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The evaluation of a pyroelectric detector with a sprayed carbon multi-wall nanotube black coating in the infrared

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ABSTRACT

The performance of a pyroelectric detector with a "sprayed" multi-wall carbon nanotube (MWCNT) coating was evaluated in the 0.9 μm–24 μm wavelength range. The relative spectral responsivity of this detector was shown to vary by 8% over this wavelength range. Its responsivity exhibited a super-linear response, while its spatial uniformity of response was strongly dependent on the modulation frequency, indicating that the thermal properties of the "sprayed" MWCNTs play an important role in the spatial uniformity of response profiles. The "sprayed" MWCNT coating is far easier to fabricate than other black coatings and it is relatively durable. This, in combination with the small variation observed in the spectral absorbance of the "sprayed" MWCNT coating over a very wide wavelength range, suggests that these coatings appear extremely promising for thermal detection applications in the infrared.
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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 so that the resulting rise in temperature per unit of incident radiant power is maximised [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 [2,3], their fibrous structure is very delicate and prone to ageing due to the collapse of this structure, particularly as a result of heating and physical contact.

The main requirements of black coatings for thermal detectors are fulfilled by the characteristics of carbon nanotube coatings [4]. Previously, we evaluated the performance of a 50 μm thick $LiNbO_3$ pyroelectric detector coated with a multi-wall carbon nanotube (MWCNT) coating, in the 0.9 μm–14 μm wavelength range [5]. That detector was coated with "vertically aligned" MWCNTs [6,7]. The relative spectral responsivity of that detector was shown to be flat over most the wavelength range examined, while the spectral flatness was shown to be comparable to the best infrared black coatings currently available. However, "vertically aligned" MWCNTs are difficult to grow because they require high temperatures which are higher than the Curie temperatures of many pyroelectric materials. Furthermore, current fabrication methods prohibit the growth of "vertically aligned" MWCNT coatings on non-flat surfaces. On the other hand "sprayed" MWCNT coatings are straight forward to apply on any surface because all that is required is for the MWCNTs to be suspended in a liquid; the suspension is then spayed on the surface to be coated (at room temperature) and the liquid is allowed to evaporate, leaving the "sprayed" MWCNT coating behind. The ease with which "sprayed" MWCNT coatings can be deposited, as well as their robustness, makes them very attractive options as black coatings in many applications.

A 10 μm thick pyroelectric detector which was coated with a "sprayed" MWCNT black coating was recently fabricated and its spectral responsivity was evaluated in the 600 nm–1800 nm wavelength range [8]. The spectral responsivity of this detector was shown to be flat over the 600 nm–1800 nm wavelength range [8]. However, the main applications of thermal detectors are in the infrared, where the advantages of alternative (photon) detector technologies are not so overwhelming [5]. The aim of this paper is to report the results of the evaluation of the spectral responsivity of the same "sprayed" MWCNT-coated pyroelectric detector in the infrared (wavelengths up to 24 μm). The results of the evaluation of the spatial uniformity of response of the same detector, repeated at a number of modulating frequencies are also reported, along with the results of the evaluation of the linearity of response characteristics of the same detector.

The pyroelectric detector was fabricated as a 10 μm thick freestanding film of $LiNbO_3$ with 250 nm thick nickel electrodes on each face of the crystal, as described elsewhere [9]. The $LiNbO_3$

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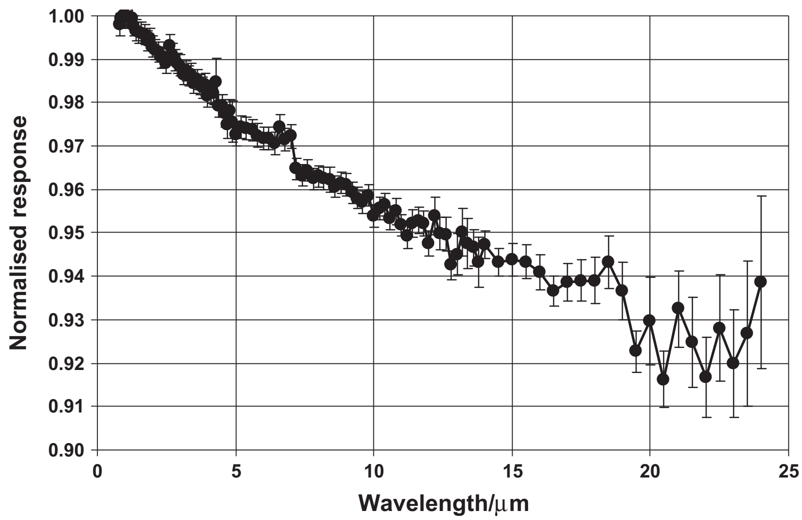

