Laser enabled ultra-high doping patterns in graphene for rewritable photodetectors

Yoonsoo Rho
University of California, Berkeley

Kyunghoon Lee
University of California, Berkeley  https://orcid.org/0000-0002-3409-9454

Letian Wang
University of California at Berkeley  https://orcid.org/0000-0002-1983-5150

Changhyun Ko
Sookmyung Women's University

Yabin Chen
Beijing Institute of Technology  https://orcid.org/0000-0002-5180-2009

Penghong Ci
Shenzhen University

Jiayun Pei
Tsinghua University

Alex Zettl
University of California, Berkeley

Junqiao Wu
University of California, Berkeley  https://orcid.org/0000-0002-1498-0148

Costas Grigoropoulos (✉ cgrigororo@berkeley.edu)
University of California, Berkeley  https://orcid.org/0000-0002-8505-4037

Article

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Abstract

Chemical doping has been extensively studied for control of charge carrier polarity and concentration in two-dimensional (2D) van der Waals materials. However, conventional routes by substitutional doping or absorbed molecules suffer from degradation of the electrical mobility due to structural disorder, while the maximum doping density is set by the solubility limit of dopants. Here, we show that laser assisted chlorination can achieve high doping concentration (> $3 \times 10^{13}$ cm$^{-2}$) in graphene monolayer with minimal mobility drop, while holding reversibility and spatial selectivity. Such superior doping scheme is enabled by two lasers with selected photon energies and geometric configurations, resulting to high Cl coverage ratio (C$_2$Cl) and subsequent local Cl-removal without damaging graphene. Based on this method, we demonstrate rewritable graphene photodetector, manifesting high quality reversible doping patterns in graphene. We believe that the presented results offer a new route for chemical doping of 2D materials that may enable exotic optoelectronic applications.

Introduction

Modulation of charge density is an important subject for fundamental research and applications in 2D van der Waals materials. Chemical doping is commonly utilized to control the sign and concentration of carriers, spanning from substitutional doping$^{1,2,3,4}$ to chemical surface functionalization through covalent bonding of absorbed molecules$^{5,6}$. However insufficient dopant concentration set by solubility limit hinders high carrier concentration$^{1,2,3,4}$, and inevitably introduced structural disorder by covalent bonding impairs charge mobility$^{1,2,3,4,7}$. On the other hand, electrostatic gating$^{8,9}$ and trapped charge in dielectric layers in heterostructure$^{10,11}$ can externally modulate the charge carriers without degrading electrical mobility, but the dielectric breakdown imposes fundamental limitations to inducing high doping density. Additionally, the associated lithography process for the formation of spatially confined gate circuitry and the use of heterostructure complicates the device fabrication platform. Although electrochemical techniques, including chemical intercalation$^{12,13}$ and electrolyte gating$^{14,15}$ have shown impressively high doping concentrations, several challenges remain regarding practical device implementation and also due to the degradation of the charge mobility by unwanted electrochemical reactions$^{14,15}$. Furthermore, they are not capable of rewritable formation of highly doped patterns for arbitrary circuitry designs.

Alternatively, surface functionalization with non-covalent bonding has been proposed as a promising candidate for non-invasive and high-doping-density scheme$^{16,17}$. One of these surface functionalization systems is chlorinated graphene where the charge transfer interaction between chlorine atoms and graphene can occur via ionic bonding, according to density functional theory (DFT) calculations$^{18,19,20,21}$. Thus, graphene chlorination is advantageous over surface functionalization through hydrogenation and fluorination, where the adsorption of H and F inevitably forms sp$^3$ type C-H and C-F covalent bonding that degrades high mobility of charge carriers$^{22,23}$. In principle, ionic bonding of Cl with graphene could make the doping process reversible, implying that writing doped patterns is also possible. Experimentally,
the chlorination via photochemical and plasma treatment has shown high coverage of chlorine on graphene (close to C₂Cl)\textsuperscript{20,21,24,25}, suggesting the possibility of heavily doped graphene devices exhibiting high performance. However, the direct light illumination in the presence of Cl₂ gas induced insulating state of graphene, indicating significant defect formation\textsuperscript{24}. Another challenge associated with plasma treatment for chlorination is the high momentum of Cl due to the external electric field that causes defect formation, unless subtle plasma power regulation\textsuperscript{20,21} or metal grid\textsuperscript{25} are applied to decelerate the radical momentum. Furthermore, simultaneous photoresist process for doped pattern generation could impair the chemical binding state of dopants and it is not appropriate for applications that require rewritable doped patterns.

