Graphene-Based Thermopile for Thermal Imaging Applications

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ABSTRACT: In this work, we leverage graphene’s unique tunable Seebeck coefficient for the demonstration of a graphene-based thermal imaging system. By integrating graphene based photothermo-electric detectors with micromachined silicon nitride membranes, we are able to achieve room temperature responsivities on the order of $\sim$$7$–$9$ V/W (at $\lambda = 10.6 \mu$m), with a time constant of $\sim$$23$ ms. The large responsivities, due to the combination of thermal isolation and broadband infrared absorption from the underlying SiN membrane, have enabled detection as well as stand-off imaging of an incoherent blackbody target (300–500 K). By comparing the fundamental achievable performance of these graphene-based thermopiles with standard thermocouple materials, we extrapolate that graphene’s high carrier mobility can enable improved performances with respect to two main figures of merit for infrared detectors: detectivity ($>8 \times 10^9$ cm Hz$^{1/2}$ W$^{-1}$) and noise equivalent temperature difference (<100 mK). Furthermore, even average graphene carrier mobility (<1000 cm$^2$ V$^{-1}$ s$^{-1}$) is still sufficient to detect the emitted thermal radiation from a human target.

KEYWORDS: Graphene, thermal imaging, infrared, detectors, thermopile, microelectromechanical Systems

Detectors sensitive in the infrared ($\lambda = 5$–$15$ μm) have a large range of applications from infrared thermography, chemical spectroscopy, and active night vision systems.1 Graphene, due to its symmetric conical band structure and broadband optical absorption, has recently been explored as a new material for infrared photon-based detectors.2-5 Current technologies, such as high performance photon based detectors (i.e., HgCdTe), often require cryogenic cooling to mitigate noise sources such as thermally excited carriers or stray blackbody optical photons. These drawbacks can be avoided at infrared wavelengths by using thermal detectors that offer higher sensitivities at 300 K. Therefore, in this work we leverage graphene’s band structure not for optical detection but rather thermal detection in the mid-infrared.4-14 By integrating graphene-based ambipolar thermopiles with silicon microelectro-mechanical (MEMS) structures, we are able to perform thermal imaging of a blackbody source, achieving sensitivities able to detect the emitted radiation from a human hand. Analysis shows the ultrahigh carrier mobility of graphene can enable intrinsic performances surpassing state-of-the-art thermopile imagers, potentially enabling new classes of low cost, transparent, and flexible thermal imagers.

Thermal infrared detectors rely upon radiative heat transfer between the image object and the detector in order to measure small changes in temperature.15-18 This transduction mechanism can take many forms such as temperature-dependent change in resistance (bolometer)10,13,14 or thermally generated voltage via the Seebeck effect (thermopiles).1,19 In the case of our device, we leverage the latter effect using a graphene based ambipolar thermocouple as the thermal readout device.10,19,20 By developing a graphene compatible wafer scale MEMS process, we are able to thermally isolate our devices and demonstrate high sensitivity thermal detection and imaging. Figure 1a shows the graphene–MEMS integration process (see Supporting Information for more details). Utilizing the underlying silicon substrate as a sacrificial release material in conjunction with a protective poly methyl-methacrylate (PMMA) layer for the graphene, we are able to release the membrane (100 nm SiO$_2$/500 nm SiN/100 nm SiO$_2$) and the graphene without the need for any wet chemical processes. The completed device diagram and optical picture of the graphene thermopile are shown in Figure 1b,c, respectively. To increase the thermal absorption area, graphene thermocouples are placed at the periphery of the central...
suspended absorber (SiN: 100 μm × 100 μm). The graphene traverses between the cold (substrate supported side) and hot reservoirs (the suspended SiN membrane side) through the thermal isolation legs (L = 64 μm, W = 16 μm). Arrays of these graphene thermopiles are fabricated simultaneously, each containing four graphene ambipolar thermocouple junctions. The fully packaged thermopile consists of two pairs of bond pads (outside the field of view in Figure 1c) for wire bonding to the individual gates (V_G1 and V_G2) and terminals (V_M1 and V_M2) of the device. Multiple thermocouples can be measured in series for multijunction measurements through external wiring of selected thermocouples (details of device characterization can be found in the Supporting Information). The room temperature electrical resistance (R) and open-circuit photovoltage (V_PH) from a two junction device, as a function of gate voltage (measured under vacuum), are shown in Figure 2a,b. The graphene is slightly p-type doped with a maximum resistance occurring at V_G1 = +10 V and V_G2 = +20 V and a field effect mobility (μ) of ∼86 cm^2 V^{-1} s^{-1}. The open-circuit photovoltage (V_PH) response from our detector was measured with a CO2 laser input (P = 280 μW), while varying V_G1 and V_G2 simultaneously (Figure 2b). The measured V_PH shows distinctive changes in polarity due to the tunable Seebeck coefficient of graphene. Figure 2c shows the measured voltage responsivity (R_V) of our devices as a function of optical modulation frequency (f_mod). At low modulation speeds (f_mod < 30 Hz), the devices achieved an R_V of 7−9 V/W, with a thermal time constant (τ_th) of 23 ms (see Supporting Information). Compared to our previous devices, this >1000× improvement in responsivity is consistent with the thermal engineering of our isolated SiN membrane (see Supporting Information). The inset in Figure 2c shows the broadband infrared transmission (τ_SiN) of the SiN membrane, which only absorbs ∼50% of the incident light at λ = 10.6 μm suggesting even larger responsivities are possible (see Supporting Information).