Fig. 1. Relative spectral responsivity of the "sprayed" MWCNT-coated pyroelectric detector normalised at 1.0 μm. Error bars represent the 1σ uncertainty of the measurements.

crystal was fabricated by crystal ion slicing, whereby the face of the $LiNbO_3$ plate was bombarded with high-energy helium atoms [10]. The CNT coating was prepared from commercially available MWCNTs produced by chemical vapour deposition (CVD). The MWCNTs were applied onto the detector by dispersing them in chloroform and airbrushing the suspension on the detector area. Full details about the preparation on the detector can be found elsewhere [4]. The thickness of the "sprayed" MWCNT coating is difficult to measure due to the delicate nature of the 10 μm freestanding $LiNbO_3$ film, but it is estimated to be in the 5 μm–10 μm range by comparison with similar films which were deposited on glass slides.

2. Detector characterisation facilities and method

The performance of the pyroelectric detector coated with the "sprayed" MWCNT coating was evaluated using the NPL infrared detector characterisation facilities [11]. The NPL infrared spectral responsivity measurement facility [12] was used to evaluate the relative spectral responsivity of the test detector in the 0.9 μm–24 μm wavelength range. This facility is based on a double grating monochromator of 0.25 m focal length, operating in the subtractive mode. All spectral responsivity measurements were completed using a 1.5 mm diameter spot illuminating the centre of the active area of the test detector. A 70 Hz modulation frequency was used in all spectral responsivity measurements. For all the radiometric evaluations described in this paper, the MWCNT pyroelectric detector was used in combination with a trans-impedance amplifier operated at a fixed gain of 10^8 V A^{-1}.

The linearity of response measurements were completed on the NPL linearity of response measurement facility [13] using a 70 Hz modulation frequency. The maximum level of spectral irradiance at which the linearity of response was restricted by the maximum spectral radiance available from the 2 mm wide element of the tungsten strip lamp operated at a 2500 K colour temperature. During the linearity characterisation, the unfiltered output of a tungsten strip lamp with a silica window was used. This was deemed acceptable because of the spectral flatness of the spectral responsivity of the MWCNT pyroelectric detector (see Section 3).

All spatial uniformity of response measurements reported were completed with a 0.16 mm diameter spot scanning the active area of the test detector. The spatial uniformity of response of the test detector was repeated at a number of modulating frequencies ranging from 4 Hz to 130 Hz. A two-slot chopper wheel driven by a frequency-stabilised chopper driver was used throughout the measurements reported in this document. For further information on the NPL spatial uniformity of response measurement facility the reader is referred to [11].

3. Results

Fig. 1 shows the relative spectral responsivity of the "sprayed" MWCNT-coated pyroelectric detector in the wavelength range of 0.9 μm–24 μm, normalised at 1.0 μm. The error bars shown in Fig. 1 represent the 1σ uncertainty of the measurements. It is important to remember that as far as the black coating is concerned, the relative spectral responsivity is sufficient to provide information on the spectral flatness of the absorbance of the coating. The absolute spectral responsivity of the test detector provides little extra information because it depends strongly on the properties of the pyroelectric crystal substrate, e.g. it crystal thickness, as well as other measurement parameters such as modulation frequency, method of modulation as well as the method of rectification. Fig. 1 shows that the relative spectral responsivity of this detector is relatively flat, with the relative spectral responsivity decreasing monotonically by approximately 8% over the wavelength range of 0.9 μm–24 μm. This, in turn, means that the absorptivity of the MWCNT coating was also relatively flat because the absorptivity of the coating is the main parameter governing the relative spectral responsivity of thermal detectors [1]. The small and smoothly varying reduction in the absorptivity of the "sprayed" MWCNT coating over such a wide wavelength range (0.9 μm–24 μm) is very promising because even good quality absorbers such as gold-black coatings also exhibit a reduction of a few percent in their absorbance with increasing wavelength [2,3].

