Terahertz Imaging and Time-Domain Spectroscopy of Large-Area Single-Layer Graphene

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Supporting Information

I. Graphene Growth

Part 1: Preparing Copper Foils

1. Obtain Alfa Aesar .025mm copper foils in a 30×30 cm sheet
2. Take copper sheet out and cut sheet into long strips with width of 2.5 - 3 inches
3. Store these strips in Tupperware (clean, airtight plastic container)
4. Take one strip of foil and cut a ribbon .5 - .75 inches by 3 inches
5. Cut the ribbon of copper into square shaped thirds, around .75 inches square
6. On one edge of the copper cut a small triangle to indicate the top orientation (*Figure S1*)
7. Place the three copper squares between two glass slides (label outside of slides "out" to note which sides are clean)
8. Use a paperclip to clip the glass slides together and flatten the copper foils

Part 2: Preparing Growth

1. Remove copper foil from glass slides
2. Treat the foil with the following baths:
    i. Acetone (10 Sec.)
    ii. Water (10 Sec.)
    iii. Acetic Acid (10 min.)
    iv. Water (10 Sec.)
    v. Acetone (10 Sec.)
    vi. IPA (10 Sec.)
3. Use nitrogen gun to gently remove remaining IPA
4. Place copper foils in the center of the 1" quartz tube that is in the furnace, with the cut out triangle oriented downstream.
5. Close the quartz tube and check for leaks.
6. Leak checking: Open all flow lines that are downstream of the flow controllers. Flow Argon at 200sccm, and squirt soap water solution around the seals to make sure there are no leaks. Turn off the Argon flow
7. Turn on the vacuum pump and allow the system to reach a base pressure < 10 millitorr.

Part 3: Growth

1. After base pressure is achieved, flow 6sccm of hydrogen. The pressure should rise to ~120 millitorr.
2. Set furnace temperature to 980°C.
3. Anneal in hydrogen at 980°C for 10 minutes.
4. After anneal, flow 157.5sccm of methane for 13 minutes. Pressure should rise to ~5.5 torr.
5. After 13 minutes, turn the furnace off, and prop the lid open 2-3 inches.
6. When temperature reaches 450°C, open the furnace completely.
7. Allow to cool down past 150°C.
8. Once cool, flow Argon at 200sccm and turn the methane and hydrogen off.
9. Allow the Argon to flow for an additional 2 minutes.
10. Turn off vacuum pump and remove your samples.

II. Graphene Transfer

To transfer the graphene from the copper foil to a prefered substrate the following method was used.

1. After growth of graphene on copper foil spin on 950MW A8 PMMA @ 4000RPM for 60 seconds.
2. Bake @ 145°C for 60 seconds.
3. Float foil on Transene CE-200 copper etchant until copper is gone. (~6 hours)
4. Scoop graphene out into six sequential baths of DI water, soaking for 2 minutes in each bath.
5. Scoop graphene out of the final bath with the target substrate. (In our case we used intrinsic undoped [1,0,0] SEMI prime Si wafers with R_0>10,000Ωcm)
6. Nitrogen dry blowing from center outward to flatten all wrinkles.
7. Allow to air dry in fume hood for 6 hours. (don't use a hot plate to “speed” this up)
8. Soak in methylene chloride for 6 hours.
9. Soak for 10 minutes in acetone.
10. Soak for 10 minutes in IPA.
11. Dry with nitrogen.

III. Fabrication of van der Pauw square devices

In order to measure sheet conductivity the following procedure was followed to make 200um van der Pauw devices.

1. Pre-bake the graphene on Si samples at 190°C for 5 minutes on a hotplate to dehydrate.
2. Allow to cool briefly and place on spin coater.
3. Completely coat the surface with P-20 HDMS primer and allow to sit for 30 seconds.
4. Spin for 30 seconds at 4000RPM.
5. Immediately spin coat with S1813 photoresist for 30 seconds at 4000RPM.
6. Expose for 6 seconds with electrode mask (Figure S2) in contact aligner.
7. Develop in MF-321 for 90 seconds
8. Thermally evaporate 1nm of Cr followed by 50nm of Au.
9. Lift off excess metal in a 24 hour bath of 70°C PG remover.
10. Rinse with DI water.
11. Nitrogen dry.
12. Repeat steps 1-7 except expose with graphene shaping mask.(Figure S2)
13. Use an RIE to etch away exposed graphene. (200mTorr, 25sccm O_2, 75W, 60 seconds)
14. Remove the remaining photoresist with a 24 hour soak in 70°C PG remover.
15. Rinse with DI water.
16. Nitrogen dry.

To verify cleanliness and proper alignment of the electrodes an atomic force microscope (Asylum Research, MFP3D) was used. An AFM image is shown in Figure S3.

IV. Sheet resistance measurements of van der Pauw squares

To obtain the average sheet resistance for our devices the following procedure was followed:

1. Apply I_{34} ~ 100 μA from electrode 3 to electrode 4 (Figure S4), and measure the potential V_{12} across electrodes 1 and 2.
2. Apply I_{41} ~ 100 μA from electrode 4 to electrode 1 (Figure S4), and measure the potential V_{23} across electrodes 2 and 3.

