Exploiting the IR Transparency of Graphene for Fast Pyroelectric Infrared Detection

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In this study, we have exploited graphene's unique combination of IR transparency and electrical conductivity to fabricate the first pyroelectric IR sensor with graphene electrodes. We find that the IR transparency of graphene enables an order of magnitude improvement in operating frequency, paving the way for faster thermal imaging than has been possible with pyroelectrics. Moreover, this is achieved without any degradation in sensitivity, as compared to pyroelectric sensors using the same polyvinylidene fluoride (PVDF) active layer. Lastly, we demonstrate that our device structure is compatible with pixelation, and fabricate an imaging system capable of capturing several thermal images from a simulated scene. Our work thus highlights a new route for the utilization of graphene for infrared sensing, with the use of organic pyroelectrics opening the door for novel curved and flexible thermal imaging applications.

Graphene, has recently generated a great deal of interest as a bolometric detector of infrared radiation. Graphene possesses a number of desirable properties for infrared sensing such as weak electron-phonon coupling and low electron heat capacity. However, its inherently low absorption remains a drawback that cannot be readily overcome and has hindered its use in large-scale, uncooled detection systems.

Here, we have identified that this perceived shortcoming is instead a unique advantage, as graphene is the only electrical conductor with uniform, near-perfect optical and IR transparency. In the IR regime, optically transparent conductors such as indium tin oxide (ITO) or silver nanowire (AgNW) films become reflective, while carbon nanotube thin films are only capable of achieving a transparency of ~50% in wavelengths near 10 µm. Thin metal films are similarly either reflective, or not as IR-transparent as graphene. Graphene, with a transparency of 97.7% in visible wavelengths and even higher transparency for doped graphene in the infrared, is thus an intriguing and unique electrode material for use in pyroelectric infrared detection.

Pyroelectric detectors operate by converting radiation into heat, which subsequently elicits a current proportional to the intensity of incident light. Conventionally, these sensors comprise a pyroelectric material sandwiched between two electrodes. The top electrode serves both as an electrical conductor, as well as an absorption layer that conducts heat from incident radiation to the pyroelectric. This mechanism hinders the response time of pyroelectric detectors and introduces heat transfer losses at the electrode–pyroelectric interface that worsen the detection.

In this study, we propose the replacement of the conventional top electrode with transparent graphene, as this should allow incident radiation to be absorbed directly by the pyroelectric. We expect this to result in faster detection, thus enabling greater spatial and time resolution in IR sensing applications such as biomedical imaging, security and surveillance, astronomy, as well as materials characterization and gas sensing. We conclude the study by demonstrating a pixelated array of our detectors for the imaging of thermal scenes.

Corona poled, 40 µm thick polyvinylidene fluoride (PVDF) films were used as the active pyroelectric layer due to their strong absorption of infrared radiation, flexibility, as well as their demonstrated compatibility with graphene. The fabricated detector array consists of nine pixels, with the top electrode being graphene and the bottom electrode a Cr/Au thin film. A schematic of the device structure, as well as pictures of the detector and its flexibility are shown in Figure 1a and b, respectively. The simplicity of device structure and roll-to-roll compatible fabrication techniques represent a considerable advantage for any future applications making use of these detectors. Figure 1c depicts the infrared absorbance spectrum of the PVDF film and the simulated IR emission of a 310 K blackbody in vacuum. Remarkably, the peak spectral radiantance of the blackbody coincides with the absorption bands of the PVDF, suggesting that our detector could be well-suited for the thermal imaging of warm bodies.

The pyroelectric response of the graphene–pyroelectric infrared (GPIR) sensors was validated by iteratively exposing them to thermal activity (Figure 1d). The positive peaks correspond to the increased oscillation of the dipoles in the PVDF

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due to the absorption of thermal energy. This oscillation causes the net surface polarization at the graphene electrode to decrease, resulting in a positive pyroelectric current. Similarly, shading the device causes cooling of polarized regions in the PVDF, which leads to a decrease in dipole oscillation. This in turn enhances surface polarization, and is recorded as a negative peak in the waveform. In both cases, the pyroelectric current is given by:

$$I_{pyro} = p \cdot A \cdot \frac{dT}{dt}$$

where $p$ is the pyroelectric coefficient of the PVDF, $A$ is the area of the device and $\frac{dT}{dt}$ is the time-varying temperature differential due to absorbed radiation.

Next, the performance of the GPIR sensors was evaluated in terms of sensitivity and frequency response. The sensitivity of sensors was quantified by the specific detectivity ($D^*$), which normalizes the noise equivalent power of the detector by the device area and noise frequency bandwidth (Supporting Information 1 for calculation and explanation). The frequency response of the GPIR sensors was quantified by the upper 3 dB cutoff frequency, $f_{3db}$, below which the device signal remains within 70.7% of its maximum.

