Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Ultra-clean high-mobility graphene on technologically relevant substrates

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Graphene transfer and cleaning process.

Graphene has been transferred from Cu to Si/SiO_2 using the semi-dry transfer method reported previously.[S1] Initially, CVD grown single layer graphene on Cu is coated with a 100 nm PMMA layer and heated at 90°C for 2 minutes. Also, an additional 1.5 µm PPC layer is employed for a stronger mechanical support to the graphene layer.[S1] The graphene/PMMA/PPC stack is then heated again to 90°C for 2 minutes. Furthermore, a PDMS frame is attached to the edge of the Cu foil. SLG electrochemical delamination is then performed in 1 M NaOH. Cu/SLG is used as the anode, and ~2.4 V is applied with respect to a Pt counter electrode. The voltage is controlled to keep the current ~3 mA to avoid excessive formation of H_2 bubbles, which may cause damage to SLG. The freestanding polymer/SLG membrane is then removed from the electrolyte, rinsed 2 times in DI water, then dried in air. Using a custom-built aligned lamination setup, the graphene/polymer stack is then transferred on a SiO_2/Si wafer heated to 90 °C. The PDMS is then peeled off and the polymer coating is removed by leaving the sample in acetone for 2 hours, then in isopropyl alcohol for 5 minutes, and finally dried under compressed nitrogen flow (1SC). To remove the remaining PMMA residues, the sample was immersed in remover AR600-71 for 3 minutes, rinsed in deionized water for 10 seconds, and finally N_2 blow-dried (second part of 2SC).

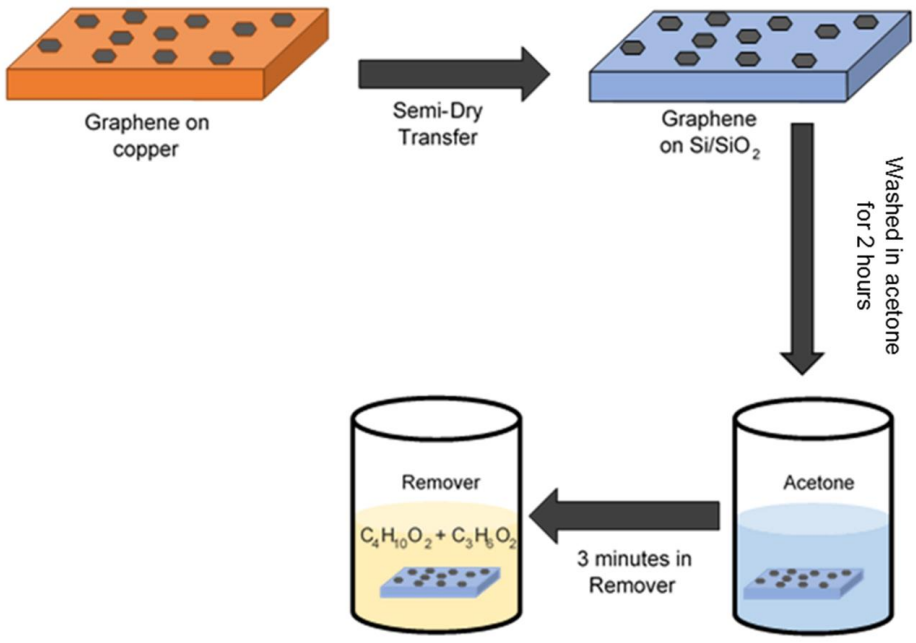

Fig. S1 Schematics of the transfer and cleaning process of CVD graphene.

Additional AFM analysis after 1SC and 2SC

Fig. S2a, b shows AFM topography images obtained at the center of the graphene crystal with RMS roughness of 3.3 nm with 1SC and 0.8 nm with 2SC which was also used for the particle analysis presented in Fig. 1d, e of main text.

