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PAPER

Compact mid-infrared graphene thermopile enabled by a nanopatterning technique of electrolyte gates

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Abstract

A central challenge in making two-dimensional (2D) material-based devices faster, smaller, and more efficient is to control their charge carrier density at the nanometer scale. Traditional gating techniques based on capacitive coupling through a gate dielectric cannot generate strong and uniform electric fields at this scale due to divergence of the fields in dielectrics. This field divergence limits the gating strength, boundary sharpness, and minimum feature size of local gates, precluding certain device concepts (such as plasmonics and metamaterials based on spatial charge density variation) and resulting in large device footprints. Here we present a nanopatterned electrolyte gating concept that allows locally creating excess charges by combining electrolyte gating with an ion-impenetrable e-beam-defined resist mask. Electrostatic simulations indicate high carrier density variations of $\Delta n \sim 10^{14} \text{ cm}^{-2}$ across a length of only 15 nm at the mask boundaries on the surface of a 2D conductor. We implement this technique using cross-linked poly(methyl methacrylate), experimentally prove its ion-impenetrability and demonstrate e-beam patterning of the resist mask down to 30 nm half-pitch resolution. The spatial versatility enables us to demonstrate a compact mid-infrared graphene thermopile with a geometry optimized for Gaussian incident radiation. The thermopile has a small footprint despite the number of thermocouples in the device, paving the way for more compact high-speed thermal detectors and cameras.

1. Introduction

Modulation of charge carrier concentration of semiconductors lies at the heart of many electronic and optoelectronic device operation principles [1, 2]. This modulation is especially essential for two-dimensional (2D) van der Waals materials [3–10] where the free carrier density change is usually much stronger (2 orders of magnitude) compared to bulk materials and can be dynamically tuned with electrostatic gating methods. In recent years, rapidly developing device concepts and applications impose stronger and stronger requirements on the spatial resolution and highest-achievable carrier concentration of gating techniques. For example, a spatially sharp ($\sim 15 \text{ nm}$) p – n junction and a high carrier density contrast across the junction is the key to the realization of concepts such as tunnel diodes [11] and negative electron refractive index [12]. A strong in-plane electric field across the junction as a result of the junction sharpness facilitates electron–hole pair separation in the photovoltaic (PV) effect [13] and can thus improve the quantum efficiency of PV-based solar cells and photodetectors [14]. Many novel device concepts also rely on the ability to create metamaterials with spatial carrier density variations down to the nanometer scale, including for instance graphene with periodically doped

nanodisk or nanoribbon arrays for complete optical absorption in the visible and near-infrared [15, 16], graphene with doped waveguide, bend and resonator patterns for a plasmon-based nanophotonic network [17], and superlattices based on graphene and other 2D materials for concepts such as electron beam supercollimation [18–21]. Implementing these concepts calls for a gating method that allows for sharp p – n junctions with narrow depletion regions (~ 15 nm), a small minimum gating feature size, large carrier density contrasts (10^{14} cm $^{-2}$), strong in-plane electric fields ($> 1 \times 10^8$ V m $^{-1}$), and the versatility to generate complex spatial doping profiles within a small area.

The state-of-the-art electrostatic gating technique for modulating charge carrier concentration and creating p – n junctions is the metal-dielectric split gate technique [22–24]. This method is based on the electric field effect [25] in which electric voltages are applied across a gate dielectric to induce extra charges on the 2D material surface. A p – n junction can be created by applying opposite electric potentials to the two sides of a boundary to induce charges with opposite polarities. Although this technique is convenient, several limitations restrict its use when more extreme requirements are desirable. In terms of carrier density contrast, dielectric-based gating can only induce a carrier concentration variation Δn of less than 2×10^{13} cm $^{-2}$ for typical dielectrics such as SiO $_2$, HfO $_2$, SiN $_x$, and hexagonal-BN, due to a maximal applicable voltage across the dielectrics before the dielectric breakdown (molecular bond breakage and defects) [26–28]. In terms of junction sharpness, the carrier density has a slowly varying profile across the junction due to electric field divergence in dielectrics, with a characteristic length similar to the thickness of the dielectric, making it hard to create sharp junctions at nanoscale without using extremely thin (a few nanometers) dielectrics which typically have undesirable leakage and tunneling currents. Furthermore, due to wire-packaging difficulties and fabrication limitation of the electrodes, complex gating patterns and device geometries with large numbers of gating electrodes at the nanoscale is practically challenging.

