

TCR, Responsivity, and Noise Properties of Carbon Nanotube-polymer Bolometric IR Detectors

Will Riedel, Gustavo E. Fernandes, Jin Ho Kim, Jimmy Xu

School of Engineering
Brown University
Providence, RI 02912 USA

william_riedel@brown.edu, gustavo_fernandes@brown.edu, jin_ho_kim@brown.edu, jimmy_xu@brown.edu

Abstract—We investigate the temperature coefficient of resistance and noise properties of polymer-infiltrated carbon nanotube membranes and their applications to infrared detection. In agreement with previous work the noise is found to be dominated by a $1/f$ contribution. We found, however, that small bolometric time constants, of ~ 10 ms, are achievable in this system in reasonably large “pixels” of $50\ \mu\text{m} \times 50\ \mu\text{m}$, which is beneficial to future applications. Contrary to our expectations, the polymer-nanotube system did not exhibit a large temperature coefficient of resistance. The possible reasons are discussed.

Keywords—Bolometer; Infrared Detection; Carbon Nanotube; polymer.

I. INTRODUCTION

Bolometric detection relies on the fact that the resistance of an object is a function of its temperature [1]. When a sensing element absorbs radiation, it heats up, increasing its temperature and changing its resistance. For short enough wavelengths (e.g., visible and near IR) conventional band gap photodetectors offer better sensitivity and speed, and are thus the preferred platform. As the wavelength increases (and the required band gap decreases), cryogenic cooling becomes a requirement for such band gap photodetectors. Bolometers, on the other hand, can operate in uncooled mode typically with wide operating temperature ranges (although they can too benefit from cooling).

There are two contributions to the resistance of a random network of carbon nanotubes (CNTs): the resistance down the length of a nanotube (i.e., the single nanotube resistance), and the contact resistances between neighboring nanotubes [2]. Because of the large conductivity of individual CNTs, the CNT network resistance is dominated by the contact resistances. Such contact resistances depend on the probability of electron tunneling between adjacent nanotubes. In a simple approximation the intertube electron tunneling probability can be modeled in the framework of a thermal activation process, i.e., it is found to be proportional to $\exp(-E/k_B T)$, where E is an activation energy corresponding to the mean potential energy of the intertube contact gaps and T is the temperature [3]. According to this simplified picture, the CNT network conductivity is proportional to $\exp(-E/k_B T)$ and its reciprocal, the resistivity, to $\exp(E/k_B T)$. The temperature coefficient of

resistance (TCR), which is given by $d\ln(R)/dT$, where R is the sample resistance, becomes proportional to $-E/(k_B T^2)$ and is thus also directly proportional to the activation energy. In principle, thus, the CNT network TCR could be increased via engineering of the activation energy E .

Various recent works have explored CNT bolometers [4-7], and found TCR values in the neighborhood of $\sim -0.5\%/K$ at room temperature. Such small TCR suggests that E is rather small for an unmodified CNT network.

However, polymers may present a readily available possibility for boosting the TCR and thus the performance of CNT bolometers. It is well known that certain polymers can be well incorporated into CNT networks [2]. Passivation of the CNTs by the polymer chains can also readily be achieved. In the latter case the polymer may infiltrate between the intertube gaps, thus providing a means to boost the intertube activation energy E . This may be expected to occur via a number of different processes including residual trapping of charges in the polymer, alteration of the intertube distances via thermal expansion, and changes in the dielectric permittivity in the intertube tunneling gap, all of which effectively change the shape and height/width of the intertube potential barriers.

In this paper, we test a simple CNT bolometric system consisting of 20 nm thin membranes of randomly oriented overlapping CNTs embedded in a polymer medium (Fig. 1). Among other bolometric parameters, we characterize its TCR, responsivity and noise figures and compare with values obtained after a hydrogel polymer is applied onto the membrane. We find that for reasonably small device sizes ($50\ \mu\text{m} \times 50\ \mu\text{m}$) very short time constants are achievable with the fabrication strategies employed here and discuss its potential implications to bolometric detection. No significant boost is observed in the TCR however, the reasons for which are discussed and believed to be related with the fabrication procedure employed. The noise figure of the CNT-polymer system shows a strong $1/f$ contribution, which is consistent with previous reports and indicates that the presence of polymer does not change the noise characteristic of the system.