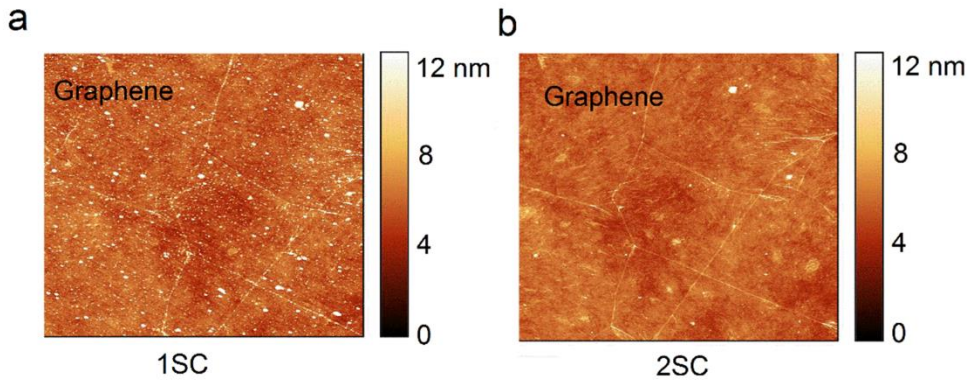

Fig. S2 (a) AFM topography image (10×10 μm^2) obtained at the center of a transferred graphene crystal after 1SC. (b) AFM topography image of the same graphene area after 2SC.

During device fabrication, RIE (O_2/Ar plasma) is used to pattern graphene, employing a PMMA etch mask. We have found that post-RIE, it is even harder to remove PMMA using 1SC, compared to post-transfer cleaning. Fig. S3a shows an AFM topography image of a patterned graphene structure after 1SC. RMS roughness of graphene surface obtained from an area of 4x4 μm^2 is 4.4 nm. As can be seen in Fig. S3b, employing 2SC, graphene surface can be cleaned just as well, with RMS roughness of the same area measured at 0.8 nm. Fig. S3c shows a line profile obtained from the same area of patterned graphene after 1SC (blue) and 2SC (red).

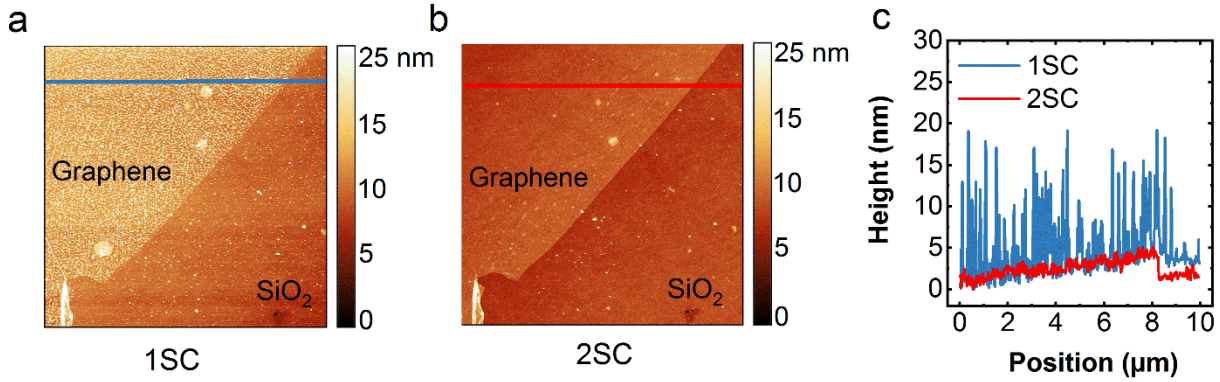

Fig. S3 (a) AFM topography image (10×10 μm^2) of patterned graphene after 1SC. (b) AFM topography image of the same graphene area after 2SC. (c) Line profiles of patterned graphene after 1SC (blue) and 2SC (red).