Here, we demonstrate a new, highly tunable doping method in graphene by laser assisted reversible chlorination. Our doping scheme can induce high doping density for practical device implementation, while possessing reversibility and spatial selectivity. We take advantage of saturable and non-invasive doping characteristics of chlorination of graphene, which is fully controlled and accessed by combining two separated laser processes using selected photon energies and geometric configurations. We achieve high doping concentration (>3×10\textsuperscript{13} cm\textsuperscript{-2} in monolayer at room temperature), while causing minimal mobility decrease. Following non-invasive Cl desorption process by photothermal CW laser annealing enables highly doped patterns in graphene. As a prime example of highly doped rewritable patterns in graphene, we demonstrate rewritable photo-active pixels in graphene photodetectors.

**Results And Discussion**

The experimental scheme for laser assisted chlorination is illustrated in Fig. 1a. We utilized ultraviolet (UV) nanosecond laser beam (\(\lambda = 213 \text{ nm (5.8 eV)}\)) which is aligned parallel to the sample surface under flowing of Cl₂ gas. The Cl₂ molecules can be photochemically dissociated by the focused UV pulsed laser and generated Cl radicals diffuse to graphene. First, we employed graphene field effect transistor device to explicitly determine the carrier density and mobility induced by laser assisted chlorination. The device was prepared based on mechanically exfoliated monolayer graphene on 20 nm thick high-k (\(\varepsilon_r \sim 20\)) HfO\textsubscript{2} layer grown on Si wafer, to access ultra-highly doped state, whereas conventional SiO\textsubscript{2} dielectric layer has limited access to doping concentration (\(\sim 5 \times 10^{12} \text{ cm}^{-2}\)) set by dielectric breakdown (Figure S1). We performed four-terminal measurement at high vacuum (<10\textsuperscript{−6} Torr) at room temperature. As doping time increased, its charge neutral point (CNP), \(V_{\text{CNP}}\), monotonically shifts to +5.6 V, indicating ultra-high p-type doping concentration (\(p > 3 \times 10^{13} \text{ cm}^{-2}\)). Meanwhile, the hole mobility (\(\mu_H\)) decreased moderately from 4,698 cm\textsuperscript{2}/V·s (pristine) to 2,551 cm\textsuperscript{2}/V·s (doped state), attributed to the increased impurity scattering (Figs. 1b and c). We note that measurement of higher doping concentration beyond this point was limited by dielectric breakdown of HfO\textsubscript{2} layer and therefore, the presented doping density is a lower bound limit. Despite the constraint, our result showed much higher doping concentration and higher mobility than liquid ionic gating\textsuperscript{26}, Xe-lamp induced Cl doping\textsuperscript{24} and Cl plasma treatment\textsuperscript{20}, while at high doping density regime, it presented charge mobility closer to the theoretical limit imposed by
phonon scattering (Supplementary Note 2)\textsuperscript{27} compared to other state-of-the-art doping methods including Li-ion intercalation\textsuperscript{12} and electrolyte gating\textsuperscript{14} (Fig. 1d).