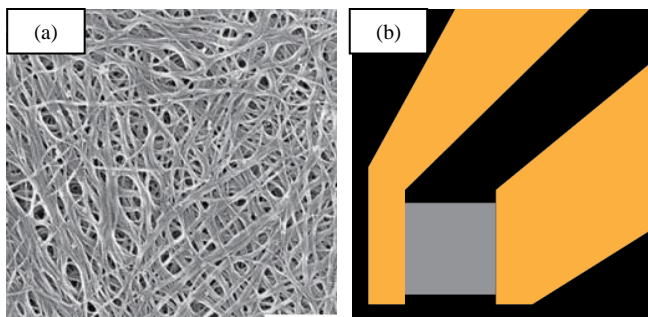


Figure 1. (a) Scanning electron microscope image of a 20 nm thick CNT membrane used in this work. The scale bar is 300 nm. (b) top-view schematic of a single device, with gold electrical contacts (orange) connected to each side of the CNT-polymer composite pixel (gray).

II. EXPERIMENTAL

A. Sample Fabrication

Square pixels of size $50\ \mu\text{m} \times 50\ \mu\text{m}$ and $200\ \mu\text{m} \times 200\ \mu\text{m}$ were fabricated as follows. First, a 20 nm thick film of carbon nanotubes was made by filtration through a membrane filter of a water-dispersed CNT solution. The commercially available CNT solution consists of sodium dodecyl sulfate (SDS) functionalized CNTs dispersed in water. The films were then transferred to a glass substrate via contact printing [8], and metallic contacts were defined directly atop the CNT film by photolithography. We used Shipley S1818 photoresist spun at 2000 rpm for 30 seconds which was exposed for 3 minutes using a Karl-Suss mask aligner. The exposed samples were then developed for 1 minute in MF-321 developer. After development, a 6 nm adhesion layer of titanium was evaporated using electron beam evaporation, followed by 75 nm of gold by thermal evaporation without breaking vacuum. Liftoff was performed in acetone to complete the contacts. Finally, a second photolithography process identical to the first was used to define the CNT pixels in the region between contacts. The remainder of the CNT membrane was etched away by plasma using a Trion reactive ion etch system. The input gas flows were 9 standard cubic centimeters per minute (sccm) argon and 13 sccm oxygen, at a pressure of 50 millitorr and input power of 100 W for 45 seconds. Next, the photoresist was removed in acetone. Wires were bonded to the contact pads using silver paste. Finally, approximately one $1\ \mu\text{L}$ drop of an aqueous poly(Nisopropylacrylamide) hydrogel solution (10 mg/mL) mixed with 1% SDS was applied to each pixel using a micropipette and the samples were annealed at $80\ ^\circ\text{C}$ for several hours to remove residual moisture from the polymer. Measurements were then repeated on the samples with polymer.

B. TCR Measurement

The sheet resistances of the samples were measured in a sealed environmental chamber kept steady at room temperature ($\sim 22\ ^\circ\text{C}$) and 1 atm. The relative humidity

(RH) value inside the measurement chamber was controlled by adjusting the flow of wet and dry N_2 (wet N_2 was obtained by flowing dry N_2 through a water bubbler) and monitored with a hygrometer. For this work the RH was fixed at 80% for all measurements, to enable partial hydration of the hydrogel medium at lower temperatures and thus to enhance the effect of hydrogel addition. The samples were mounted on a thermoelectric heater/cooler plate inside the chamber which allowed the sample temperature to be varied. Sheet resistance measurements were taken at sample temperatures between 2 and $45\ ^\circ\text{C}$ in increments of $1\ ^\circ\text{C}$. Two source measure units (Model 236, Keithley) were used for the electrical measurements. The sample temperature was adjusted and controlled via a temperature controller (LDC 3722B, ILX Lightwave) and monitored by a thermocouple that was mounted onto the Al block that served as sample stage in the chamber.

