PHYS 449 Lab Book

# Paper Summaries

1. Raman spectra of twisted CVD bilayer graphene (<https://www.sciencedirect.com/science/article/pii/S0008622317307467>):

A polycrystalline Cu foil (99.8%, Alfa Aesar) was cleaned in acetic acid, acetone and IPA to remove any surface oxides. The cleaned Cu foil was loaded into the CVD chamber and the furnace temperature was ramped to 1030 °C while flowing Ar (300 sccm) and H2 (15 sccm) at ambient pressure. The foil was annealed for 2 hours under the same flow rates. For the growth of graphene, methane (90 ppm) along with Ar (300 sccm) and H2 (15 sccm) was introduced into the chamber for 12 minutes.

1. Twist angle dependent absorption feature induced by interlayer rotations in CVD bilayer graphene (<https://www.degruyter.com/document/doi/10.1515/nanoph-2021-0190/html?lang=de>):

Grown on annealed copper substrate (Alfa Aesar #46365, purity of 99.8%, and thickness of 25 μm) in a low-pressure chemical vapor deposition system with a tube furnace. Firstly, the LPCVD system was evacuated to 0.5 Pa, and then the Cu substrate was annealed at 1060 °C for 100 min under 50 sccm H2 with a pressure of about 50 Pa. One additional step was also adopted by flowing 1 sccm O2 for 10 min to reduce the nucleation density. With the slight incorporation of the oxygen on the Cu surface, the flakes grow under the typical condition of 300 sccm H2 and 0.3 sccm CH4. After 3-h growth, the system was cooled down to room temperature with the gas flowing.

1. Raman mapping investigation of chemical vapor deposition-fabricated twisted bilayer graphene with irregular grains (<https://pubs.rsc.org/en/content/articlehtml/2014/cp/c4cp03386h>):

Bilayer graphene was synthesized using low-pressure CVD on a copper foil (thickness of 25 mm, 99.9% purity). The flux of hydrogen was maintained at 96 sccm during the entire heating process, and 6 sccm methane was introduced at the growth temperature of 1045 **°**C and maintained for 90 min.

1. Growth of twisted bilayer graphene through two-stage chemical vapor deposition (<https://iopscience.iop.org/article/10.1088/1361-6528/aba39e/meta>):

A pretreated (polished and cleaned) Cu foil was placed on a SiC boat for thermal processing in a cold-wall rapid thermal apparatus (As-Micro RTP System, ANNEALSYS). The major thermal process for CVD graphene growth includes four stages: A ramping (10 min) to target temperature, a constant temperature period at 1000 ◦C for 30 min under a common gas ratio to allow for preferred form of multilayer growth, and another 30 min or 1 h of growth under various gas ratio in order to tune the areal proportion of multilayer grains, followed by a cooling to room temperature for 15 min. During stage 1, The copper substrate was mildly oxidized by exposure to hot Ar (500 sccm, 960 mtorr) that contains low concentration of residual oxygen. After the ramping period, graphene film was grown with CVD involving H2/CH4 ratio = 30:1 for 30 min so that there are usually more than one small multilayered grains under a single layer graphene grain while the front and back-sides of the Cu substrate are not fully covered by graphene. After that, various gas mixtures with H2/CH4 ratio from 20:1 to 40:1 (H2 = 20∼40 sccm, CH4 = 1 sccm) are injected into the chamber to allow for various form of grain-grain interactions between the bilayer grains. For the above steps, the chamber pressure (1.4 torr) is maintained by the accompanying Ar flow. After graphene growth, a fast cooling (cooled down to below 800 ◦C within 1 min) is applied by switching off the heating lamp with continuous Ar, H2 and CH4.

1. Selectively enhanced photocurrent generation in twisted bilayer graphene with van Hove singularity (<https://www.nature.com/articles/ncomms10699>):

The tBLG was grown on copper foil in a home-made low-pressure CVD system. The growth was carried out under the flow of H2 and CH4 (600:1 in volume) with a pressure of 600 Pa at 1030 **°**C for 40 min.

1. Angle-Resolved Raman Imaging of Interlayer Rotations and Interactions in Twisted Bilayer Graphene (<https://pubs.acs.org/doi/full/10.1021/nl301137k>):

Large grain graphene was grown on copper foil in a hot wall tube furnace, which was heated while flowing H2 and CH4. Growths were conducted in a copper enclosure that was inserted into the furnace. Three different growth parameters: (1) 980ºC, 60 sccm H2, 1 sccm CH4, 90 min; (2) 950ºC, 120 sccm H2, 6 sccm CH4, 90 min; or (3) 930ºC, 120 sccm H2, 6 sccm CH4, 90 min.