In this paper we present a nanopatterned electrolytic gating concept that allows for a junction sharpness down to 15 nm and a minimum gating feature size of 30 nm. In contrast to dielectric-based gating, electrolyte gating can concentrate excess charges directly on the surface of the 2D material and reach a capacitance of $C = 3.2$ μ F cm $^{-2}$ (250 times higher than a typical 300 nm SiO $_2$ gate) [29–31], which enables carrier density modification up to $\Delta n = 10^{14}$ cm $^{-2}$. Since patterning of electrolyte is challenging, a general method for local electrolyte gates at nanoscale has not been demonstrated so far. To achieve this goal we introduce a lithographical masking technique based on e-beam over-exposed poly(methyl methacrylate) (PMMA) that can screen ions in electrolyte. This e-beam patterned mask can prevent the mask-protected areas from being in contact with, and thus modulated by, the electrolyte gate. Hence this technique effectively creates lithographically-defined local electrolyte gates. Previously, masking of the contacts to create electrolyte gating channels or lateral doping profiles at micrometer scale has been shown with materials such as SU-8 and hydrogen silsesquioxane (HSQ) [32–35]. However, SU-8 is more commonly used as a photoresist for microstructure patterning. Previous works have demonstrated SU-8 as an e-beam resist for nanometer size patterning, but only for large pitch structures (\sim hundreds of nm) [36], which makes it unsuitable for creating nanoscale electrolyte gates. HSQ is a high resolution e-beam resist that is capable of creating sub-10nm patterns. However, no previous studies have been performed on the usage of HSQ as a mask for electrolyte at the nanoscale or investigated HSQ's impenetrability against electrolyte ions. Here we demonstrate patterning of electrolyte gates at the nanoscale. To argue that this technique can create nanometer-sharp junctions and spatial carrier density profiles with feature sizes down to tens of nanometers, we study the junction profile and provide several experimental proofs for the ion-impenetrability of the mask.

2. Methods

2.1. E-beam cross-linked PMMA

950PMMA A Resist from MicroChem (Westborough, Massachusetts, USA) is first spun on 2D material samples. Different dilution concentration and spin speeds are used to create PMMA thin films of different thicknesses according to the spin speed curves⁸. Since volatile groups (CO $_2$, H $_2$, CH $_3$ O) and cross-linked carbon–carbon covalent bonds form during the e-beam irradiation, resultant cross-linked PMMA loses thickness compared to the original PMMA [37]. This thickness ratio was characterized to be ~ 0.6 using a Dektak stylus profiler. The resist is then baked on a hotplate at 180 °C for 2 min and exposed to electron beams with an energy of 125 keV at a dose of $\sim 80\,000$ μ C cm $^{-2}$ (or electron beams with an energy of 30 keV at a dose of $\sim 20\,000$ μ C cm $^{-2}$). Finally, the resist is developed with a mixture of isopropyl alcohol and deionized water (3:1 mixing ratio) at the temperature of 4 °C for 2 min. The unexposed PMMA thin film is removed by acetone followed by a quick rinse in isopropyl alcohol.

⁸ PMMA Data Sheet, Microchem.

2.2. Solid polymer electrolyte PEO–LiClO₄

Poly(ethylene oxide) (PEO) powder (average M_v 100,000), lithium perchlorate (LiClO₄) powder (99.99% purity) (both from Sigma Aldrich, St. Louis, Missouri, USA), and methanol are mixed in a weight ratio of 0.2:0.024:7.6. The solution is then warmed up to 60 °C and subsequently centrifuged at 14 000 rpm for 5 min to separate the long chain polymers from the liquid. The clear and transparent solution can then be spun coat or drop cast onto a sample and dried for 5 minutes before it is ready for use.

3. Results

Figure 1(a) illustrates the technique for a graphene sheet. When a voltage is applied between the electrolyte top gate and the graphene, ions in the electrolyte accumulate on the graphene surface, only in regions that are uncovered by the PMMA mask, creating an electrolyte gating pattern defined by the shape of the mask. An additional SiO₂ back gate allows weak p or n doping of the regions covered by the mask.