Raman analysis for 1S and 2S cleaning during the transfer and lithography process

For better understanding of the effects of polymer deposition on high quality graphene and subsequent cleaning, we have performed extensive Raman mapping on the same 12x12 μm^2 graphene area during device fabrication. A Raman map was obtained after each of the 2 cleaning steps following every graphene fabrication procedure (transfer, patterning and metallization). The collected data is presented in table S1 and Fig. S4. For clarity, in Fig. S4 we present the average values with respective error bars instead of the numerous data points obtained from Raman mapping.

Table. S1. Average Raman Fit Parameters from Figure S4 (a–d)

Graphene cleaning stage	Pos (G) (cm^{-1})	Pos (2D) (cm^{-1})	FWHM (2D) (cm^{-1})	I(2D)/I(G)	A(2D)/A(G)
Transfer+1SC	1586.5±0.76	2679±1.38	30.5±1.03	2.8±0.19	5.7±0.35
Transfer+2SC	1583.4±1.29	2674.9±1.8	28.06±1.85	3.13±0.48	6±0.38
Etching +1SC	1586.7±0.72	2678.4±1.18	25.7±1.32	2.3±0.31	6.7±0.77
Etching+2SC	1582.9±0.74	2675.2±1.28	24.6±0.79	3.6±0.42	7.3±0.35
Lift-off+1SC	1583.2±1.34	2673.7±2.34	25.9±1.1	3.1±0.2	7.2±0.34
Lift-off+2SC	1581.9±0.78	2673.9±1.27	23.6±1.28	4.6±0.71	7.9±0.6

The general trend of the data is that after each processing step (i. e., transfer, RIE, metallization) and 1SC cleaning, a blue shift of peak positions and a reduction in 2D/G peak intensity and area ratio is observed, compared to pristine graphene. This indicates increasing doping and strain, though this effect is reversed simply by applying the second cleaning step. 2D width, which is correlated to the nanometric strain fluctuations within the laser spot[S2], gradually improves after each step, reaching the lowest value of 23.6 cm^{-1} after metal liftoff and 2SC. This likely indicates that polymer re-deposition releases some of the strain induced in graphene during transfer, without releasing extra contamination due to the effective cleaning by the remover. We note that this 2D width is lower than is generally observed for exfoliated graphene on SiO_2.