C. Responsivity Measurement

The photoresponse was measured at constant current by measuring the voltage drop across the films with a lock in amplifier (SRS830, Stanford Research). Two-point measurements were deemed adequate based on negligible contact resistance found through four-point measurements in previous studies. Illumination was provided by a 650 nm laser diode with a power intensity $3\text{W}/\text{cm}^2$. The measurements were performed at room pressure with the atmosphere in the environmental chamber kept at a constant temperature of $22\ ^\circ\text{C}$. The sample temperature was controlled independently.

Previous measurements showed that the Seebeck coefficient for CNT's is $\sim 30\ \mu\text{V}/\text{K}$ [10]. With an estimated temperature change in the sample of less than 1 K at DC, the resulting potential is too small to affect the measurement, so no adjustment was made for the Seebeck voltage.

From this data, one can construct plots of the responsivity as a function of the modulation frequency of the laser diode, from which the thermal conductance and capacitance of the sample through non-linear curve fitting, as described below.

III. RESULTS AND DISCUSSION

Fig. 2 shows the resistance and TCR for the $50\ \mu\text{m}$ sample of as a function of temperature. The resistance varies nearly linearly with temperature, and the TCR fluctuates near $-0.2\%/^\circ\text{C}$, which is similar to results for pure carbon samples [4-6]. The behavior is consistent over the entire measured temperature range. We note that the negative TCR obtained indicated that the conductivity in these CNT membranes is indeed dominated by contact effects (instead of by the $2/3$ metallic CNTs traditionally present in such membranes). However, the addition of polymer did not significantly improve the TCR compared with previous studies on CNT films [4-6]. The choice of high relative humidity for the measurement was made so that the hydrogel would

experience hydration and swelling, especially at the lower temperatures (i.e., at or below the dew point temperature), and thus significantly alter the intertube distances. However, no signature of such a process was observed.

The photoresponse also did not show any major enhancements. Fig. 3 shows the measured responsivity as a function of modulation frequency for the 50 μm sample at 15 °C. The device exhibits behavior that conforms to the well known responsivity formula [1]:

$$\mathfrak{R} = \frac{i_b R \alpha \eta}{G \sqrt{1 + \omega^2 \tau^2}} \quad (1)$$

where i_b is the bias current, α is the TCR, η is the absorption coefficient, G is the thermal conductance and $\tau = C/G$, where C is the thermal capacitance. However, the drop off is more gradual than that of the model. In this case the model was weighted to fit the low frequency behavior more closely so as to not underestimate the time constant. The obtained values of G can C for both samples are given in Table 1.

The time constants obtained from fitting (Table I) are very fast for a bolometric system. Although the response speed is partially the result of high thermal conductance due to the direct contact of the devices with the substrate, there is much room for design adjustment in our structures to improve the poor responsivity while still maintaining an effective time constant. For example, in order to improve the responsivity, the substrate thermal conductivity could be reduced, or alternatively the thermal coupling between film and substrate could be modified by addition of a thin thermally insulating film between the substrate and the CNT membrane.

To complete our analysis, we investigate the noise behavior of these bolometers. The plots of the predicted and measured noise levels for the 50 μm device are plotted vs. frequency in Fig. 4. The magnitude of noise decreases with frequency, indicating that 1/f noise is indeed the dominant source. Additionally, the measured noise agrees reasonably well with the empirical formula previously established by Snow [9] for pure CNT devices:

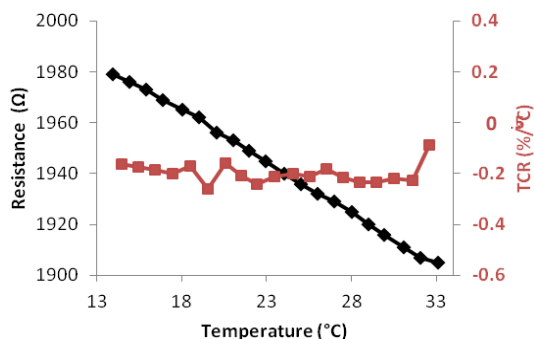


Figure 2. Resistance (black) and TCR (red) vs. Temperature for device of side length 50 μm.