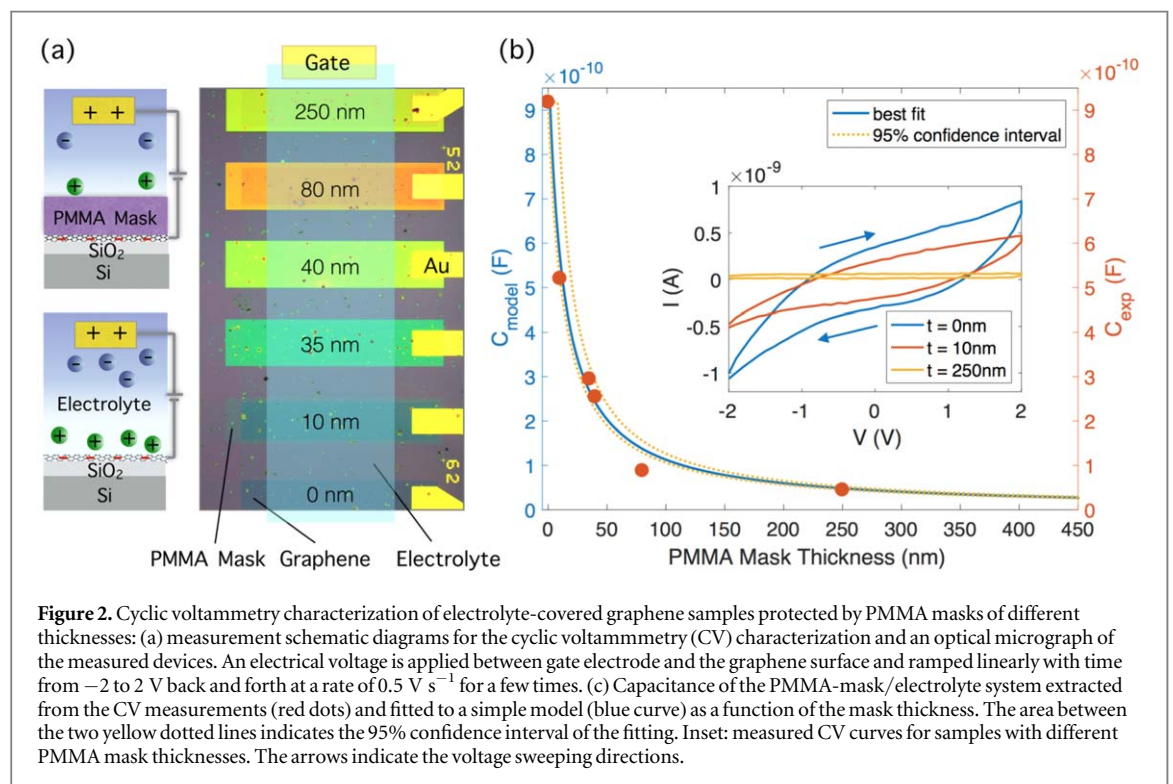
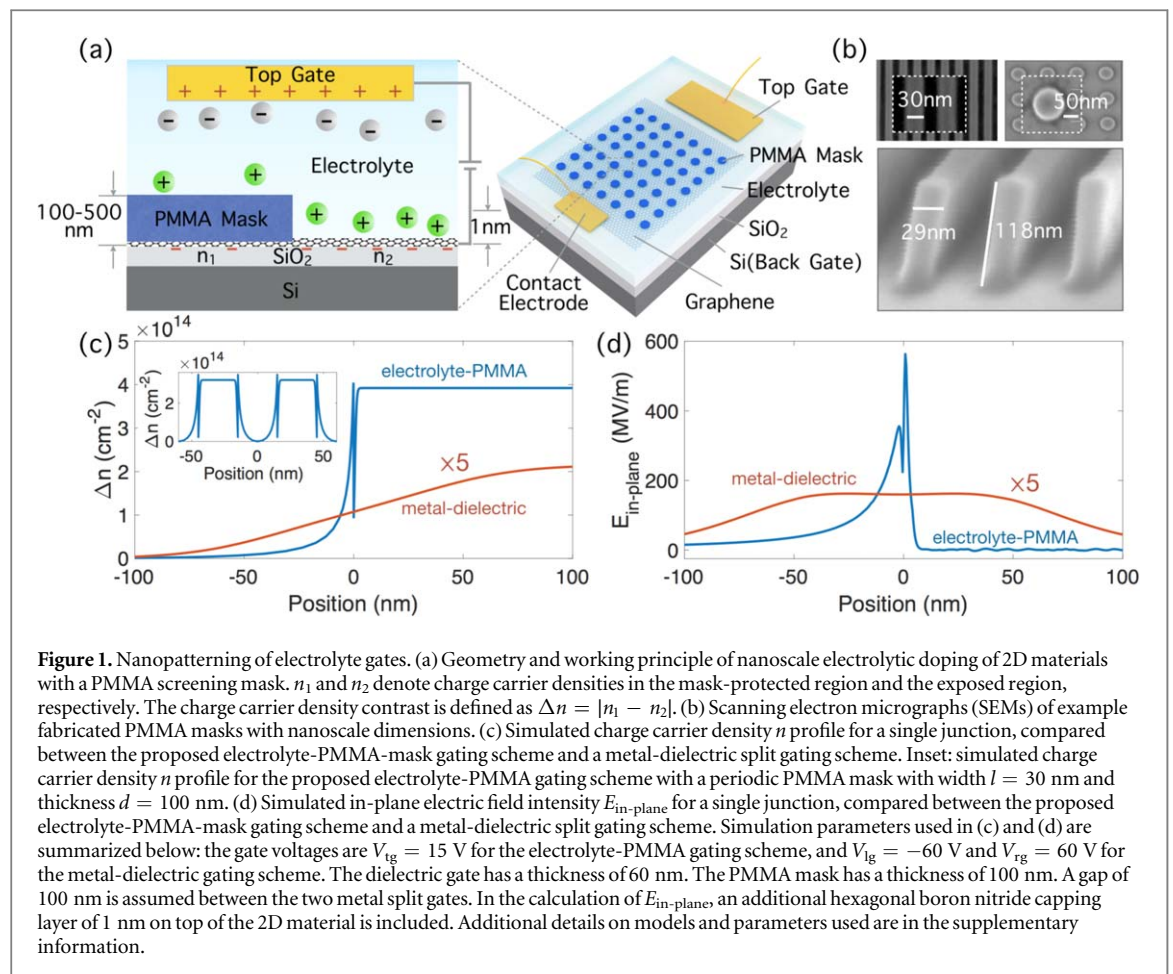
For an electrolyte gate voltage of 15 V, a carrier density contrast of $\Delta n \sim 10^{14} \text{ cm}^{-2}$ can be created at the PMMA mask boundary across only $\sim 15 \text{ nm}$, as shown in the blue curve in figure 1(c), produced by finite element simulations with COMSOL-Multiphysics [38]. Plotted in figure 1(d) in the blue curve is the calculated in-plane electric field intensity across the junction, showing a maximum magnitude as high as $E_{\text{in-plane}} = 550 \text{ MV m}^{-1}$ at the close vicinity of the mask boundary. The simulation assumes a Stern–Gouy–Chapman electrical double layer model [39] of the electrolyte ions and calculates the electric potential and the flux of ions under the influence of both ion diffusion due to the ionic concentration gradient and ion migration due to the electric field. This process is governed by the Poisson–Nernst–Planck equations. The discontinuity in the carrier density profile is caused by the difference in the electric permittivity between electrolyte medium and cross-linked PMMA mask ($\epsilon_{\text{PEO}} = 5$ and $\epsilon_{\text{PMMA}} \sim 20$). Additional details about the double layer model and parameters used in the simulation are in the supplementary information.

