanotubes has been achieved by a variety of methods, including laser vaporization, arc-discharge evaporation, and various chemical-vapour-deposition (CVD) techniques. In our proof-of-concept investigations, purified, bulk SWNTs were applied to a thermal detector with a simple airbrush technique.[5] The promising results of these preliminary investigations motivated the development of hot wire CVD (HWCVD) techniques for the synthesis of nanotube films directly on thermal-detector surfaces, which we have documented recently.[6]

Presently we summarize our production techniques and present new work that documents the process of growing carbon multiwall nanotubes (MWNTs) directly on the detector material by the process of gas phase CVD.

The synthesis of the SWNTs was accomplished by use of a laser vaporization method. The laser vaporization process is similar to that described by Guo et al., in which an alexandrite laser emitting at 755 nm with a power density of 40 W/cm^2 was used to vaporize a graphite target doped with cobalt (Co; 0.6% relative atomic mass) and Ni (0.6% relative atomic mass).[7] The crude soot was produced at 1200 °C with 500-torr argon (Ar) flowing at 100 cm^3/min (units based on standard air). The SWNTs were purified with a nitric acid (HNO_3) reflux for 16 hours, followed by air oxidation at 550°C for 30 minutes.[8] The purified SWNTs were dispersed in chloroform by use of a cup-horn sonicator connected to an ultrasonic processor. During the entire sonication period (two hours), the suspensions were kept in a water bath cooled to 15 °C. The SWNT (0.1 % by weight) suspension was then applied from 3 × 2 aliquots by use of an airbrush and dried under a steady stream of nitrogen. In one case the suspension was formed from SWNTs dispersed in choloroform and in another case the SWNTs were dispersed in fluoroalkanelsulfonic acid (Nafion).[8]

HWCVD, which uses a tungsten filament for the decomposition of various precursor gases, has recently been used for continuous gas-phase production of both SWNTs and MWNTs.[9,10] However, by coating various substrates with a transition-metal catalyst (instead of supplying this catalyst in the gas phase), carbon nanotubes can be directly grown onto surfaces using the HWCVD technique. To demonstrate the process, 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 approximately 20 A, 25 V, and at 1700 °C as determined by an optical pyrometer. Nickel (Ni) films were used as a substrate catalyst, ranging in thickness from 5 to 10 nm. Graphitic MWNTs with a modest amount of non-nanotube carbon impurities were produced in an atmosphere of 1:5 methane:argon at 150 torr with the furnace at 400 °C.

Conventional catalytic CVD (not HWCVD) processes require relatively high temperatures, reducing atmospheres, and the presence of metal catalysts on the crystal surface, which, when combined, can undesirably increase the electrical conductivity of a pyroelectric material such as lithium niobate ($LiNbO_3$) or lithium tantalate ($LiTaO_3$). However, CVD nanotube growth furnaces are commercially available, and thus we are motivated to adapt the processing of CVD to thermal detectors. To demonstrate the CVD process, the deposition of Fe catalytic films on $LiNbO_3$ pyroelectric crystals and silicon (Si) substrates (control sample for comparison) were optimized initially, and eventually the process was adapted to copper (Cu). The experiments began by varying the Fe film thickness over the range from 3 to 7 nm. The substrate with a catalyst film was placed on a quartz platform and loaded into the quartz reaction tube located in a high temperature tube furnace. Prior to the synthesis of carbon nanotubes, the quartz tube was purged by argon. Then the gas mixture of methane, ethylene and hydrogen was introduced at different flow rates. After the process was complete, the furnace was cooled to room temperature in the flow of argon. In various experiments, the temperature range was from 700 to 900 ^{o}C and the duration of reaction was varied from 5 to 30 min.

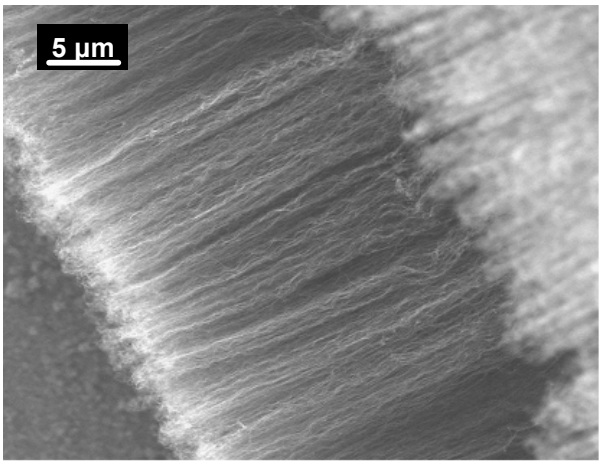

Figure 1. SEM images of vertically aligned MWNTs grown on 3 nm Fe film with a Si_3N_4 barrier layer (100 nm), a deposition temperature of 725 °C, and methane, ethylene and hydrogen gas flow rates of 100, 400 and 500 sccm respectively, for 10 min.