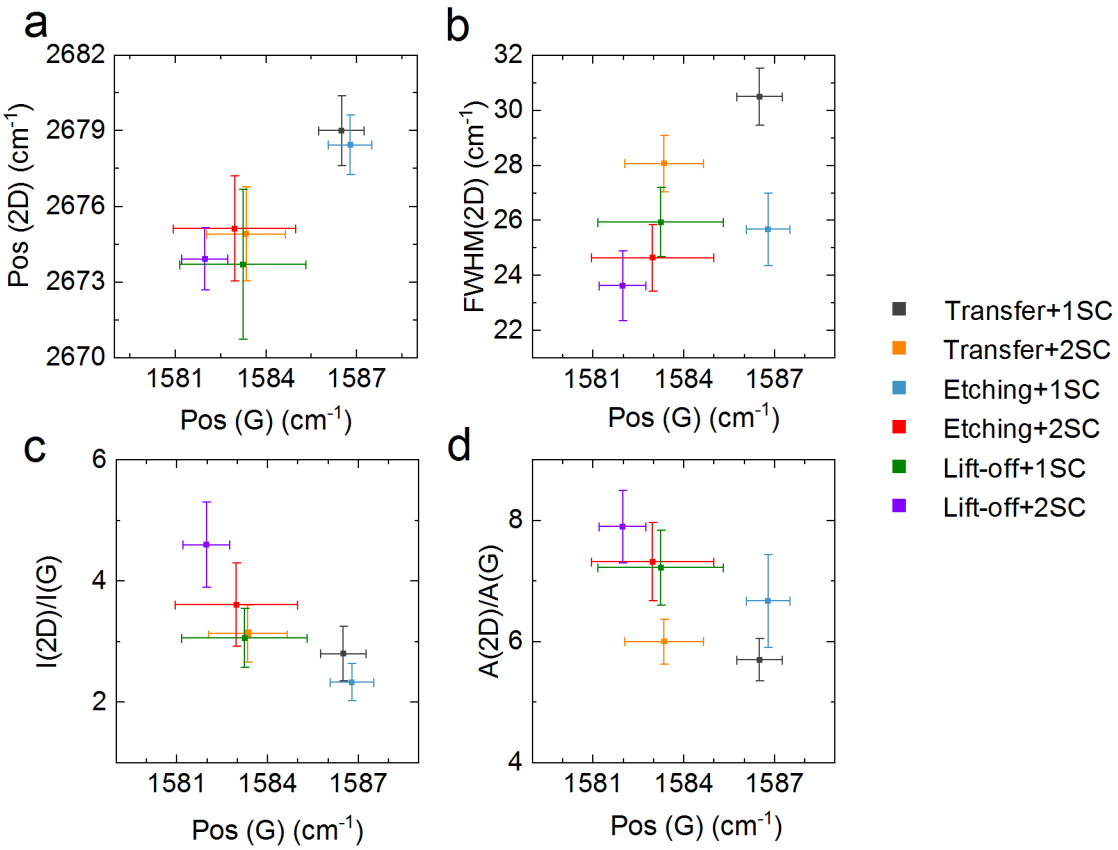

Fig. S4 Raman correlation plots after 1SC and 2SC at each transfer/processing step. (a) Pos (2D) as a function of Pos (G). (b) FWHM (2D) as a function of Pos (G). (c) 2D vs G peak intensity ratio as a function of Pos (G). (d) 2D vs G peak area ratio as a function of Pos (G).

Doping estimation from Raman 2D/G peak area ratio

As discussed in the main text, we use the methodology of Basko *et al*[S3] to estimate the doping in our samples during various fabrication steps from Raman 2D and G peak area ratio. We account for the different dielectric constant $\varepsilon(SiO_2) = 3.9$. We also note that using the electron-phonon scattering rate $\gamma_{e\text{-}ph} = 33$ meV from ref. S4 tends to overestimate the doping in our samples (when comparing Raman and electrical measurements). In fig. S5 we plot square root of Raman 2D and G peak area ratio as a function of sample doping obtained from measurements of 10 samples fabricated using 1SC and 2SC processing. As can be seen from the figure, doping dependence in our samples is described much better using $\gamma_{e\text{-}ph} = 28$ meV (blue solid line) instead of $\gamma_{e\text{-}ph} = 33$ meV (red dashed line).

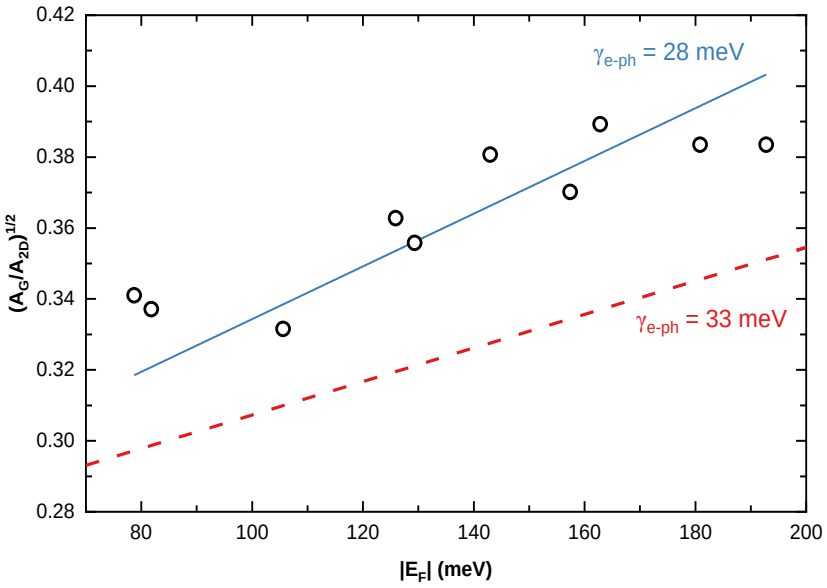

Fig. S5. Square root of Raman 2D and G peak area ratio as a function of sample doping obtained from field effect measurements (black circles). Red and blue lines show fits obtained with two different values of $\gamma_{e\text{-}ph}$, as in Ref. S4.