However, due to the already drastic improvement in responsivity, demonstration of active thermal imaging using graphene is now possible. While many previous works utilized narrow line width and high intensity laser sources (~mW), in this work optical detection of a low power, incoherent, broadband blackbody source (Omega − 1″ diameter) is achieved, mimicking the properties of real-world thermal sources. Figure 3a shows our device characterization system for coupling the incident blackbody source with our detector (see Supporting Information). The V_PH (f_mod = 173 Hz, integration time (τ_int) = 1s) of a single graphene thermocouple was measured as a function of increasing blackbody temperature (T_0) from 372 to 534 K with the device at room temperature and under vacuum. As expected from Planck’s law for an ideal blackbody source (P ∝ T_0^4), the measured photovoltage response of our devices (V_PH ∝ T_0^{3.54}) follows a similar relationship. To perform active thermal imaging, a thermal target is placed in the imaging plane of IM1 (Figure 3c). Due to the packaging of the device inside of the cryostat, the thermal image was scanned across IM1 rather than scanning the position of the detector, which given the one-to-one mapping between conjugate image planes are equivalent operations. The thermal image was a stainless steel
aperture that was illuminated by a blackbody source ($T_0 = 472$ K) and scanned in the IM1 plane using a series of linear actuators (Thorlabs). Figure 3d,e shows the measured magnitude and phase of the photovoltage response as a function of scan position (step size $= 0.5$ mm for $x$ and $y$). The image shown clearly reproduces the starting aperture; however, the image’s spatial resolution is limited mainly by the step size of the scan, rather than the detector.

To evaluate the technological applications of this type of detector, the ultimate intrinsic performance of these graphene-based devices is evaluated. A common figure of merit for comparing various thermal detectors is detectivity ($D^*$). Assuming a thermo-electric detection mechanism and the device is Johnson noise limited,1,19,22 the material-dependent components of $D^*$ are the Seebeck coefficient ($S$) and the bulk resistivity ($\rho_\text{sh}$) (eq 1), ignoring emissivity ($\epsilon$) for now since the optical absorption is assumed to be done by the membrane or absorbing material, which is different than the sensing material

$$D^*_{\text{thermopile}} \propto \frac{S}{\sqrt{\rho_\text{sh}}}$$

(eq 1)

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Figure 4. Performance analysis of graphene thermopile. (a) Plot of graphene Seebeck coefficient (S) as a function of bulk resistivity (ρ0). Graphene Seebeck coefficient and resistance are computed utilizing a square-root charge model assuming various values of carrier mobility (μ = 1000, 8000, 50 000 cm^2 V^-1 s^-1) and a charge impurity at the charge neutrality point of n0 = 5 × 10^11 cm^-2. (b) Computed detectivity (D*) of a graphene thermopile assuming a device area (A0) = 100 × 100 μm^2, a thermal isolation leg with an aspect ratio of L/W of 5, thickness of thermal isolation membrane of 250 nm, and a thermal conductivity of 10 W m^-1 K^-1. (c) Noise equivalent temperature difference (NETD) computed directly from experimental data from Figure 3b: (blue squares) with a focal length (f) of 50.8 mm, optical absorption of silicon nitride (τSiN) from Figure 3c, and starting mobility (μ0) from Figure 2a. Red circles indicate the expected improvement in NETD due to reducing the focal length by a factor of 2, as well as assuming a 100% optical absorption (τideal) after atmospheric and window (ZnSe) transmission. The green open circles represent the additional change to NETD of the red circles due to improving the quality of the graphene mobility by 100x.