The presented high carrier density with high mobility implies that the laser assisted chlorination process fully takes virtue of non-invasive bonding characteristics of chlorination of graphene. To understand the chemical trend in doping, we carried out Raman and X-ray photoelectron spectroscopy (XPS) analysis based on mechanically exfoliated graphene monolayer on SiO\textsubscript{2}(300 nm)/Si wafer (Fig. 2). Raman spectra near G and 2D peaks (Fig. 2a) showed that both peaks significantly blue shifted from 1584 and 2678 cm\textsuperscript{-1} to 1600 and 2689 cm\textsuperscript{-1}, respectively, while \(I_{2D}/I_G\) intensity ratio reduced from 2.8 to 1.0, indicating strong p-type doping effect\textsuperscript{28,29} (Fig. 2a). Also, no sign of defects (e.g., D peak (~ 1350 cm\textsuperscript{-1})) was observed as shown in full spectra in Figure S2. As described in Fig. 2b, the changes in Raman spectra showed monotonic shift and saturation after 5 min. We note that this trend contrasts previous reports on chlorination by plasma treatment, wherein the excessive processing time decreased the doping density\textsuperscript{20}. We attribute this difference to the significantly low momentum energy of Cl radicals generated by laser, owing to the short mean free path of Cl atoms (~ 100 nm in the limit of ideal gas approximation at 400 Torr\textsuperscript{30}), as well as the absence of external driving force such as electric field. UV nanosecond laser in parallel direction can excite Cl\textsubscript{2} electronic energy state (ground \(^1\Sigma_g \rightarrow \) excited \(^1\Pi_u\)) and break Cl\textsubscript{2} bonding\textsuperscript{31,32} without affecting surface. The generated Cl radicals diffused to the graphene surface while experiencing significant momentum reduction.

XPS analysis also revealed clear evidence of high coverage of chlorine without structural damage (Fig. 2c). As presented in the C 1s XPS spectra of pristine graphene, the narrow sp\textsuperscript{2} C-C bonding peak (at 284.4 eV) was clearly observed.\textsuperscript{33} After chlorination process, C-Cl and C-O\textsubscript{x} bonding states were evident at 286.5 and 288.3 eV, respectively\textsuperscript{33}, without sign of sp\textsuperscript{3} C-C bonding formation at 285.4 eV. In addition, the Cl 2p peak was observed after doping. The C:Cl elemental ratio was estimated to be 43.5 % based on the intensity of C and Cl peaks (Figure S4), which is close to the highest reported experimental values\textsuperscript{20,21}. However, we note that the observed high Cl coverage ratio in graphene deviates from the theoretical prediction based on free standing graphene\textsuperscript{18}: a maximum of 12.5 % Cl coverage ratio was predicted as stable stoichiometry in chlorinated graphene, when it forms ionic bonding by charge transfer complex. Higher coverage ratio exceeding this value would result in a weaker non-invasive bonding state, termed as ‘non-bonding’ where Cl element likely escape from graphene by forming Cl\textsubscript{2} molecule, due to the weak interaction between Cl and graphene. Meanwhile, recent experimental study on chlorination of graphene by plasma doping suggested potential substrate effect by showing changes in maximum Cl coverage ratio depending on the type of substrate (dielectric or metal)\textsuperscript{21}. This result implies that the substrate may affect the Cl-graphene interaction, which induced the observed unexpectedly high Cl coverage ratio.

Based on the suggested Cl binding mechanisms, we obtained the theoretically estimated doping concentration in graphene. The charge transfer rate between Cl and graphene is small in case of non-bonding state (0.03e per single Cl) due to the weak interaction\textsuperscript{18}. Considering carbon density of graphene,
(3.82 × 10^{15} \text{ cm}^{-2}), in case of C_2Cl ratio, the charge density, p can be as high as 5.73 × 10^{13} \text{ cm}^{-2}, despite the small charge transfer rate. In case of ionic bonding (charge transfer complex), which can induce 12.5% of maximum Cl coverage ratio (C_8Cl), the charge transfer rate is 0.27e per single Cl^{18}, which can result in p = 1.27 × 10^{14} \text{ cm}^{-2}. Thus, we expect that the combination of non-bonding and ionic bonding states of Cl can readily induce the experimentally observed high doping concentration.