A previous evaluation [8] showed that the spectral responsivity of this detector was flat in the 600 nm–1.8 μm wavelength range. Our evaluation shows that the spectral responsivity of the same detector varies by approximately 0.5% over the 0.9 μm–1.8 μm range. This is well within the uncertainty of the previous study [8] hence the results of the two studies are in agreement.

Fig. 2 shows the linearity factor of the sprayed MWCNT-coated pyroelectric detector as a function of the lock-in amplifier output (all measurements were normalised to a lock-in amplifier sensitivity setting equal to 1 V). Measurements were repeated with three different illumination conditions corresponding to a 1 mm

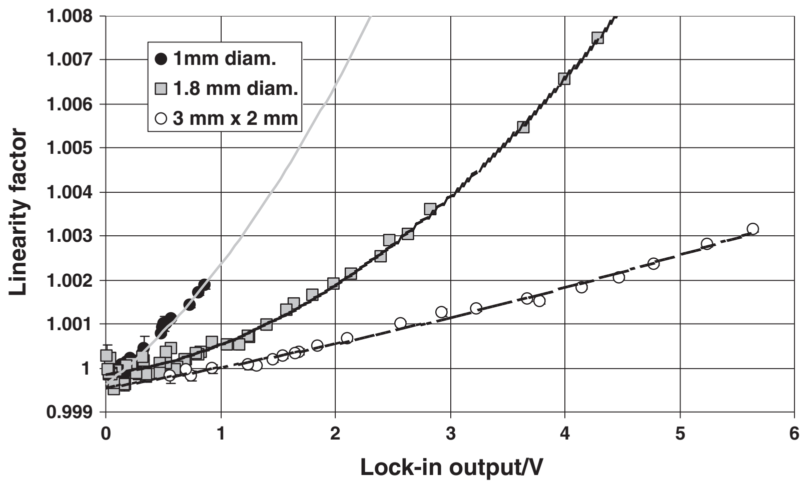

Fig. 2. Linearity factor of the "sprayed" MWCNT-coated pyroelectric detector as a function of the lock-in amplifier output for the three different spot sizes illuminating the active area of the detector. Also shown are the best quadratic fits to the data.

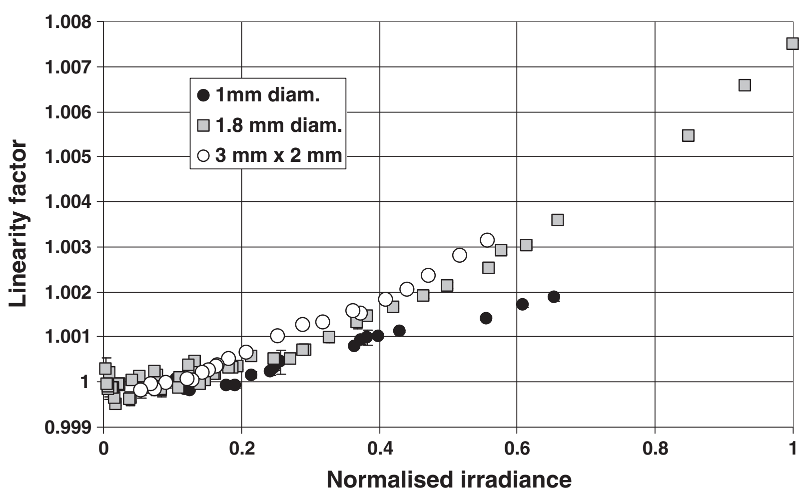

Fig. 3. Linearity factor of the pyroelectric detector coated with "sprayed" MWCNTs as a function of normalised irradiance for three different spot sizes illuminating the active area of the detector.

diameter spot, a 1.8 mm diameter spot and a 3 mm by 2 mm rectangular spot illuminating the active area of the detector. Spatial variations of the irradiance within the areas of these spots were lower than 5%. The error bars shown in Fig. 2 represent the standard deviation of eight measurements of the linearity factor at each output voltage. Fig. 2 also shows the best quadratic fits to the data. Fig. 2 demonstrates that the linearity characteristics of this detector exhibit a super-linear behaviour, i.e. its response increases as the incident radiant power increases. A similar super-linear behaviour has also been observed in DLATGS [14] as well as $LiTaO_3$ [15] pyroelectric detectors coated with metal-black coatings. A super-linear behaviour was also observed in a $LiTaO_3$ pyroelectric detector coated with a single wall CNT coating [16].