For comparison, the simulated doping contrast and the in-plane electric field are much lower in a metal-dielectric split gate, as indicated in the red curves in figures 1(c) and (d), rescaled for better visibility with a factor of 5. A carrier density contrast of at most $\Delta n = 2 \times 10^{13} \text{ cm}^{-2}$ (1 order of magnitude lower than that with the electrolyte-PMMA-mask technique) across a length scale of $\sim 100 \text{ nm}$ is induced when a voltage of $\sim 60 \text{ V}$ is applied, corresponding to an in-plane electric field of $E_{\text{in-plane}} = 3 \times 10^7 \text{ V m}^{-1}$. This simulation assumes a dielectric constant of 3.9 (SiO₂) and a thickness of 60 nm for the gate dielectric, and a gap of 100 nm between the two gate electrodes, which are typical values in the literature [22, 23]. The dielectric thickness and the gap width between the gate electrodes are the limiting factors for the junction sharpness. To achieve a sharpness of $\sim 15 \text{ nm}$, both the dielectric and the gap width have to be similar in size too (see supplementary information). The former would result in undesirable leaking and tunneling currents and the latter is currently challenging from a fabrication standpoint.

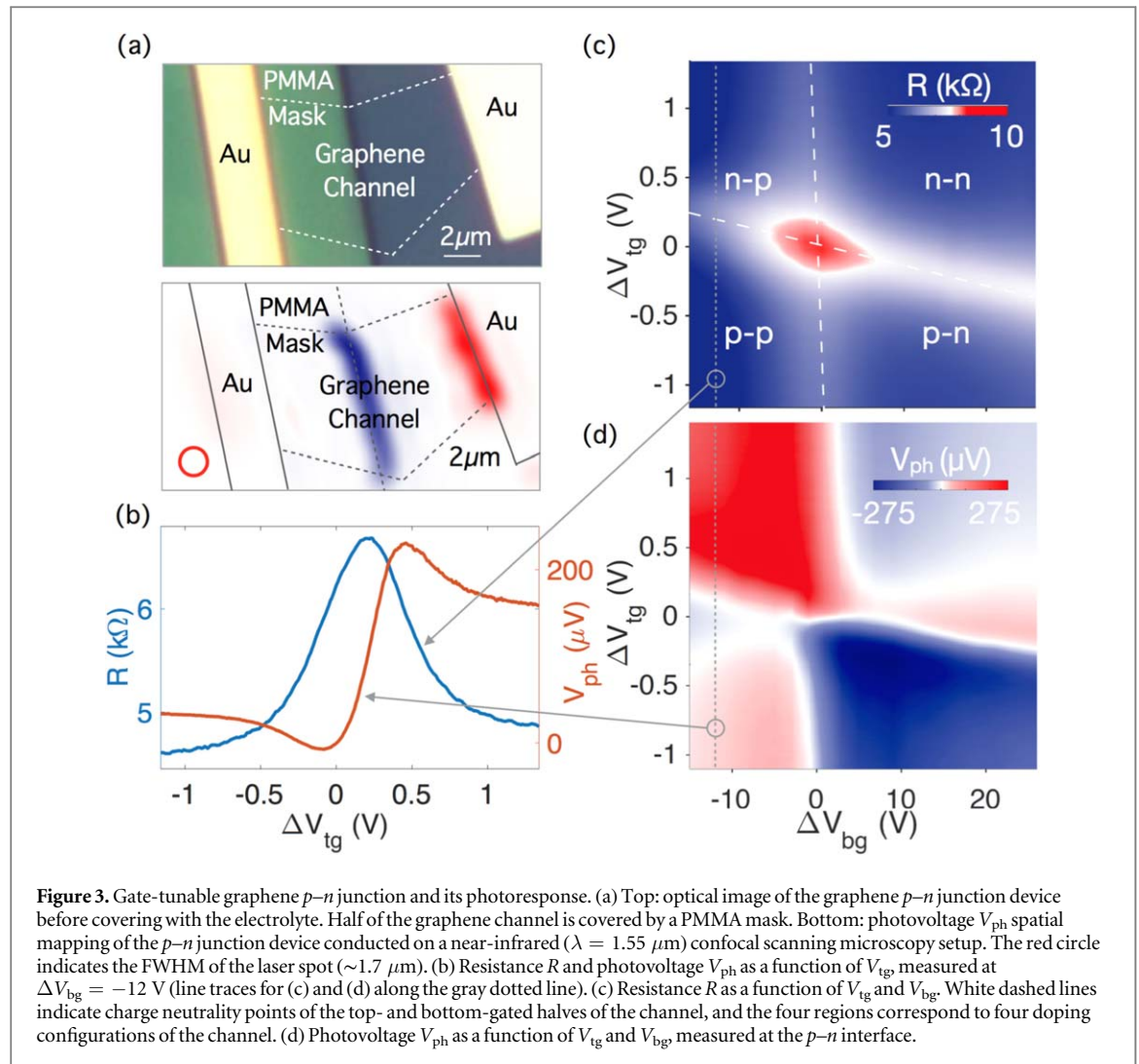
In summary, our nanopatterned electrolyte gating technique can enable nanometer-sharp junctions, and carrier density contrast and in-plane electric field orders of magnitude higher than split metal gate structures.

To implement this electrolyte gating technique with the screening mask, the choice of material for the mask is essential and several requirements need to be met. To ensure high spatial carrier density modulation resolution, the lithographical resolution of the mask has to be high. To ensure correct junction profile results calculated, the assumptions made in the simulation have to be experimentally verified for the mask of choice, which include the mask's impenetrability to ions in the electrolyte, the straightness of the mask sidewalls, and the ability for the electrolyte to fill, wet and maintain contact with finely patterned nanostructures.