The Cl dopant can be reversibly removed by photothermal process. We introduced CW green laser (\lambda = 532 \text{ nm (2.3 eV}) at normal direction with 2 \mu m (1/e^2) of focal size (Fig. 3a). After Cl removal by laser (25 mW and 1 min), the G and 2D Raman peaks downshifted to 1588 and 2677 cm^{-1}, respectively, and the I_{2D}/I_G intensity ratio restored to 2.5 without D peak generation, corresponding to the pristine graphene state. By subsequent re-chlorination process, hole doped state was uniformly restored over the entire graphene sheet (Fig. 3b). Based on this procedure, arbitrary doped patterns can be reversibly formed without defect as demonstrated in Fig. 3f. To elucidate the effect of CW green laser in the Cl removal process, we carried out heat transfer simulation and Kelvin probe force microscopy (KPFM) mapping. KPFM mapping was performed to resolve the spatial distribution of changes in chemical potential of graphene due to the removal of Cl beyond the optical diffraction limit of Raman probing. From the simulated temperature profile (Fig. 3c), the full width half maximum (FWHM) of developed steady state temperature profile on graphene was estimated as \sim 1.2 \mu m (Supplementary Note 10). Meanwhile, KPFM images obtained from Cl-removed spot (Fig. 3d) showed a wider distribution (\sim 1.7 \mu m, at 25 mW for 1 min) as depicted by plotting the line profile overlaid on the temperature distribution induced by the laser (Fig. 3e). Such trend suggests that the laser induced Cl desorption was dominated by thermal process. Photochemical routes typically tend to generate features smaller than the Gaussian profile laser beam focal spot size^{32,34}.

Such rewritable and highly doped patterns in graphene can demonstrate writing and erasure of photoactive junction in graphene-based photodetector as schematically depicted in Fig. 4a. We mapped the photocurrent response from the two-terminal graphene device fabricated on hBN/SiO_2(300 nm)/Si substrate with Pd electrodes. A CW laser beam (532 nm) with 1 \mu m (1/e^2) spot size at 100 \mu W power was raster scanned while collecting source drain current with zero bias voltage. The positive current indicates the excited hole moving toward source. As shown in Fig. 4b-i, pristine graphene showed significant photocurrent at metal/graphene junctions in opposite polarities due to the built-in potential developed by Fermi level pinning^{35}. Furthermore, irregular photocurrent appears at the graphene channel area, attributed to the local electron-hole puddle or unexpected local doping during the electron beam lithography process. After chlorination process (Fig. 4b-ii), photocurrent at the channel area was eliminated as the high doping concentration overwhelmed any non-uniform doping fluctuation in graphene. Also, the distance between the photocurrent peaks appeared at two opposite metal/graphene junctions of the chlorinated device increased to 7.1 \mu m, whereas its pristine state showed 5.8 \mu m, as depicted in Fig. 4c. The high doping concentration rendered sharp band bending near electrodes and the peak position of the photocurrent shifted toward the metal^{35,36}. After local Cl-removal at the center of the
channel area, the photocurrent clearly appeared in a symmetric distribution of opposite polarities (Fig. 4b-iii). The formation of p-p\(^{-}\)-p junctions in the graphene channel resulted in opposite band bending as schematically described in Fig. 4d-iii.

We attribute the observed photocurrent in channel area to the photothermoelectric (PTE) effect, which originates from the local non-uniformity in Seebeck coefficient modulated by the gradient of density of states, represented by Mott formula\(^9,37\). It has been reported that PTE effect at graphene unipolar junctions (i.e., p-p\(^{-}\) or n-n\(^{-}\) junctions) imposes photocurrent directions opposite to photovoltaic (PV) effect\(^38\), where the excited charges are drifted by built-in chemical potential. Considering the chemical potentials developed in p-p\(^{-}\)-p junctions as illustrated in the energy band diagram in Fig. 4d, if the PV effect dominates the photocurrent, the photocurrent should flow in opposite directions to our experimental results, implying that the observed photocurrent at doped junctions is driven by PTE effect. On the other hand, at metal/graphene junction, the photocurrent mechanism cannot be differentiated solely by its flow direction as the photocurrents by both PV and PTE effects have the same direction\(^39,40\). (Supplementary Note 13)