Our early experiments on carbon nanotube growth revealed that while MWNTs readily grow on Si substrates at 750 °C, Fe films on $LiNbO_3$ did not support nanotube synthesis because at 700 – 750 °C iron diffuses into $LiNbO_3$ crystals and thus does not remain as a stable thin film on the surface. To address this problem we have created an additional processing step: deposition of a thin (20 nm) silicon nitride (Si_3N_4) barrier layer, which prevents catalyst diffusion into the pyroelectric at elevated temperatures. We also incorporated a final step of annealing in air at 400 °C for 5 hrs to partially restore the stoichiometry of the $LiNbO_3$ and thus restore the desirable electrical properties of the pyroelectric. The scanning electron

microscope image in Fig. 1 shows a representative area with vertically aligned MWNTs on $LiNbO_3$. A photographic image of a completely packaged $LiNbO_3$ pyroelectric detector is shown in Fig. 2.

Figure 2. Photographic image of completely packaged pyroelectric detector with MWNT coating prepared by CVD.

Calorimeters developed at NIST in the past incorporated an optical receiver cavity in which incoming light is absorbed and converted to heat. Typically such a cavity was fabricated from electroformed Cu and coated with carbon-based paint.[3] Black paint has a relatively high thermal mass compared to carbon nanotubes. Therefore, in addition to growth of MWNTs on pyroelectric materials as described above, we have undertaken experiments on the growth of carbon nanotubes on Cu in the interest of building more accurate calorimeters. In our early attempts to produce MWNTs, the surface quality of our substrate (for example, the pyroelectric crystals) was typically an optical-quality (polished) surface. In our investigation of Cu substrates, we found that the growth and orientation of MNWTs was dependent on surface roughness. At this early stage, we believe that the surface roughness, with variations on the order of the barrier and catalyst thickness, defies deposition of a barrier layer and a catalyst that is relatively uniform and free of defects. We do not rigorously define a required surface quality in the present work. However, on scratched or matte Cu substrate surfaces, we observed only random and sparse nanotubes grown in non-uniform patches. On surfaces that are predominately specular reflectors, the length and appearance of MWNTs approaches that of our samples prepared on polished quartz, silicon, and $LiNbO_3$. A photographic image of a MWNT coating on a Cu is shown in Fig. 3.

Figure 3. A photographic image of MWNTs grown on a Cu disk (the disk is 40 mm in diameter and 1 mm thick). The image shows a scratch on the left side and the absence MWNTs (non-black) where the Si_3N_4 barrier layer was absent.

Measurements

The performance of the SWNT and MWNT pyroelectric detectors over the wavelength range from 0.8 μm to 1.8 μm were characterised by use of the NIST spectral responsivity calibration service. This measurement facility is based on a grating monochromator and a pyroelectric trap reference detector.[9] The results of these measurements are plotted in Fig. 4. The results of the responsivity of each pyroelectric detector coated with CNTs are compared with a pyroelectric detector that is identical with the exception of a gold black coating in place of the CNT coating. We consider the gold black coating to be state of the art for coatings having high absorption efficiency and the process by which this coating was created is documented elsewhere.[10]

The CNTs on pyroelectric detectors for which measurement results are shown in Fig. 4 are based on a lithium tantalate ($LiTaO_3$) disk 12 mm in diameter and 60 μm thick, with nickel (Ni) electrodes 10 mm in diameter and 25 nm thick on each face. The CNTs on a pyroelectric detector for which measurement results are shown in Fig. 5 are based on a $LiNbO_3$ pyroelectric detector that is 250 μm thick and 3 mm in diameter with Ni electrodes 10 mm in diameter and 25 nm thick on each face.

The performance of the MWNT pyroelectric detector was characterised by use of the NPL infrared detector characterisation facilities [9, 11]. The NPL infrared

spectral responsivity measurement facility is based on a double grating monochromator of 0.25 m focal length operating in the subtractive mode. Full details on this facility can be found elsewhere [10], [12]. The results of these measurements are plotted in Fig. 5.