AFM and Raman analysis of wet-transferred graphene after 1SC and 2SC.

We demonstrate that graphene processing using 2SC can be used not only for single-crystal graphene after semi-dry transfer, but also for wet-transferred polycrystalline graphene.

Polycrystalline monolayer graphene was grown on copper foil (Alfa Aesar 46365) as reported previously.[S4] It was coated with a 200 nm layer of PMMA (AR-P 679.02, Allresist). Cu foil was etched using a copper etchant solution (30 g/L Ammonium persulfate in H_2O, Sigma-Aldrich), leaving a membrane of PMMA/Graphene floating on the surface of the etchant solution. The membrane was rinsed 3 times in deionized water to remove etchant residues. Si/SiO_2 was then used to pick up the membrane from the water and dried in ambient conditions for 1h. The sample was then baked on a hotplate at 120°C for 15 minutes to improve graphene adhesion. Subsequently, the PMMA was removed using 1SC, followed by AFM and Raman characterization. The second cleaning step was then performed and the sample was again characterized using AFM and Raman spectroscopy.

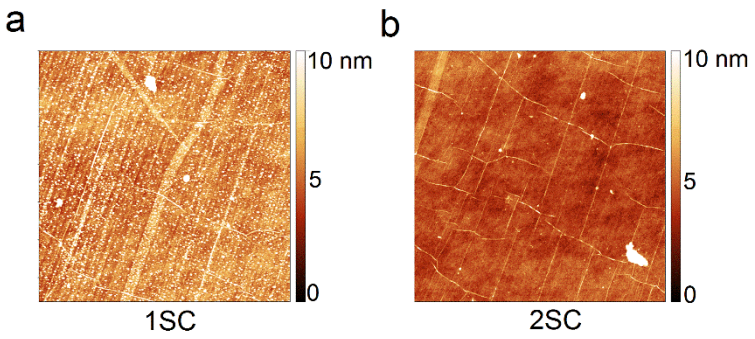

Fig S6. (a) AFM topography image (6×6 μm^2) taken after transferring polycrystalline graphene on SiO_2/Si after 1SC and (b) 2SC.

