Infrared responsivity of a pyroelectric detector with a single-wall carbon nanotube coating

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The performance of a 10 mm diameter pyroelectric detector coated with a single-wall carbon nanotube (SWCNT) was evaluated in the 0.8 to 20 μm wavelength range. The relative spectral responsivity of this detector exhibits significant fluctuations over the wavelength range examined. This is consistent with independent absorbance measurements, which show that SWCNTs exhibit selective absorption bands in the visible and near-infrared. The performance of the detector in terms of noise equivalent power and detectivity in wavelength regions of high coating absorptivity was comparable with gold-black-coated pyroelectric detectors based on 50 μm thick $LiTaO_3$ crystals. The response of this detector was shown to be nonlinear for DC equivalent photocurrents $>10^{-9}$ A, and its spatial uniformity of response was comparable with other pyroelectric detectors utilizing gold-black coatings. The nonuniform spectral responsivity exhibited by the SWCNT-coated detector is expected to severely restrict the use of SWCNTs as black coatings for thermal detectors. However, the deposition of SWCNT coatings on a pyroelectric crystal followed by the study of the prominence of the spectral features in the relative spectral responsivity of the resultant pyroelectric detectors is shown to provide an effective method for quantifying the impurity content in SWCNT samples.

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1. Introduction

Coatings applied to thermal detectors must combine high absorptivity and low thermal mass to ensure that a large fraction of the incident radiation is converted to heat and that the heating is maximized per incident radiant power [1]. These requirements are particularly important in the infrared where there is limited availability of black coatings having characteristics that match these priorities. While the absorptivity of gold-black coatings in the infrared is very good [2–4], their fibrous structure is very delicate and prone to aging due to the collapse of this structure, particularly as a result of heating and physical contact. Lehman *et al.* recognized that the characteristics of carbon nanotube coatings fulfill the main requirements of black coating for thermal detectors [5,6]. The fabrication and evaluation of two pyroelectric detectors with two different types of carbon nanotube coatings were reported in the 600 to 1800 mm wavelength range [5,6]. However, the main applications of thermal detectors are in the infrared where the advantages of alternative (photon) detector technologies are not so overwhelming. Previously we evaluated the performance of a pyroelectric detector with a multiwall carbon nanotube in the 0.9 to 14 μm wavelength range [7]. The relative spectral responsivity of that detector was shown to be flat over most of the wavelength range examined, and the spectral flatness was shown to be comparable with the best infrared black coatings currently available [4]. Our aim is to report the evaluation of a pyroelectric detector with a single-wall carbon nanotube (SWCNT) coating in the infrared.

2. Detector Preparation and Evaluation

The deposition of the SWCNT coating has been described previously [5]. Briefly the synthesis of the SWCNTs was accomplished using a laser vaporization method similar to that of Guo *et al.* [8], whereby an alexandrite laser operating at a wavelength of 755 mm and a power density of 40 W cm^{-2} was employed to vaporize a graphite target doped with cobalt (0.6% relative atomic mass) and nickel (0.6% relative atomic mass). The crude soot was produced at 1200 °C with 500 Torr argon flowing at 100 cm^3 min^{-1} (units based on standard air). The SWCNTs were purified with a HNO_3 reflux for 16 h followed by air oxidation at 550 °C for 30 min as described in earlier work [9]. The purified SWCNTs were dispersed in chloroform using a cup-horn sonicator connected to an ultrasonic processor. During the entire sonication period (2 h), the suspensions were kept in a water bath cooled to 15 °C. The SWCNT (0.1% by weight) suspension was then applied from 3 × 2 aliquots using an airbrush and dried under a steady stream of nitrogen, with the pyroelectric crystal maintained at an ambient temperature so a thin $LiTaO_3$ crystal could be used. The active area of the SWCNT-coated pyroelectric detector was 10 mm in diameter and, the thickness of the $LiTaO_3$ crystal was 60 μm.

The performance of the SWCNT-coated pyroelectric detector was evaluated using the National Physical Laboratory's (NPL's) infrared detector characterization facilities [10]. The NPL infrared spectral responsivity measurement facility is based on a 0.25 m focal length double grating monochromator operating in the subtractive mode. For full details of this facility [10] and the NPL spatial uniformity of response measurement facility [11], please refer elsewhere. The NPL linearity of response measurement facility [12] is based on the double aperture method [13] and employs reflective neutral density filters deposited on wedged zinc selenide substrates to attenuate the incident radiation. The maximum level of spectral irradiance at which linearity measurements were made was restricted by the maximum spectral radiance of the tungsten strip lamp with a 2 mm wide element.