Fig. 2 shows that the plots of the linearity factor [13] of the sprayed MWCNT-coated pyroelectric detector as a function of the lock-in amplifier output corresponding to the different illumination conditions have very different slopes. The same data were therefore plotted as function of normalised irradiance and the results are shown in Fig. 3. Fig. 3 shows that the plots corresponding to the different illumination conditions show a much better overlap/agreement indicating that the linearity factor of this detector is a function of the incident irradiance rather than incident radiant power/lock-in amplifier output. Again, this behaviour is in agreement with that exhibited by a gold-black-coated DLATGS as well as some $LiTaO_3$ pyroelectric detectors evaluated previously [14,15].

Fig. 4 shows the normalised response of the "sprayed" MWCNT-coated pyroelectric detector, measured at different points on the active area of this detector. Fig. 4 shows the spatial uniformity of response at a total of eight different modulation frequencies in the 4 Hz–130 Hz range. A 0.16 mm in diameter spot was used for all spatial uniformity of response measurements reported in this document. Fig. 4 shows that the spatial uniformity of response of the test detector progressively deteriorates as the modulation frequency increases.

4. Discussion

The spatial non-uniformity of response of a pyroelectric detector can arise from the pyroelectric crystal itself (e.g. thickness variations) or from spatial variations in the properties of the black coating [17]. Typically we expect the absolute responsivity of the detector to decrease with increasing modulation frequency, and