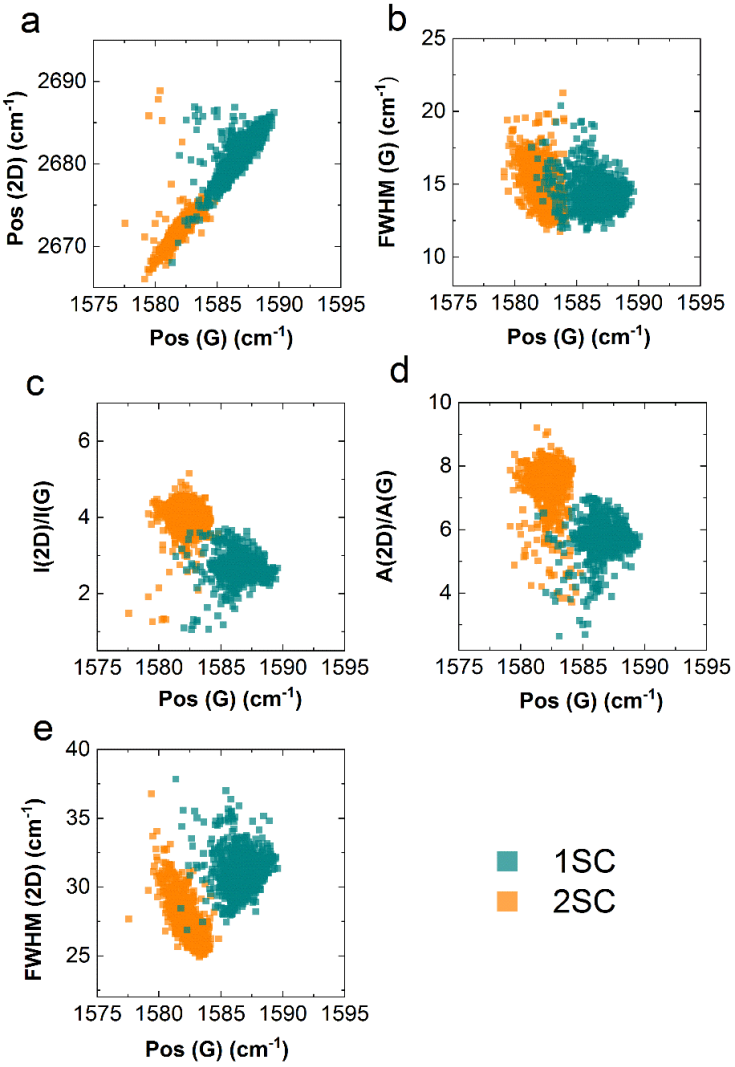

Fig. S7 (a) Pos (2D) as a function of Pos (G). (b) FWHM (G) as a function of Pos (G). (c) I2D/IG ratio with respect to the Pos (G). (d) Area ratio of 2D and G peaks and e) FWHM of 2D-peak as a function of Pos (G) of polycrystalline graphene after 1SC and 2SC.

As is visible from AFM and Raman analyses, the effect of 2SC in removing polymer residues, reducing strain, and doping, is similar also when applied to continuous polycrystalline graphene, and not only for graphene single crystals.

XPS parallel imaging for 2S cleaning taken in the C1s and Si2p region

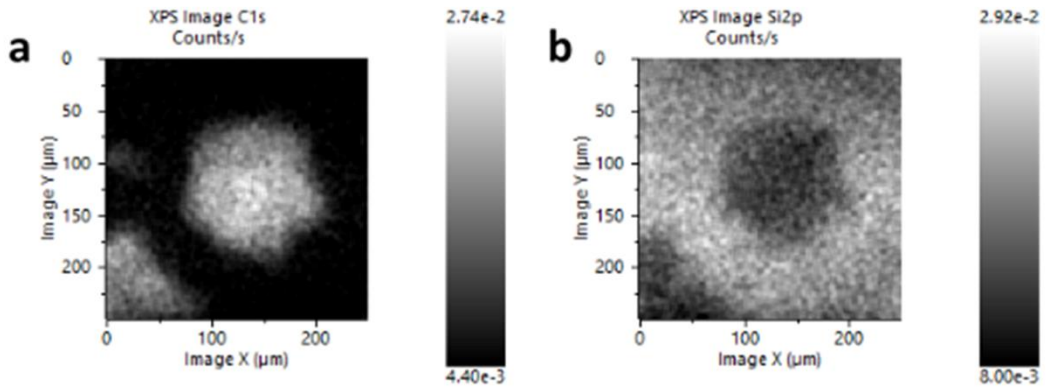

Fig. S8 Parallel XPS Imaging of a graphene crystal after transfer to SiO_2/Si and 2SC measured at binding energies of (a) 284.5 eV and (b) 102.5 eV.

In Fig. S8, we show two different images taken on the same region (250x250 μm^2) of a sample, centered on an individual flake after 2 SC at different binding energies in order to obtain a chemical map of C1s and Si2p intensities. In Fig. S7(a) the higher intensity of carbon gives a clear view of the flake. Nevertheless, such contrast might be related to topographic effects. However, in Fig. S8(b), the intensity of the Si2p peak related to the Si substrate is obviously higher outside of the flake. Such data suggest that the Si2p peak intensity is screened by the graphene flake. This indicates that, indeed, chemical mapping is performed.

References

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