During this evaluation the SWCNT pyroelectric detector was used in combination with an E690 transimpedance amplifier assembled for the NPL by Vinculum Services of Royston, United Kingdom. The amplifier was maintained at a gain of 10^8 VA^{-1} throughout the measurements described here. All measurements presented here were performed at a 70 Hz modulation frequency.

3. Results

A. Relative Spectral Responsivity and Specific Detectivity Measurements

Figure 1 shows the relative spectral responsivity of the SWCNT pyroelectric detector in the 0.8 to 5 μm wavelength range, normalized at 0.8 μm. The plot shows that the relative spectral responsivity of this detector exhibits significant fluctuations in this wavelength range. Since the detector responsivity is proportional to the coating absorptivity, the variations are attributable to the coating [1]. The presence of these spectral features is significant since they provide information about the purity of the coating, as highlighted in Section 4. Figure 2 shows the relative spectral responsivity of the same detector extended to a wavelength of 20 μm, again normalized at 0.8 μm. Figure 2 shows that for wavelengths longer than 4 μm, the responsivity of the detector decreased monotonically up to 20 μm, the longest wavelength studied.

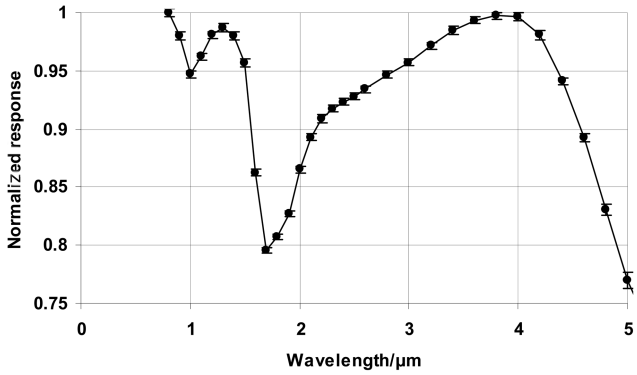

Fig. 1. Relative spectral responsivity of the SWCNT-coated pyroelectric detector in the 0.8 to 5 μm wavelength range normalized at 0.8 μm. The error bars represent the 1σ uncertainty of the measurements.

The DC equivalent [14] absolute spectral responsivity of the SWCNT-coated pyroelectric detector in combination with the Vinculum transimpedance amplifier with a 10^8 V/A gain at 0.9 μm for a 70 Hz modulation frequency was measured by comparison with the NPL standards to be 64.5 VW^{-1}. The noise voltage spectral density of the detector–amplifier combination at 70 Hz was measured to be 2.1 $\mu V\,Hz^{-1/2}$. Ignoring the noise contribution due to the transimpedance amplifier (the noise was dominated by the pyroelectric detector), the specific detectivity (D^*) of the SWCNT pyroelectric detector

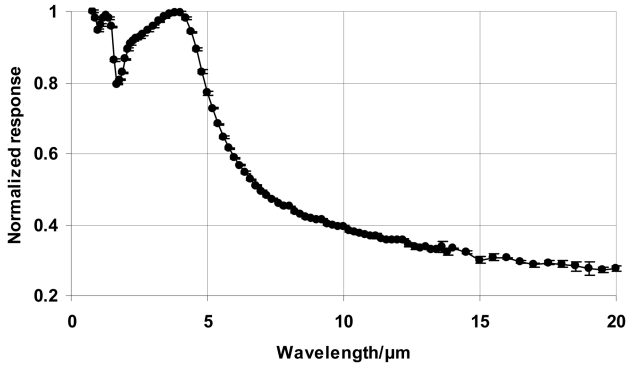

Fig. 2. Relative spectral responsivity of the SWCNT-coated pyroelectric detector in the 0.8 to 20 μm wavelength range normalized at 0.8 μm.

at 0.9 μm at 70 Hz was estimated to be 2.7×10^7 cm $Hz^{1/2}\,W^{-1}$. This is slightly lower compared with gold-black-coated $LiTaO_3$ pyroelectric detectors of similar crystal thicknesses [15].

B. Spatial Uniformity of Response

In the NPL spatial uniformity of response measurement facility, radiation from various sources (tungsten strip lamps and glow bars) is imaged on a pinhole, and radiation passing through this pinhole is reimaged using a pair of optically polished off-axis parabolic mirrors, so the image of the pinhole is formed in the plane of the active area of the detector being tested. The test detector is mounted on a motor-driven X–Y translation stage, so the image of the pinhole sequentially illuminates different parts of the active area of the detector. A beam splitter located just in front of the test detector directs approximately 50% of the incident radiation onto another (reference) detector, which is stationary. Its purpose is to measure any drifts in the radiant power of the beam incident on the test detector, so their effect on the test detector can be corrected. The operation of this facility is fully automated.