Next, the re-chlorination process can reversibly erase the photocurrent junction formed at channel area and the photodetector was ready for generation of a new photoactive pixel (Fig. 4b-iv). The line profiles of the photocurrent maps show the identical shapes in the chlorinated and re-chlorinated states of the photodetector (Fig. 4c). Thus, this result shows that the developed laser assisted reversible chlorination mechanism enables rewritable photoactive pixels in graphene photodetectors.

**Conclusion**

In summary, we proposed a new doping approach of graphene via laser assisted surface functionalization by chlorine. The parallel UV nanosecond laser enabled saturable ultrahigh doping concentration (>\(3\times10^{13}\) cm\(^{-2}\) as a lower bound limit) while showing minimal mobility drops in graphene. Then, the normal CW green laser subsequently induced local Cl-removal, enabling highly doped rewritable patterns in graphene. The Raman and XPS studies revealed that the chlorination and Cl-removal processes were free of structural damage on graphene. Further, using this method, rewritable photoactive pixel was demonstrated in graphene photodetector. We note that the presented approach is fundamentally different from previously reported studies on laser assisted chemical processing of 2D van der Waals materials that rely on direct illumination of single laser beam at the presence of doping source\(^41,42\), which induced unintentional chemical reactions degrading mobility and limited the doping concentration (Figure S9). Thus, we believe that the presented two laser beam assisted surface functionalization offers a new approach to systematically test and incorporate various dopant elements into 2D van der Waals materials. These efforts will allow, in general, the writing of a wide variety of local electronic functionalities, enabling exotic optoelectronic applications.

**Experimental Method**
• **Preparation of monolayer graphene flake**

We utilized both mechanically exfoliated and CVD grown graphene monolayers. The exfoliated graphene was used for Raman analysis, KPFM, and FET device fabrication while CVD graphene was employed for XPS analysis.

• **Chlorination and Cl-removal processes**

As-prepared graphene monolayer was placed in the laser chemical processing chamber equipped with quartz windows for access of laser beams from various geometric configurations. The 1 \% of Cl\textsubscript{2} diluted in He flows at 50 sccm at controlled pressure (400 Torr). The parallelly irradiated UV nanosecond laser beam (4 mJ, \(\lambda\)=213 nm (5.8 eV) with pulse width \(~\)16 ns at 11 Hz repetition rate) (Coherent) was focused at 500 \(\mu\)m above the graphene surface through spherical lens (f\textsubscript{~}100 mm). For the Cl-removal process, a CW laser at 532 nm of wavelength was focused by objective lens (NA=0.55) at graphene at ambient condition.

• **Raman, KPFM and XPS Characterization**

Graphene samples for Raman, KPFM and XPS characterization were prepared on SiO\textsubscript{2}(300 nm)/Si wafers. Raman spectroscopy system equipped with 532 nm excitation laser beam source at 0.5 mW and 1800 grating (Renishaw) was utilized. KPFM mapping was conducted by AFM system (Vistascope, Molecular Vista) and the details of electrical setup are in Supplementary Note 12. XPS analysis was performed by PHI 5600 XPS apparatus.

• **Device fabrication and measurement**

Mechanically exfoliated Graphene monolayer was dry transferred on HfO\textsubscript{2}/Si. Using e-beam lithography (EBL), shape and dimensions of graphene and Pd electrodes were defined, followed by oxygen etching and lift-off processes, respectively. All FET device characterization was performed based on four-point probe measurement at high vacuum (310\textsuperscript{8} Torr) and at room temperature. The details of fitting of electrical transport curve are in Supplementary Note 7.

• **Photocurrent measurement**

The photocurrent device was prepared by same procedure used for FET device fabrication. A CW 532 nm laser was mechanically chopped at 730 Hz. The source-drain voltage was zero and the back gate was grounded. The generated photocurrent was filtered at 730 Hz using lock-in amplifier.