1. Hetero-site nucleation for growing twisted bilayer graphene with a wide range of twist angles (<https://www.nature.com/articles/s41467-021-22533-1>):

tBLGs were grown on 50 μm thick Cu foil in a low-pressure CVD system. Cu-foil pieces were placed in a quartz-tube furnace and sequentially heated to 800 °C for 30 min (500 sccm Ar), annealed for 10 min at 800 °C (500 sccm Ar), heated to 1020 °C for 10 min (500 sccm H2), and annealed for 30 min at 1020 °C (500 sccm H2). Graphene growth proceeded by introducing 12CH4 or 13CH4 after the flow of H2 was stable at the appropriate value

1. Observation of tunable electrical bandgap in large-area twisted bilayer graphene synthesized by chemical vapor deposition (<https://www.nature.com/articles/srep15285#Sec7>):

Initially, 25-μm-thick Cu foil (99.8%, Alfa Aesar) was cleaned in the dilute HCl/H2O (1:10) solution for 3 min and then washed by deionization (DI) water several times to remove the residual acid solution and then was dried by nitrogen gas. Secondly, decaborane was dissolved into anisole solvent (0.03 g/ml) and then spin-coated onto the surface of Cu foil at 3000 rpm for 30 s. Thirdly, the Cu foil was loaded into the silica tube of the CVD system with a vacuum background of 7 × 10−4 Pa and then the growth chamber was heated to 1000 °C and held for 20 min with 30 sccm Ar and then the CH4/H2 (15/30 sccm) replacing Ar was introduced into the tube for graphene growth at 1000 °C for 20 min.

1. Quantum Hall effect in Bernal stacked and twisted bilayer graphene grown on Cu by chemical vapor deposition (<https://journals.aps.org/prb/abstract/10.1103/PhysRevB.85.201408>):

The graphene samples studied here are grown on a 25-μm thick Cu foil at a temperature of 1035 **°**C by CVD, using a mixture of methane and hydrogen at partial pressures of 0.02 and 0.03 mbar, respectively.

1. Synchronous growth of 30°-twisted bilayer graphene domains with millimeter scale (<https://iopscience.iop.org/article/10.1088/2053-1583/abda0e/meta#tdmabda0es2>):

By introducing decaborane as co-catalyst, twisted BLG domains were synthesized by a facile CVD process with a gas mixture of Ar, H2 and diluted CH4 (200 p.p.m. methane balanced in Ar). Firstly, the 25 μm-thick Cu foil (99.8%, Alfa Aesar) was washed in HCL/H2O solution (1:10), washed with deionized water several times to remove the remaining acidic solution, and dried with N2. Secondly, for decaborane (B10H14, 0.03 g ml−1 in anisole solution), which was employed as the cocatalyst, spin coating on Cu foil at 3000 rpm for 30 s is very important for the formation of tBLG domains. Thirdly, the Cu foil was loaded into the quartz tube of the CVD system, and then, the growth chamber was heated to 1050 °C with 100 sccm Ar and held for 20 min. Next, the gas mixture of Ar (100 sccm), H2 (100 sccm) and diluted CH4 (25 sccm) was introduced into the tube for graphene growth for different times at 1050 °C.

1. Temperature dependent Raman scattering of directly grown twisted bilayer graphene film using LPCVD method (<https://www.sciencedirect.com/science/article/pii/S0008622321002761>):

Various samples of tBLG film have been synthesized using 25 μm thick [polycrystalline](https://www.sciencedirect.com/topics/engineering/polycrystalline) [copper foil](https://www.sciencedirect.com/topics/engineering/copper-foil) (Alfa Aesar, purity 99.999%) as a substrate. Prior to growth, the copper has been cleaned with [acetone](https://www.sciencedirect.com/topics/engineering/acetone), deionized water, acetic acid, and IPA, successively. The different samples have been grown by varying the annealing time of copper from 30 to 50 min. The annealing has been performed in the presence of a mixture of Ar and H2 gas for 30-50 min at 1000 °C. After annealing, the Ar gas has been turned off and pressure adjusted to 14.5 ± 0.5 Torr using the flow of H2 gas before introducing the methane gas. The partial pressure ratio (PH2:PCH4=2:1) has been maintained at a pressure of 17 ± 0.3 Torr after introducing the methane (CH4) gas in the chamber, and the growth has been carried out for 3 min at 1000 °C.