One suitable candidate for the mask is e-beam cross-linked PMMA. In addition to being a high resolution e-beam resist [40, 41], the e-beam cross-linking of this material produces a high carbon atom density material matrix that is nearly impermeable to electrolyte ions. Commonly used as a positive-tone e-beam resist, PMMA becomes negative-tone when exposed at a much higher electron dose ($\sim 20\,000 \mu\text{C cm}^{-2}$) which cross-links macromolecules and transforms the resist into higher-density graphitic nanostructures through a carbonization process [42, 43, 37]. Cross-linked PMMA has good solvent resistance and its atoms are connected by shorter-range carbon–carbon covalent bonds (bond lengths 120–154 pm) instead of van der Waals force between molecules as in normal PMMA [37], making it an effective screening mask impermeable to ions ($\sim 1 \text{ nm}$) in the electrolyte. Atomic force microscopy shows a continuous and smooth resist surface (root mean square surface roughness of 0.32 nm) without major defects or pinholes, indicating uniform dielectric thickness and promising high insulation (see supplementary information). Cyclic voltammetry (CV) measurements of graphene samples covered by masks of different thicknesses (illustrated in figure 2(b)) show strongly reduced charging current for mask-protected samples, as shown in the inset of figure 2(c). The subsequent calculation and model fitting of the capacitance of the electrolyte/PMMA-mask system (figure 2(c)) confirm that cross-linked PMMA is indeed largely impermeable to electrolyte, with an ion infiltration layer thickness of only $1.5 \pm 3.4 \text{ nm}$ (see



supplementary information for a detailed discussion of the model). In separate experiments, we use scanning-electron-microscopy to image the cross section of patterned cross-linked PMMA nanowires covered with electrolyte, verifying the electrolyte's ability to wet and fill narrow slits of at least 20 nm and remain good contact



with finely patterned nanostructures (see supplementary information). These experimental findings validate assumptions we made in the simulation and support the calculated results.

The spatial carrier density modulation resolution of the local electrolytic gates is determined by two factors: the e-beam lithography resolution of the screening mask and the sharpness of the junction. As shown in the simulation, the junction sharpness is $\sim 15 \text{ nm}$, and the e-beam resolution has previously been demonstrated to be sub-10 nm [42], so the spatial modulation resolution using this technique is limited by roughly twice the junction sharpness, which is 30 nm. The simulation in the inset of figure 1(c) indicates a well-defined carrier density modulation profile resulting from periodic local electrolyte gates with a half-pitch of 30 nm. Figure 1(b) shows SEM images of examples PMMA mask on graphene with this resolution and different geometries, including disks and ribbons. The cross section of the resist mask ribbons indicates straight sidewalls.

As proof-of-principle studies, we apply this technique to demonstrate the dynamical tuning of a graphene p - n junction. The device, shown in figure 3(a) (top panel), consists of a graphene channel covered in half by a PMMA mask. The graphene is exfoliated onto a 285 nm SiO_2 substrate thermally grown on doped Si. It is then patterned by e-beam lithography and reactive ion etching into a channel roughly $10 \mu\text{m}$ in length and $5 \mu\text{m}$ in width. A pair of Cr/Au contacts and a PMMA mask are then defined by e-beam lithography. Solid polymer electrolyte PEO-LiClO₄ is then drop-casted to cover the entire device.

Large-range doping level control of the two regions in a p - n junction can be achieved by tuning electrolyte top gate and SiO_2 back gate voltages, where V_{tg} controls the mask-uncovered region and V_{bg} mostly controls the mask-covered region. Figure 3(c) shows the channel resistance R versus V_{tg} and V_{bg} , showing four distinct characteristic regions that indicate gate-voltage-tunable charge density at a p - n interface [44]. Two intersecting lines of high resistance (white dashed), representing charge neutrality points of the two regions respectively, divide the resistance map into four low-resistance regions: p - n , p - p , n - p , and n - n . A vertical line trace of the 2D resistance map along the dotted gray line, shown in the blue curve of figure 3(b), exhibits distinct Dirac peak indicating modulation of graphene's Fermi level across the charge neutrality point.