Figure 3 shows the normalized responsivity of the SWCNT-coated pyroelectric detector measured at different points on the active area of this detector using a 0.6 mm diameter spot. A spatial nonuniformity of approximately 3% is typical for pyroelectric detectors of this size [3].

C. Linearity Characteristics

Radiometrists quantify the deviation from linearity of photodetection systems using a parameter called the linearity factor, $L(V_{A+B})$ [11]. It represents a measure of the linearity of the detector for an output of $(V_A + V_B)/2$, and its value is calculated from the relationship

$$L(V_{A+B}) = \frac{V_{A+B}}{(V_A + V_B)}, \tag{1}$$

where V_A and V_B represent the dark-corrected output signals from the photodetection system when two optical signals, A and B, illuminate the photodetection system, respectively, whereas V_{A+B} represents the dark-corrected output signal from the same photodetection system when A and B illuminate the photodetection system at the same time. The definition requires V_A to be approximately equal to V_B. The linearity factor at a specific output voltage essentially provides a measurement that is the average deviation of the absolute responsivity from nominal over a range of 2:1 at that specific output voltage.

Figure 4 shows the linearity factor of the SWCNT-coated pyroelectric detector–amplifier combination. The abscissa represents the DC equivalent photocurrent [14] generated by the optical radiation incident in a 2 mm diameter spot on the active area of the detector. The error bars represent the standard deviation of eight measurements of the linearity factor at each photocurrent value. The data shown in Fig. 4 were acquired using the unfiltered output of a 2 mm wide tungsten strip lamp with a silica window. Since the spectral responsivity of this detector exhibits strong fluctuations (see Fig. 2), its linearity factor was quantified as a function of the DC equivalent photocurrent generated by the pyroelectric detector. Using the unfiltered output of the lamp, evidence of superlinearity can be seen for DC equivalent photocurrents higher than approximately 1 nA . A similar superlinear behavior has also been observed [16] in the response of $LiTaO_3$ pyroelectric detectors coated with metal-black coatings. When bandpass filters were used to select pseudomonochromatic radiation, the generated DC equivalent photocurrent was much lower than 1 nA, and no measurable deviation from linearity could be observed in the response of the SWCNT-coated pyroelectric detector.

D. Temperature Coefficient of Response

The temperature coefficient of response of the SWCNT-coated pyroelectric detector was measured by measuring the responsivity of the detector at a

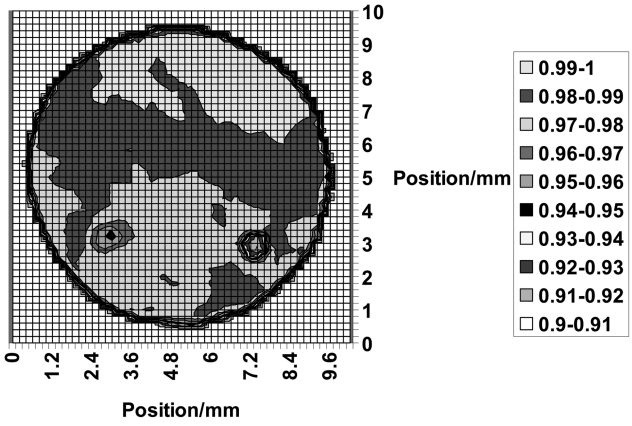

Fig. 3. Spatial uniformity of response plot of the SWCNT-coated pyroelectric detector acquired with a source wavelength of 1.25 μm and a 0.6 mm diameter probe spot.

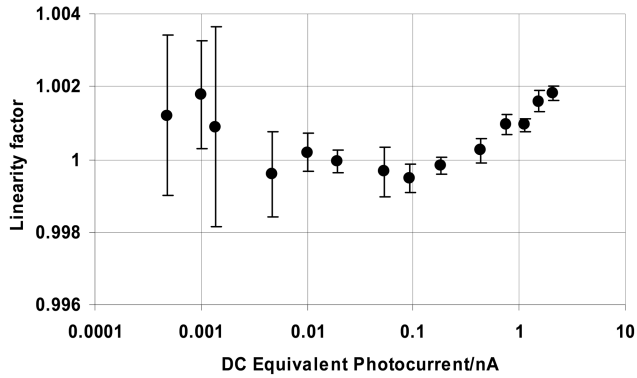

Fig. 4. Linearity characteristics of the SWCNT-coated pyroelectric detector. The error bars represent the standard deviation of eight measurements of the linearity factor at each DC equivalent photocurrent value.