Table 1. Device Simulation Parameters

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is 2–8 × 10^8 cm Hz^{-1/2} W^{-1} for a single monolayer of graphene is already on par or superior to comparable sized thermopile devices assuming electrical noise limited devices. While D* allows us to compute the intrinsic material-dependent sensitivities of these detectors, the imaging system’s ability to differentiate between various blackbodies is better captured by a different figure of merit: noise equivalent temperature difference (NETD) shown in eq 2

\[
\text{NETD}(T_0) = \frac{V_{\text{noise,peak}}}{\frac{dV_{\text{PH}}}{dT}(T_0)} \times \frac{f_L^2}{N t D^*} \left( T_0 \right)
\]

where f_L is the total integrated optical absorption in the absorber region and f_L is the focal length. Using eq 2 and Figure 3b, the experimentally measured NETD of our system is 30–40 K (Figure 4c, blue squares); however, this value only sets an upper bound for the minimal NETD. Equation 2 also shows how NETD is dependent on other external factors of the system including both the imaging optics and the optical absorption of the infrared absorber. Figure 4c (red circles) plots the improvement (×16~20) to the NETD simply by reducing the focal length from 50.8 mm to 25.4 mm and enhancing the absorption of the SiN to 100% (i.e., deposition of carbon black) (see Supporting Information). While these extrinsic improvements can achieve a NETD of ~1 K, the mobility of the graphene in our devices ~100 cm^2 V^-1 s^-1 is still far from ideal due to doping, defects, and tears associated with transfer and device fabrication. However, improved transfer techniques in conjunction with h-BN29 suggest a 100x improvement in carrier mobility of the graphene can easily be achieved, which results in an NETD of 30–150 mK, a value that can still be lowered through improvements to the thermal isolation. In spite of these possible routes for improvement, the measured NETD of our current device already suggests the possibility of resolving the thermal radiation of a human subject (~320–330 K). Figure 5 shows the measured V_{PH} using a human hand as the thermal source instead of the calibrated blackbody source used earlier (Figure 5a). While a longer integration time (10 s) was necessary (potentially due to the variability in the position of the human hand), Figure 5b,c clearly shows that the detected presence and absence of the human hand in both the averaged phase and magnitude of V_{PH}. When the infrared radiation from a warm body is more than the ambient noise, the lock-in amplifier output tends to a constant value with a set phase. However, without a thermal source the phase of the output is unlocked and is a random value (−180°, 180°), which results in an averaged value of zero.

In conclusion, by integrating graphene technology with standard silicon MEMS fabrication, we are able to demonstrate real-world technological applications for graphene thermal imagers, imaging blackbody objects, and sensing and detecting human heat signatures. While these demonstrations have utilized current graphene technologies, improvements in graphene transfer and synthesis continue to rapidly advance, and graphene’s ultimate detector performance can exceed conventional technologies due to graphene’s unique high carrier transport, low thermal mass, and ambipolar band structure, which could be utilized for many other

Seebeck coefficient and resistance are computed utilizing a square-root charge model assuming various values of carrier mobility (μ = 1000, 8000, 50 000 cm^2 V^-1 s^-1) and a charge impurity at the charge neutrality point of n0 = 5 × 10^11 cm^-2. Therefore, as shown in Figure 4a, high mobility graphene (μ > 10 000 cm^2 V^-1 s^-1) can actually outperform other thermocouple materials, even conventional silicon based thermopiles (see Supporting Information). However, while D* depends on the ratio of S/√ρ_0 for graphene, D*thermopile ∝ √μ (see Supporting Information). Therefore, as shown in Figure 4a, high mobility graphene (μ > 10 000 cm^2 V^-1 s^-1) can actually outperform other thermocouple materials, even conventional silicon based thermopiles (see Supporting Information). However, while D* depends on the ratio of S/√ρ_0 for graphene, D*thermopile ∝ √μ (see Supporting Information).
applications in the infrared including materials inspection or even biological applications. Furthermore, utilizing back end of the line (BEOL) compatible processes with complementary metal oxide semiconductor (CMOS) technology also suggests an easy process integration path for future graphene-thermopile based focal plane arrays (FPA). 25,30 While in this work we have used an electrostatically tunable thermocouple, complementary dopants (p and n type) applied to a single layer of graphene may also be sufficient for forming a thermal sensor, which given the optical transparency of both the SiN and the graphene could enabled stacked multilayer photodetectors. 31 Finally, given that doping graphene can be done very easily by tailoring the surrounding environment (such as spin on dopants), one could also imagine completely low temperature polymer based thermopiles where the thermal isolation could be formed from a simple casting/stamping, enabling extremely low cost and transparent sensors for thermal imaging and sensing applications.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b01755.

Details with regards to device fabrication, electrical and optical characterization systems, thermal time constant extraction, analysis of improvements due to thermal isolation by suspension, derivations for D* and NETD for graphene, and comparison between graphene and silicon based thermopiles (PDF)

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Notes

The authors declare no competing financial interest.

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