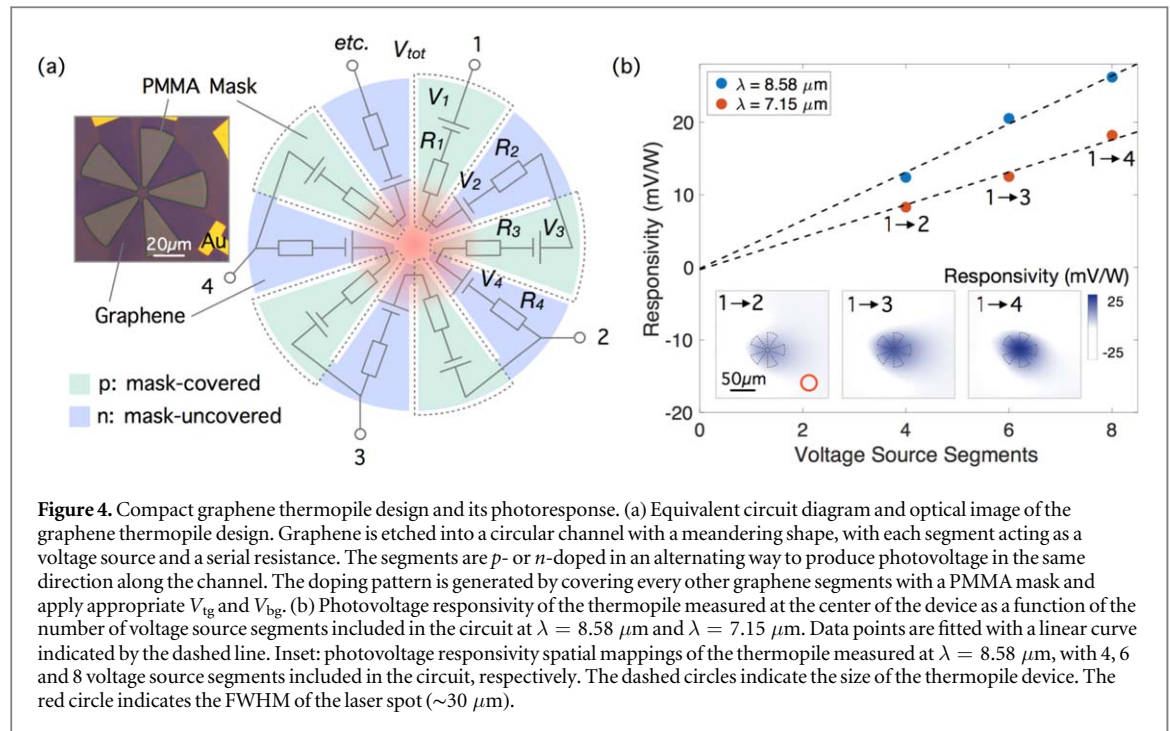


Figure 4. Compact graphene thermopile design and its photoresponse. (a) Equivalent circuit diagram and optical image of the graphene thermopile design. Graphene is etched into a circular channel with a meandering shape, with each segment acting as a voltage source and a serial resistance. The segments are *p*- or *n*-doped in an alternating way to produce photovoltage in the same direction along the channel. The doping pattern is generated by covering every other graphene segments with a PMMA mask and apply appropriate V_{tg} and V_{bg} . (b) Photovoltage responsivity of the thermopile measured at the center of the device as a function of the number of voltage source segments included in the circuit at $\lambda = 8.58 \mu\text{m}$ and $\lambda = 7.15 \mu\text{m}$. Data points are fitted with a linear curve indicated by the dashed line. Inset: photovoltage responsivity spatial mappings of the thermopile measured at $\lambda = 8.58 \mu\text{m}$, with 4, 6 and 8 voltage source segments included in the circuit, respectively. The dashed circles indicate the size of the thermopile device. The red circle indicates the FWHM of the laser spot ($\sim 30 \mu\text{m}$).

Photoresponse observed at the graphene *p*–*n* junction can also be dynamically tuned by the gate voltages. Figure 3(a) (bottom panel) shows the spatially-resolved open-circuit photovoltage map of the device under zero bias voltage across the channel, conducted on a near-infrared ($\lambda = 1.55 \mu\text{m}$) confocal scanning microscopy setup at room temperature. As the laser excitation is scanned over the device, a large photovoltage V_{ph} is observed at the electrolyte gate defined junction. This photovoltage V_{ph} at the junction as a function of V_{tg} and V_{bg} , plotted in figure 3(d), exhibits a distinct six-fold pattern with alternating photovoltage signs, showing a strong dependence of the photoresponse on the relative doping level of the graphene junction. This six-fold pattern indicates a photo-induced hot carrier-assisted photoresponse process at the graphene *p*–*n* junction known as the photo-thermoelectric (PTE) effect [45]. A vertical line trace of the 2D photovoltage map along the same dotted gray line, plotted in the red curve of figure 3(b), shows typical non-monotonic gate voltage dependence as a result of the PTE effect.

Leveraging the spatial gating versatility of this technique and the PTE effect in graphene, we design and demonstrate a compact mid-infrared graphene thermopile. The thermopile has 8 thermocouples connected in series and arranged in a geometry that optimizes voltage collection for free-space incident radiation with a Gaussian profile. The geometry flexibility of the patterned electrolyte gating technique eases the fabrication process and results in a small device footprint that is comparable to the diffraction limited beam size of mid-infrared light.

In this design a complex doping pattern of graphene is created to enhance the thermopile's photovoltage responsivity. For PTE effect, the photovoltage generated can be expressed as $V_{ph} = \int S(n, x) \Delta T(x) dx$, where S is the Seebeck coefficient of graphene, a function of charge carrier density, and ΔT is the increase in electron temperature from the environment. For free-space incident light that has a spherical Gaussian profile, the temperature gradient points in the radial direction, so the photovoltage is maximized when it is collected radially.