Pyroelectric signal measurements were obtained by illuminating GPIR sensors with chopped radiation from a cavity blackbody source. Refer to experimental methods for further details of the measurement and acquisition setup. The signal of the detector for various blackbody temperatures as a function of chopping frequency is plotted in Figure 2a. The highest signal measured was 52.4 pA at a blackbody temperature of 1200 °C and a chopping frequency of 33 Hz. Signal was found to decay exponentially with frequency, with the $f_{3dB}$ calculated to be 681 Hz (Supporting Information 3 for time constant analysis). This frequency is considerably higher than conventional PVDF sensors, which typically exhibit a decay below 100 Hz. The $f_{3dB}$ frequency is also higher than that in recent works demonstrating improved response times ($f_{3dB} \sim 300$ Hz) in pyroelectric sensors with patterned top electrodes, suggesting that...
the IR transparency of graphene is indeed having an effect on detector performance.

We then verified that the high f_{3dB} frequency does not arise at the expense of detector sensitivity. Signal data was used in conjunction with noise measurements to calculate the signal-to-noise ratio (SNR) and specific detectivity, D*. SNR as a function of the chopping frequency and the blackbody temperature is plotted in Figure 2b. SNR was observed to peak to a value of 75 dB at 1200 °C and 183 Hz. The highest SNR does not coincide with the point of highest signal due to the higher contribution from 1/f noise at frequencies below 180 Hz (Supporting Information 4 for further analysis). At frequencies above 180 Hz the contribution from 1/f noise diminishes but the decay in signal leads to a drop in SNR.

Specific detectivity D* of the GPIR sensors is presented as a function of chopping frequency for various blackbody temperatures in Figure 2c. The maximum was calculated to be 7.42 × 10^6 cm·Hz^{1/2}/W, which occurs at 100 °C and a chopping frequency of 183 Hz. This sensitivity is comparable to that of other PVDF detectors, which report D* between 10^6 and 10^7 cm·Hz^{1/2}/W.[26–28] As with device signal, D* was also observed to remain consistent until a f_{3dB} of ~700 Hz. This is higher than conventional PVDF detectors whose D* starts decaying at frequencies below 100 Hz. Overall, D* was observed to peak between 160 Hz and 200 Hz; a frequency range that is also higher than for other PVDF pyroelectric sensors, which have reported peak sensitivities between 60 Hz and 100 Hz.[26–28] These comparisons determine that GPIR sensors allow faster thermal imaging than previously reported PVDF-based pyroelectric detectors, without any degradation in sensitivity.

We propose that the improved operating frequency of GPIR sensors compared to conventional pyroelectric (PIR) sensors is directly due to graphene’s unique combination of IR transparency and electrical conductivity. We explain this by contrasting their operation principles (Figure 3). In a PIR detector, incident radiation is absorbed by the top electrode, typically Ni-Cr or Au-black, which then converts it into heat (Figure 3b1). The heat needs to be subsequently conducted to the pyroelectric layer for detection (Figure 3b2); a process that relies strongly on the thermal resistance of the interface between the top electrode and the pyroelectric layer.[31] Doing so not only results in heat losses to the environment and external circuitry, but also introduces a delay between the radiation being absorbed and an electrical signal being generated. It has been demonstrated that patterning the top electrode enhances response time by allowing a portion of incident radiation to be directly absorbed by the pyroelectric. However, this comes at the expense of effective detector area since those regions are no longer electrically connected.[10] A trade-off thus arises between having sufficient metalized area for signal capture, and having sufficient exposed pyroelectric surface for improved frequency response.

In the case of GPIR sensors, this trade-off is made irrelevant, as the transparency of the top graphene electrode allows radiation to be directly absorbed by the entire pyroelectric layer. This is achieved without intermediate transfer losses and also without any delay between the radiation being absorbed and the heat being conducted (Figure 3e). Furthermore, the pyroelectric signal is collected over the full electrode area because of the graphene coverage of the pyroelectric, as compared to patterned top electrodes. As such, GPIR sensors combine the beneficial

![Figure 3. (a–c) Operation of a conventional PIR sensor. (a) Chopper closed, no incident radiation. (b1) Chopper open, radiation strikes the absorbing layer, with a portion of heat convectively dissipated to the environment. (b2) Conduction of heat from absorbing layer to pyroelectric, illustrating heat lost due to the thermal resistance of the interface and to electrical circuitry. Pyroelectric material eventually undergoes temperature change, and positive current signal observed. (c) Chopper closed. Pyroelectric material cools, and negative current signal observed. (d–f) Operation of a GPIR sensor. (d) Chopper closed, no incident radiation. (e) Chopper open, radiation is immediately absorbed by pyroelectric layer, which undergoes temperature change. Strong positive current signal observed. (f) Chopper closed. Pyroelectric material cools. Negative current signal observed.](image-url)
aspects of both fully covered (complete area utilization) and partially covered (direct absorption) electrode sensor structures. This translates into faster heat-to-signal conversion without degradation in sensitivity, which enables sustained device performance at higher frequencies. While the work presented here validates this hypothesis for PVDF-based detectors, we expect the result to hold for other pyroelectric active layers as well.