• **Data availability**

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

**Declarations**
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Author Contributions

C.G., J.W., Y.R., and K.L. conceived the experiments and idea. C.G., Y.R., and L.W. contributed to developing the laser chemical doping process. A.Z., Y.R., K.L., and C.K. contributed to device fabrication. Y.R. and K.L. conducted all device fabrication and measurement. Y.R., Y.C., P.C., and J.P. contributed to the sample preparation and characterization. Y.R., K.L., J.W., and C.G. co-wrote the manuscript, with inputs and comments from all authors.

Conflicts of Interest

The authors declare no competing financial interest.

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**Figures**
Figure 1

The schematics of laser assisted surface functionalization by chlorine and demonstration of high doping concentration and high mobility. a) The illustration schematically depict UV nanosecond laser irradiated in parallel direction for Cl radical generation. b) Electrical transfer curves of graphene on HfO2 (20 nm)/Si wafer at pristine state, and after chlorination for various processing times from 30 s to 340 s. The inset in panels b) shows the optical microscope images of fabricated devices. The red dashed line delineates the graphene monolayer. The scale bar is 3 μm. c) Hole doping concentration, p and mobility, μ extracted from electrical transfer curves shown in panel b) depending on the processing times. d) Plots of doping concentration and mobility of this work and previous works. The data were extracted from following references: Phonon limited theoretical model27, Xe-lamp assisted Cl doping24, Cl-plasma treatment20, electrolyte gating14, 26, and Li-ion intercalation13.
Figure 2

Non-invasive and saturable characteristics of chlorination process. a) Raman spectra near G and 2D peaks of pristine and chlorinated graphene monolayer at various doping time. b) The plot of chlorination time versus Raman I2D/IG ratio and G and 2D peak positions (inset). c) XPS data before and after chlorination process near C 1s and Cl 2p peaks. Curves obtained by peak deconvolution of C 1s peak from chlorinated graphene are overlaid.
Figure 3

Reversible Cl removal process by CW green laser. a) The illustration schematically depicts site-selective reversible Cl-removal by CW green laser irradiated in normal direction. b) Raman spectra near G and 2D peaks of pristine, chlorinated, Cl removed, and re-chlorinated graphene monolayer. c) Steady state temperature profile of Graphene/SiO2/Si multilayer under the illumination of 35 mW of laser power. d) KPFM image obtained from Cl-removed area. The scale bars in panel c) and d) indicate 1 μm. e) Normalized temperature profiles ((T-T_0)/(T-T_0 )_Max, where T_0 is initial temperature) along r direction from center of graphene in panel c) in case of 35 mW of laser power, and normalized KPFM values along A-B lines in panel d). f) I2D/IG maps of graphene at various processing states. After reversible Cl-removal in designed patterns, “LTL” (a logo standing for the Laser Thermal Laboratory) can be clearly depicted from Raman maps in panel iii). v) Optical microscope image of graphene and the white dashed box indicates the Raman mapping region. The scale bars in panel f) are 4 μm.
Figure 4

Demonstration of rewritable photoactive junction using chlorination and local Cl-removal processes. a) Schematics of photocurrent mapping set up and optical microscope image of real device prepared on hBN/SiO2(300 nm) dielectric layer. The white dashed line delineates graphene monolayer b) Photocurrent mapping images of the i) pristine, ii) chlorinated, iii) local Cl-removed, and iv) re-chlorinated graphene photodetector. The green circle in panel iii) indicates the area where CW laser irradiated for Cl-removal process. The scale bars indicate 2 µm. c) Line profiles of photocurrent across the device (metal-graphene-metal, along the A-B line in panel b-i)) at each processing step obtained from photocurrent maps in panel b). d) Energy band diagrams of graphene device and direction of photocurrent at junctions in pristine i), chlorinated ii), and local Cl removed iii) states.

Supplementary Files

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