The designed thermopile geometry, whose equivalent circuit diagram is illustrated in figure 4(a), consists of several thermocouples connected in series whose photovoltages are all collected in the radial direction. Each graphene segment is considered a voltage source with a resistance. For the photovoltage to sum up along the meandering graphene channel, each segment is *p*- or *n*-doped in an alternating fashion so that neighboring photovoltages point in opposite directions (Seebeck coefficient has opposite signs). The alternating doping is achieved using our gating technique by covering every other segments with the PMMA mask and applying positive V_{tg} and negative V_{bg} respectively. Compared to existing graphene thermopiles such as that in [46], this approach eliminates the need for embedded gates and external wiring of thermocouples, enabling a compact thermopile based solely on graphene.

Spatially-resolved open-circuit photovoltage mapping of this thermopile is conducted on a confocal scanning microscopy setup with a mid-infrared laser source at two wavelengths $\lambda = 8.58 \mu\text{m}$ and $\lambda = 7.15 \mu\text{m}$. The photovoltage between several sets of terminals (indicated with numbers in figure 4(a)) are measured to study

the individual contributions of thermocouples. As the laser spot is scanned over the device, a maximal photovoltage V_{ph} is observed at the center of the thermopile, as shown in the photovoltage spatial maps in the inset of figure 4(b). The spatial maximum for responsivity is then plotted as a function of the number of voltage source segments between the terminals. The well-fitted linear relation at both wavelengths confirms the summation of photovoltages from each individual segment. The maximal responsivity of this device is 26.2 mV W^{-1} at $\lambda = 8.58 \text{ }\mu\text{m}$, when 8 voltage segments are included in the device. Compared to a previous graphene thermocouple with only one single $p-n$ junction, studied in similar conditions [47], the carefully designed doping pattern of graphene results in an about 7 times enhancement in photovoltage responsivity. Further optimization of parameters including device dimension and the number of voltage segments can be done to achieve higher responsivity (see supplementary information for a detailed discussion), and the device can be suspended as in [46] to benefit from higher temperature gradient as well.

4. Discussion

The flexibility to tailor the dimension and geometry of electrolyte gates on 2D materials at the nanoscale with strong doping ability expands the possibility of 2D-material-based tunable optoelectronic devices. The broadband optical transparency of the PMMA mask also ensures unaffected performance of optical designs such as waveguide and resonator modes and allows non-interfered optical spectroscopy. Moreover, although electrolyte and cross-linked PMMA can be sources of disorder that might degrade the quality of the gated material, when high sample mobility is desirable this limitation can be overcome by protecting the sample with a monolayer or few-layer hexagonal boron nitride before deposition of the electrolyte and the mask [48]. These are important practical considerations that can be crucial for the experimental implementation of many novel device concepts. Plasmonics in graphene would be an example. To achieve a plasmonic resonant wavelength of $5 \text{ }\mu\text{m}$ or less, graphene nanostructures need to have a feature size as small as 30 nm combined with high carrier densities. This typically requires direct patterning of the graphene sheet, which on this small scale would create significant edge scattering and reduce carrier mobility, limiting the quality factor of the graphene plasmonic resonances [49]. The nanoscale electrolytic gating scheme proposed here would be an alternative and promising way of generating tunable graphene plasmons with an improved quality factor and a broader wavelength range.

5. Conclusion

To conclude, we have proposed and numerically simulated a nanopatterned electrolyte gating method of 2D materials that allows for a carrier density contrast of more than $\Delta n = 10^{14} \text{ cm}^{-2}$ across a length of 15 nm and an in-plane electric field of 550 MV m^{-1} . We have developed an experimental implementation of this technique using cross-linked PMMA as the resist mask and verified its spatial patterning resolution of 30 nm , its impenetrability to electrolyte ions, the straightness of the mask sidewalls, and the ability for the electrolyte to fill, wet and maintain contact with finely patterned mask nanostructures. Taking advantage of the spatial versatility of this gating technique, we have designed and demonstrated a compact mid-infrared graphene thermopile whose geometry is optimized for free-space Gaussian incident radiation. The thermopile has a small footprint despite the number of thermocouples in the device that are connected in series, paving the way for more compact high-speed thermal detectors and cameras. This nanopatterned electrolytic gating scheme is a promising and versatile experimental approach to numerous 2D material-based device concepts in tunable nanophotonics and optoelectronics, and can potentially be used for other low-dimensional material classes too.

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