Lastly, we constructed a proof-of-concept array of our GPIR sensor to demonstrate that our structure was compatible with pixelation, and used it to image a thermal scene (Figure 4). First, dark current measurements were conducted at each of the 9 pixels to establish the baseline signal. The array was then selectively exposed to blackbody radiation at 1200 °C and the current was again recorded. The response of the pixels was calculated as the difference between light and dark currents. This procedure allowed us to quantify the amount of leak current in shaded pixels due to thermal crosstalk. Panels 4a to 4c illustrate the illumination of the letters H, O and T on the pixels, while Panels 4d to 4f depict their response. Illuminated pixels were found to generate an average signal of 82 pA with a standard deviation of ±3 pA. The average leak current for all shaded pixels, i.e., the center pixel in letter ‘O’, was observed to be 11% of illuminated device response. These results show the robustness of our methods for the fabrication of large area array detectors.

To summarize, in this study we have been the first to recognize and exploit graphene’s unique combination of IR transparency and electrical conductivity for pyroelectric infrared detection. We find that replacing the conventional electrode with graphene enables considerably faster detector operation, with our GPIR sensor capable of maintaining its sensitivity to an upper cutoff frequency \( f_{\text{DB}} \sim 680 \, \text{Hz} \). Moreover, high frequency operation does not come at the expense of sensitivity; our sensor, even at 680 Hz, maintained a \( D^* \) comparable to the peak detectivities achieved by PVDF-based detectors in literature. We propose that faster operation is due to direct absorption of radiation within the entire surface area of the pyroelectric, in contrast to detectors using absorbing or patterned electrode structures. Future work could seek to further investigate this effect by integrating transparent graphene electrodes with other pyroelectric active layers, and indeed, into other classes of photodetectors as well. Lastly, we demonstrate that our detector is capable of accurate thermal imaging, with minimal thermal crosstalk observed between shaded and illuminated pixels. We expect the simplicity of our detector structure and fabrication process, the flexibility of the materials, in conjunction with the unique absorption spectrum of PVDF, will allow our detector to unlock previously unfeasible applications in fields ranging from biomedical imaging, defense, materials characterization and gas sensing.

**Experimental Section**

CVD-grown graphene on copper foil was cut into the appropriate size and transferred with a polymer mediated process. A 400 nm thick PVDF-TrFE:DMF transfer layer was spin-coated on CVD graphene followed by an annealing step. Backside graphene was etched by oxygen plasma and then the copper foil was etched in ammonium persulfate solution. The graphene/PVDF-TrFE stack was then rinsed in DI water.

A pre-poled, 40 µm PVDF film was cut into the appropriate size. 5 nm chromium and 50 nm gold were selectively deposited by thermal evaporation to one side of the PVDF film to form the rear electrode. Another mask was used to selectively deposit 5 nm chromium and 50 nm gold on the other side of the PVDF film, to form gold the contacts for the top graphene electrodes. The PVDF film was used as a substrate to scoop the floating graphene/PVDF-TrFE stack. Graphene was patterned and isolated into 1 cm × 1 cm pixels by etching with oxygen plasma.

The response of the GPIR sensors was evaluated by illumination with a collimated IR beam (collimation angle of 0.2 mrad) emanating from a cavity blackbody source at temperatures from 100 °C to 1200 °C, in 100 °C increments. A mechanical chopper was placed near to the source point to generate signal pulses at frequencies ranging from 33 Hz to

![Graphical representation of the experimental setup](image)

Figure 4. (a–c) Photographs of selectively shaded portions of incoming radiation at 1200 °C to form letters on the surface of the GPIR detector. (d–f) Response of pixels in the GPIR detector array, taken as the difference in light and dark currents, to incident radiation.
1 kHz. Device signals were captured in ambient conditions at room temperature using a lock-in amplifier phase-locked to the chopper frequency. The use of lock-in amplification allowed us to reduce known coupling effects from the piezoresponse of the device due to acoustic noise.[33] Noise measurements were taken with a blocked beam at varying reference frequencies and blackbody temperatures, in order to account for any residual piezoeffects due to acoustic noise.

IR absorption of devices was characterized using a FTIR Spectrometer in a nitrogen atmosphere at room temperature.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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