For all of the NIST-referenced spectral responsivity evaluations, the pyroelectric detectors (gold black, SWNT and MWNT coated), was used in combination with a transimpedence amplifier operating at 10^{-10} A/V with a lock-in amplifier referenced to a chopping frequency of 15 Hz.

For all the NPL-referenced radiometric evaluations described in this paper, the MWNT pyroelectric detector was used in combination with a trans-impedance amplifier operating at 10^{-8} A/V and referenced to a modulation frequency of 70 Hz.[13]

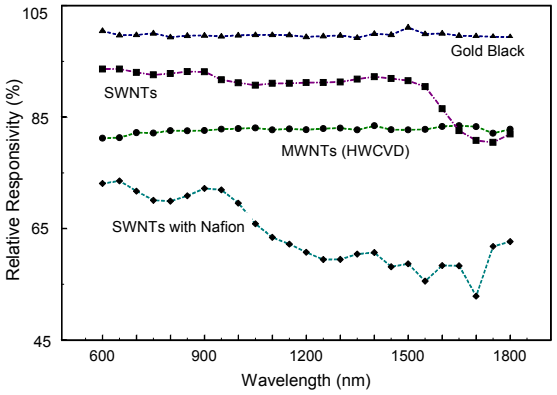

Figure 4. Fig. Spectral responsivity of four pyroelectric detectors that were identical except for the thermal absorber coating. Error bars are not shown for clarity. The relative expanded uncertainty for the spectral responsivity measurement is 1.24 %. The level of confidence for the relative expanded uncertainty is approximately 95 %.

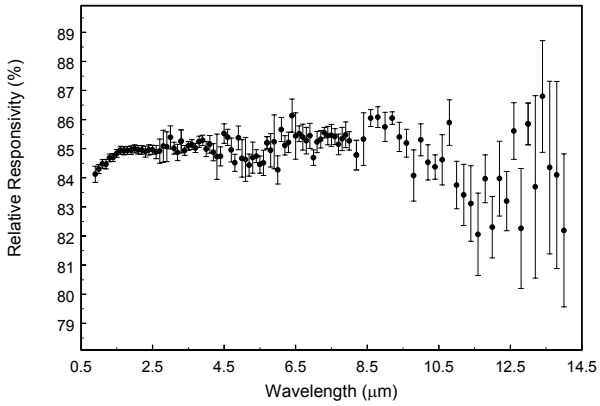

Figure 5. Relative spectral responsivity of $LiNbO_3$ pyroelectric detector coated with MWNTs. The uncertainty of the measurement varies with wavelength and is indicated by the error bars. The level of confidence for the relative expanded uncertainty is approximately 95 %.

Discussion

The first observation we make from our spectral responsivity measurements in the visible and near infrared is that different coatings, representing different coating processes, yield detectors having different spectral responsivity. So far, none of the CNT coatings have the same absorption efficiency as gold black. We have begun to investigate various models by which we might make engineering judgements to modify the coating topology to improve the coating absorptivity. For example, Garcia-Vidal et al., present an effective medium approximation to calculate a dielectric function for aligned CNTs that accounts for the tube diameter and spacing.[14] Our goal is to create a CNT coating that has an absorption efficiency (greater than 99 %) that meets or exceeds that which we can achieve with gold black and thus have the ability to build thermal detectors having a relative responsivity greater than 99 %. Our experiments thus far indicate that changing process parameters modifies the coating topology. In addition, to justify the value of CNT coatings, we must maintain the advantages of exceptionally high thermal conductivity and damage threshold claimed in the literature.[4],[15]

To date we have not attempted to produce a copper calorimeter cavity, so we cannot comment on the absorption properties and conversion efficiency of

MWNTs on Cu. In principal, the spectral responsivity of thermal detectors depends on the optical properties of the detector coating. Therefore we expect the relative spectral responsivity of a cavity calorimeter coated with CNTs to be similar to that which we have demonstrated on pyroelectric materials.

Conclusion

From our processing experiments, imaging and detector responsivity measurements we have demonstrated that CNTs can be employed as a thermal detector coating. With novel processing steps we have adapted the process by which we grow MWNTs by CVD to include the addition of a Si_3N_4 barrier layer and qualitatively correlated tube growth with the surface finish of the detector platform. In the near future we plan to document damage studies of both SWNTs applied by airbrush as well as MWNTs grown directly on the detector substrate.

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