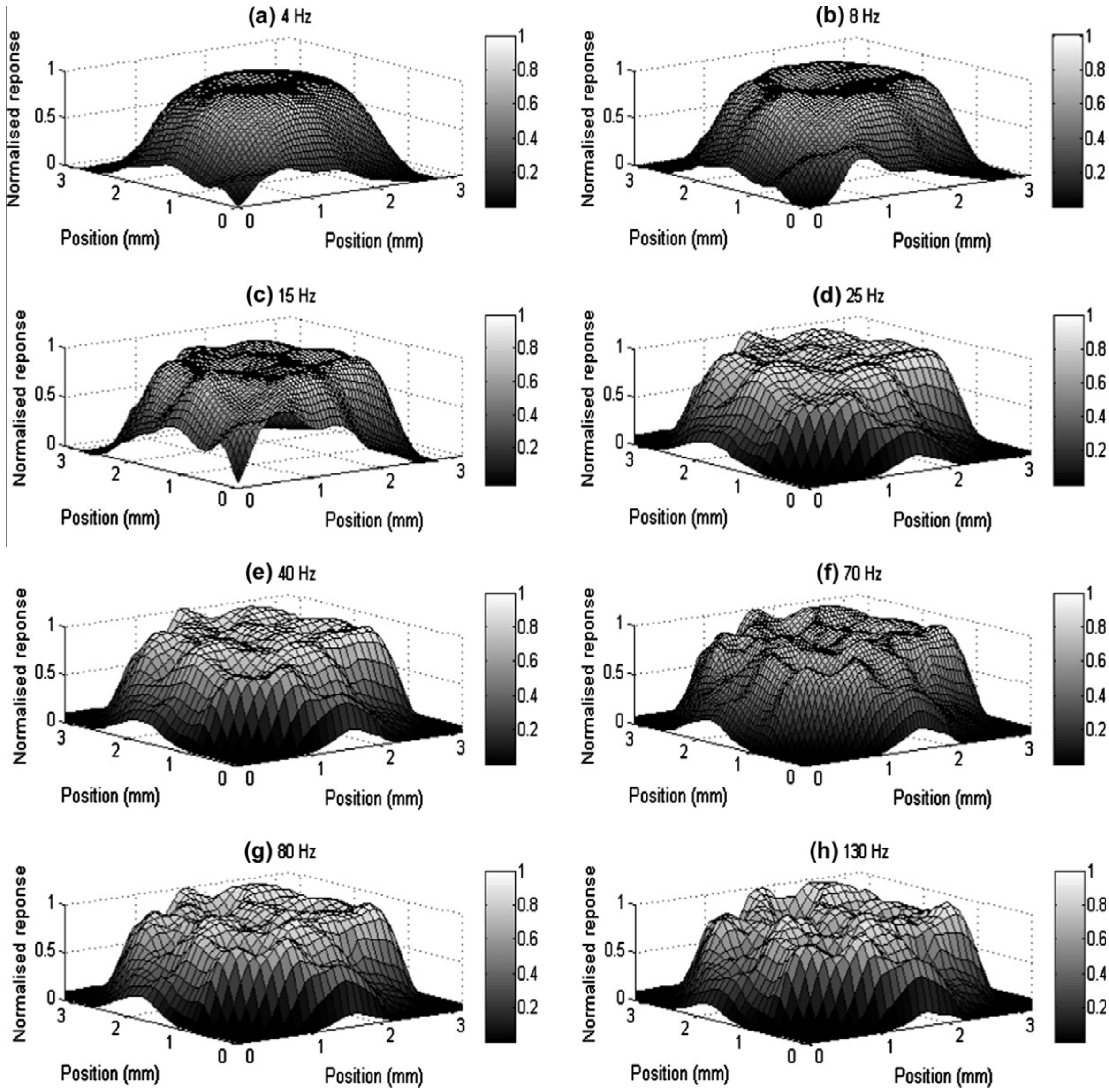

Fig. 4. Spatial uniformity of response of the "sprayed" MWCNT pyroelectric detector at eight different modulating frequencies in the 4 Hz–130 Hz range.

the spatial uniformity of response to improve (with increasing frequency) because heating of the detector does not extend through the thickness of the pyroelectric crystal. Unpublished measurements of the spatial uniformity of pyroelectric detectors based on 50 μm thick $LiTaO_3$ crystals coated with gold-black coatings show that the spatial uniformity of response of these detectors improves slightly as the modulation frequency increased from 4 Hz to 80 Hz.

The observation in Fig. 4 that the spatial uniformity of the test detector deteriorates at higher frequencies is new and contradicts what we expect for conventional black coatings [18]. Fig. 4 shows variations in spatial uniformity increasing from less than 10% at 4 Hz, to more than 60% at 130 Hz. We expect a conventional black coating, such as gold-black, to have a thermal conductivity of approximately 0.2 W/mK [1], and a MWCNT coating to be approximately 20 W/mK [19]. Therefore the results are not unexpected when we consider the relatively high thermal conductivity of the MWCNTs based on the analytical treatment by Peterson et al. [20] and the idea of thermal decay length in the context of pyroelectric films described by Muralt [21]. On this basis we can make some assertions regarding the spatial non-uniformity and frequency response of a thin pyroelectric detector. The thermal decay length is represented by $\lambda_{th} = (2\kappa/\omega c_p)^{1/2}$, where κ is the thermal conductivity, ω is the angular frequency of the modulated light input and c_p is the heat capacity per unit volume of the material. For black coatings such as gold-black or carbon paint, λ_{th} is comparable to that of the pyroelectric crystal [20]. Therefore, the one-dimensional heat transfer model is valid and spatial uniformity variations are attributable to the thickness variations of the coating and detector. In the case of the MWCNT coating, however, λ_{th} is nearly one hundred times greater than that of the detector material. At higher chopping frequencies, heat is more readily diffused laterally across the coating, rather than being coupled into the underlying detector. Thus, we believe the measurement resolves variations in coating thickness and non-uniform contact between the MWCNT bundles and the underlying pyroelectric crystal.

5. Conclusions

The relative spectral responsivity of the "sprayed" MWCNT-coated pyroelectric detector was shown to vary by 8% in the 0.9 μm–24 μm wavelength range. This change in the absorbance of sprayed MWCNT coatings over such a wide spectral range is more than tolerable in a large number of radiometric applications. The responsivity of the same detector was shown to exhibit a super-linear response, in common with other pyroelectric detectors evaluated previously. The linearity factor was shown to be a function of irradiance rather than the total radiant power incident on the detector. The spatial uniformity of response exhibited a strong dependency on the modulation frequency, indicating that thermal diffusivity of the MWCNT coating plays an important role in the spatial uniformity of response profiles observed for the test detector, at low modulation frequencies. These observations indicate that the frequency of response of a pyroelectric detector can be a useful measurement tool in future work to determine the thermal properties of MWCNTs alone.

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