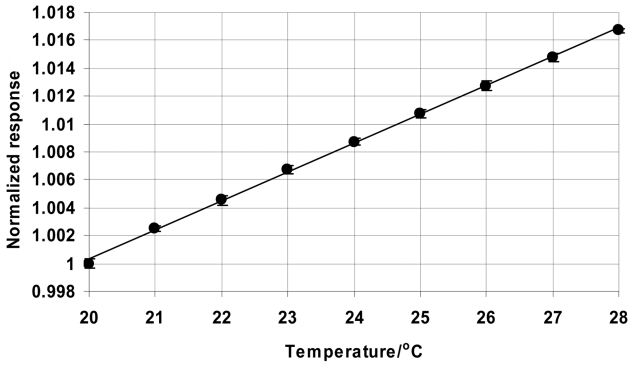

Fig. 5. Normalized response at different temperatures and best straight line fit.

number of temperatures in the 20 °C to 28 °C temperature range (see Fig. 5). From the slope of this plot, the temperature coefficient of response was estimated to be 0.21% $°C^{-1}$. This is similar to the values of the temperature coefficient of response measured for gold-black-coated $LiTaO_3$ pyroelectric detectors [15].

4. Discussion

From the standpoint of improving the detector coating, it is important to note that, as with other black coatings, morphology is critically important to the absorption efficiency and spectral flatness. Becker *et al.* have shown that topology and extent of percolation will enhance the absolute absorptivity of the detector coating [17]. So a highly purified SWCNT coating might be optimized for high absorption efficiency by increasing the porosity. The present work correlates with previous studies of absorptance in the near infrared of SWCNTs made by laser vaporization.

Figure 1 shows that the responsivity of this detector decreases at wavelengths around 1 and 1.7 μm. This suggests that the spectral absorbance of the SWCNT coating decreases for wavelengths around 1 and 1.7 μm. Absorbance measurements of SWCNT samples measured spectrophotometrically typically indicate that the absorbance of SWCNT coatings increases for wavelengths around the 1 and 1.7 μm bands, in apparent contradiction to the measurements reported here. The direct absorbance measurements of SWCNTs in suspension by Landi *et al.* [18] have shown that spectral nonuniformity is characteristic of purified bulk SWCNTs, where the resolution of the known intrinsic excitonic transitions becomes prominent with greater purity. It is apparent from the absorptivity measurements of Landi *et al.* [18] that the presence of impurities reduces the prominence of spectral features that characterize SWCNTs. The nonuniform spectral responsivity of the SWCNT-coated pyroelectric detector shown in Fig. 1 can possibly be explained by a nonuniform reflectance of the SWCNT coating [5]. Measurements by Barnes *et al.* [19] indicate a reflectance component in addition to an absorbance component at the same band regions. The work of neither Landi *et al.* [18] nor Barnes *et al.* [19], however is for an opaque film such as that on the pyroelectric detector. Whether the spectral features are dominated by reflectance or absorbance (and inequivalence) is a matter for further investigation.

It is possible that additional spectral features (rather than a monotonic decrease) beyond 5 μm would be apparent with a thicker detector coating. The thickness of the SWCNT coating is difficult to determine by optical methods because of its high absorption efficiency, and mechanical methods are difficult because the coating is readily damaged by a mechanical stylus. Using a thickness gauge we estimate that the thickness of the coating is approximately 2 μm. This is merely an estimate and is given without bounds of uncertainty. The monotonic decrease of the responsivity at wavelengths >4 μm is possibly due to the fact that the coating is not sufficiently optically thick to absorb longer wavelength photons. A thicker coating, however, may contribute to nonequivalence, that is, radiation absorbed by a thicker coating may be dissipated or reradiated before being absorbed by the pyroelectric material.

5. Conclusions

The performance of a 10 mm diameter pyroelectric detector coated with a carbon single-wall nanotube coating was evaluated in the 0.8 to 20 μm wavelength range. The relative spectral responsivity of this detector exhibited significant fluctuations over the wavelength range examined. These fluctuations are in agreement with independent spectrophotometer-based measurements [18]. The presence of these fluctuations is expected to restrict its use as a black coating for thermal detectors. The performance of the detector (in terms of noise equivalent power and D^*), however, was comparable to gold-black-coated pyroelectric detectors based on 50 μm thick $LiTaO_3$ crystals. The spatial uniformity of response of this detector was similar to other large area pyroelectric detectors utilizing other types of black coatings. The carbon nanotube coatings were reported to be much more durable than other infrared black coatings commonly used to coat thermal detectors in the infrared, such as metal-blacks. Despite the ease with which SWCNT coatings can be prepared, it is unlikely they will find applications in thermal detectors for radiometric applications because of the large fluctuations in the spectral absorbance in the infrared. However, we have shown that the deposition of SWCNT coatings on a pyroelectric crystal followed by the study of the prominence of the spectral features in the relative spectral responsivity of the resultant pyroelectric detectors provides an effective method for quantifying the impurity content in SWCNT samples.

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