Eight devices were measured in this way (Table 1). The devices were positioned across the graphene film (the same film that was imaged by THz). We note that all of the $I(V)$ relationships were linear within the measurement range (0 – 100 μA).

The van der Pauw square devices were built on a high-resistivity Si substrate. Therefore, a small amount of the current (approximately 3%) leaked through the bulk substrate, rather than passing through the graphene. We estimated the magnitude of the shunt current by measuring control structures on high-resistivity Si. The geometry of the control structure was identical to Fig. S4, except the graphene was not present. In control devices we found two point resistances (V_{34}/I_{34} etc.) > 30 kΩ. In contrast, the two-point resistances of the graphene devices were ~ 1 kΩ.

V. Figures

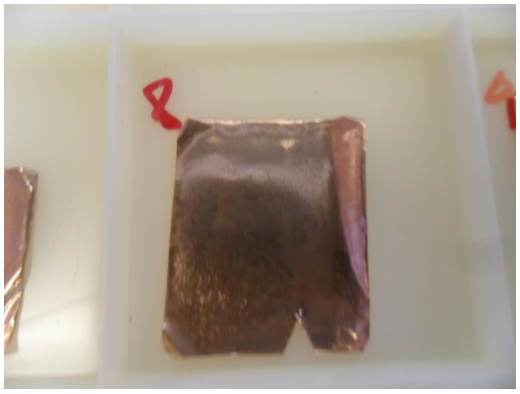

Figure S1. Copper foil with CVD graphene grown following the methods from section I.

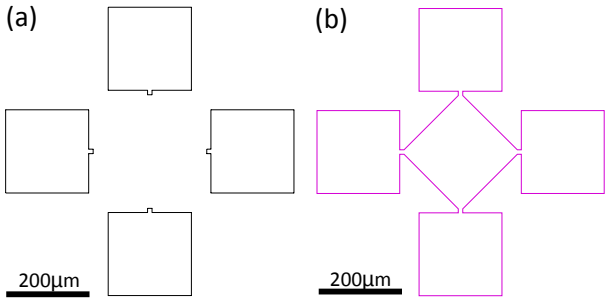

Figure S2. Mask patterns for van der Pauw devices (a) Electrodes (b) Graphene shaping

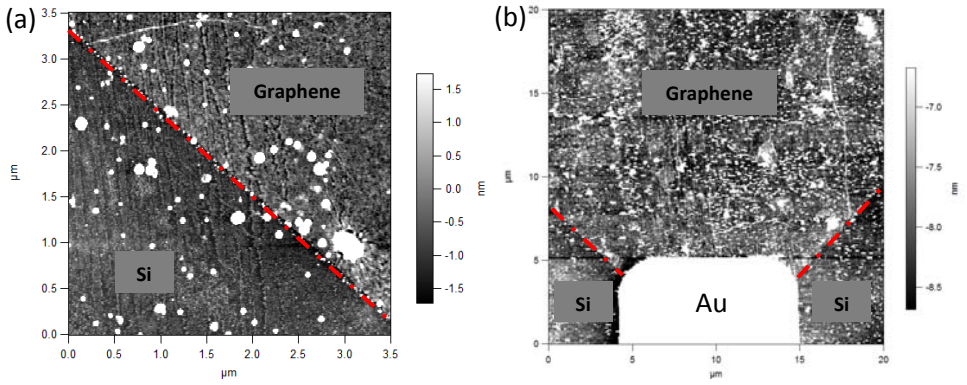

Figure S3. Atomic force microscope images of completed devices on Si with no oxide layer. The edge of the graphene is highlighted with the dashed red line. (a)Zoomed in image of graphene edge (b) Alignment of electrodes to graphene

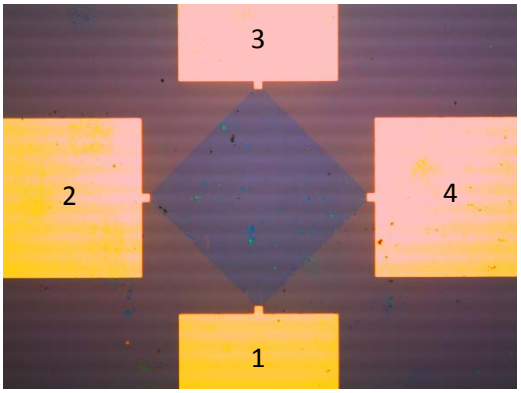

Figure S4. A completed van der Pauw device. The gold contact pads are each 200 x 200 µm. The device in this image was made on a Si/SiO_2 substrate (300nm oxide layer) so that the graphene would be visible.

Table 1: Four-point measurements of van der Pauw squares (high resistivitiy Si substrate)

Device	$\frac{V_{1,2}}{I_{3,4}}(\Omega)$	$\frac{V_{2,3}}{I_{4,1}}(\Omega)$	$\rho(\Omega) = \frac{\pi}{ln(2)}\left(\frac{\frac{V_{1,2}}{I_{3,4}} + \frac{V_{2,3}}{I_{4,1}}}{2}\right)$
F-9	125	149	622
F-11	151	161	707
H-12	164	168	751
I-13	184	169	798
K-5	126	131	582
L-9	134	159	665
O-10	134	128	593
O-11	133	145	629