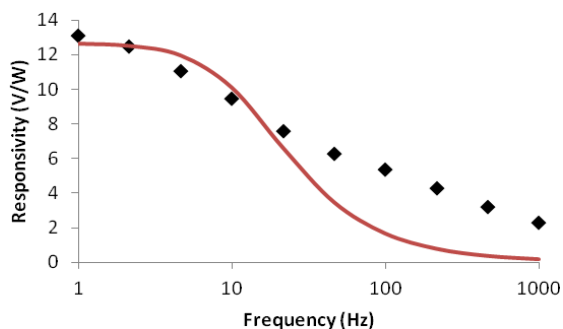


Figure 3. Responsivity vs. Frequency for device of side length 50 μm. Black dots are the measured values, red line is the modeled behavior using parameters estimated by curve fitting. Here the time constant $\tau = 12$ ms.

$$V_{1/f}^2 = (9 \cdot 10^{-11}) \frac{RV^2}{L^{1.3}f} = (9 \cdot 10^{-11}) \frac{R^3 i_b^2}{L^{1.3}f} \quad (2)$$

where L is the side length of the sample, V is the applied voltage bias, and f is the frequency of modulation. The addition of the polymer does not appear to have a substantial effect on the noise levels in the system. Near DC, the signal-to-noise ratio of the detector is only about 10, contributing to poor performance at this frequency. At higher frequencies, however, this ratio improves, and the NEP and detectivity improve as well.

Interestingly, when the photoresponse measurements are made using only a standard resistor, 1/f noise still dominates the system at low frequencies, although the magnitude is lower.

TABLE I. MEASURED DEVICE CHARACTERISTICS

	200 μm sample	50 μm sample
Thermal Conductance (μW/K)	422	38
Thermal Capacitance (μJ/K)	14	0.46
Time Constant τ (ms)	34	12
Responsivity (V/W)	1.1	12.6

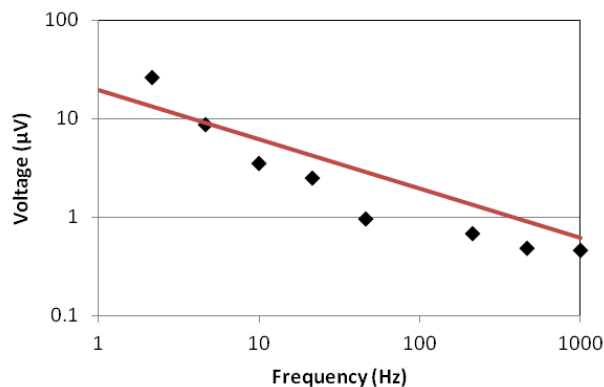


Figure 4. Noise voltage vs. Frequency for devices of side length 50 μm . The black data points indicate measured values, and the red line indicates the empirical formula given by Snow et al.

IV. CONCLUSION AND FUTURE WORK

CNT-polymer composite bolometric detectors as small as 50 μm x 50 μm were fabricated and characterized. Measurements revealed that the polymer does not have a significant impact on the TCR or time constant of the devices. Short time constants near 10 ms were achieved, suggesting the potential for use in high speed bolometric imaging applications, which are sought after.

Contrary to our expectations, the inclusion of a humidity absorbing polymer did not lead to large TCR or indeed any dramatic changes in behavior of these bolometers compared to previous reports on CNT bolometers. We hypothesize that this may have been a result of our device fabrication strategy. Although aqueous solutions of CNT were used to fabricate the CNT membranes, the subsequent processing with acetone and the liftout procedure may have stripped the surfactants (SDS) off the CNTs thus rendering them hydrophobic, which may ultimately have prevented the water based polymer solution from infiltrating into the membrane and indeed filling the intertube contact gaps.

Further work is thus necessary in order to make the fabrication procedure compatible with polymer addition. Possibly, soaking the patterned devices with SDS just prior to polymer application may improve polymer infiltration into the CNT membrane. The sensitivity could also be improved through suspension of the devices, but this will inevitably come at a cost in terms of response time.

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