1. Designed growth of large bilayer graphene with arbitrary twist angles (<https://www.nature.com/articles/s41563-022-01361-8#Sec7>):

A piece of polycrystalline Cu foil (25 μm thick, 99.8%, Sichuan Oriental Stars Trading, #Cu-1031) was placed on a flat quartz substrate and then loaded into a hot-wall tube furnace. The furnace was ramped to 1020 °C in 1 h and maintained at this temperature for 2 h under 500 s.c.c.m. Ar and 50 s.c.c.m. H2. Then, the system was flushed with Ar and heated to 1050 °C under 500 s.c.c.m. Ar and 10 s.c.c.m. H2. During growth, 1 s.c.c.m. of 1% CH4 (diluted by Ar) was introduced as the carbon source for 6 h, and the furnace was heated to 1074 °C for 30 min to form the bilayers.

1. Twinning and Twisting of Tri- and Bilayer Graphene (<https://pubs.acs.org/doi/full/10.1021/nl204547v>):

Graphene was grown on Cu foil (99.8% Alfa Aeasar, #13382) in a hot wall tube furnace, which was heated while flowing H2 at a pressure of ~2 Torr.

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# Comparing Methods:

|  | Copper purity | Copper thickness | Gasses Used | Temperature (**°**C) | Pressure (Pa) | Annealing time (min) | Growth time (min) | Crystal Size (microns) |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 1 | 99.8% | x | Ar, H2 | 1030 | ambient | 120 | 12 | 25-30 |
| 2 | 99.8% | 25 microns | H2 | 1060 | 50 | 100 | 180 | ~30 |
| 3 | 99.9% | 25mm | H2 | 1045 | “Low- pressure” | x | 90 | x |
| 4 | x | x | H2, CH4 | 1000 | 186 | x | 60-90 | 40 |
| 5 | x | x | H2, CH4 | 1030 | 600 | x | 40 | 15-20 |
| 6 | x | x | H2, CH4 | 930, 950, 980 | x | x | 90 | x |
| 7 | x | 50 microns | Ar, H2 | 800 → 1020 | “Low- pressure” | 60 | x | ~20-25 |
| 8 | 99.8% | 25 microns | Ar, H2, CH4 | 1000 | 7x10-4 Pa | x | 20 | x |
| 9 | x | 25 microns | H2, CH4 | 1035 | 2-3 | x | x | ~30 |
| 10 | 99.8% | 25 microns | Ar, H2, CH4 | 1050 | x | x | 20 | ~1000 |
| 11 | 99.999% | 25 microns | Ar, H2 | 1000 | 2266 | 30-50 | 3 | x |
| 12 | 99.8% | 25 microns | Ar, H2 | 1074 | x | x | 30 | ~20 |
| 13 | 99.8% | x | H2 | x | 266 | x | x | ~10 |

# Protocol:

* Heat Oven to 1050C
* Set up 3 beakers for methanol, DI water and acetic acid
* Cut a section of copper (remember to use the plastic tweezers when handling Cu)
* Bathe sample piece in methanol (green bottle) for 10s, then clean with DI water
* Bathe sample piece in Acetic Acid (flammable compartment) for 10min, clean with DI water, dry with N2
* Keep rising with DI water and drying with N2 until acetic acid smell is gone
* Make sure H2 and CH4 tubes are connected properly to gas cylinders and open valve fully (to low pressure)
* Pump down the system
* Run gas through the lines to clean em out (5 time,5 ch4,20 h2)
* Set up flow rates on computer
* Put sample piece in quartz cylinder
* Turn on pump to drop pressure
* Leave at low pressure for a couple minutes
* Start gas flow program on computer
* Put on face shield
* Dispose of chemicals and clean glass dishes used for cleaning the copper
* Remove cylinder from oven and wait to cool (use facemask)
* End program & turn off pump
* Depressurize by opening valve
* Remove cylinder and remove copper sample
* Close valve
* Turn on hot plate and set to ~200C
* Place sample and control piece on hot plate and wait ~10min
* Close gas cylinders, set oven to 0C
* Transfer samples to petri dish

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# Transfer Protocol:

* Grab glass sheet
* Set up white sheet to work on
* cut piece of copper with graphene on it
* Flatten copper with glass sheet with side you want to transfer facing up
* Barely tape edges of copper to glass sheet
* Get PMMA from flammables shed
* Turn on pump
* Put sample in middle of spinner
* Set to 3k rpm for 30s
* Put on lid and start spinning
* Let PMMA cure overnight OR
  + Set hot plate to 180C if you dont plan to let PMMA cure overnight
  + Put sample on hot plate for 90s
* Measure out 15g of ammonium peroxydisulfate into beaker
* Pour about 100ml-20ml of DI water, label with chemical identification form
* Unpeel tape to remove copper piece
* Cut off sides of copper that were taped down to leave only coated copper left
* Put copper in solution with PMMA side UP
* At the 5 and 10min mark,, rinse underside of copper to remove other side of graphene
* Let it sit in solution for around 2hrs, until you can't see anymore copper, not even any little specs (needs to be completely clear)
* Preparing the Silicone substrate
* Get the diamond scribe and splitters
* Score the silicone wafer using a glass piece as a ruler and the diamond scribe
* Use the splitters to split off your piece
* Transfering the PMMA to the silicone
* Fill 2 beakers with DI water
* Use glass plate to scoop PMMA out of solution and into first beaker
* Transfer from first beaker into second beaker
* Use silicone to pick up the PMMA and either leave to dry overnight or set hot plate to 60C and leave for 3-5min until turns greenish colour
* Dissolving the PMMA
* Fill beaker with acetone from flammable cabinet
* Put samples in to dissolve overnight or put on hot plate for ~30min at 65C
* Cover with parafilm as to not evaporate the acetone while you wait
* Fill small beaker with IPA (yellow bottle top) and dunk sample into it
* Rinse sample with DI water then dry with N2 blowgun

# Growths:

## 07/10/2022

Time (mins): 30 5 inf

H2 (sccm): 20 30 20

CH4 (sccm): 0 3 0

Pressure: ~2.9x10-1

Temp: 1050 C

## 17/10/2022

Time (mins): 30 4 inf

H2 (sccm): 40 40 40

CH4 (sccm): 0 3 0

Pressure: ~8.5x10-1 torr

Temp: 1050 C

## 28/10/2022

Growth 1:

Time (mins): 30 4 inf

H2 (sccm): 10 10 10

CH4 (sccm): 0 2 0

Pressure: annealing: 1.1x10-1 growing: 1.5x10-1

Temp: 1050 C

Growth 2:

Time (mins): 30 4 inf

H2 (sccm): 10 10 10

CH4 (sccm): 0 2 0

Pressure: annealing: 1.1x10-1 growing: 1.5x10-1

Temp: 1050 C

(smaller piece)

Growth 3:

Time (mins): 30 4 inf

H2 (sccm): 10 10 10

CH4 (sccm): 0 1 0

Pressure: same

Temp: 1050 C

Growth 4:

Time (mins): 30 2 inf

H2 (sccm): 20 30 20

CH4 (sccm): 0 3 0

Pressure: 2.9e-1

Temp: 1050 C

Growth 5:

Time (mins): 30 1 inf

H2 (sccm): 20 30 20

CH4 (sccm): 0 3 0

Pressure: 2.8e-1, 5.3e-1

Temp: 1050 C

Growth 6:

Time (mins): 30 1 inf

H2 (sccm): 20 30 20

CH4 (sccm): 0 3 0

Pressure: 2.9e-1, 5.4e-1

Temp: 1050 C

(Smaller piece)

## 04/11/2022

Growth 1:

Copper: 046986 25micron 99.8%

Time (mins): 35 4 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 4 0

Pressure: 3.7x10-1

Temp: 1030 C

Growth 2:

Copper: 046986 25micron 99.8%

Time (mins): 35 2 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 4 0

Pressure: x10-1

Temp: 1030 C

Growth 3:

Copper: 046986 25micron 99.8%

Time (mins): 35 4 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 4 0

Pressure: 3.8x10-1

Temp: 1030 C

Eric Growth:

Time (mins): 30 5 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

## 09/11/2022

Growth 1:

Copper: 046986 25micron 99.8%

Time (mins): 35 5 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 4 0

Pressure: ????x10-1

Temp: 1040 C

Growth 2:

Copper: 046986 25micron 99.8%

Time (mins): 35 5 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 4 0

Pressure: 3.0x10-1 , 4.0x10-1

Temp: 1040 C

## 10/11/2022

Growth 1:

Copper: 046986 25micron 99.8%

Time (mins): 35 4 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 4 0

Pressure: 2.9x10-1 , 3.9x10-1

Temp: 1040 C

Growth 2:

Copper: 046986 25micron 99.8%

Time (mins): 35 3 inf

H2 (sccm): 20 40 20

CH4 (sccm): 0 4 0

Pressure: 2.9x10-1 , 9.5x10-1

Temp: 1060 C

Growth 3

Copper: 046986 25micron 99.8%

Time (mins): 35 5 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 4 0

Pressure: 3.0x10-1 , 3.9x10-1

Temp: 1040 C

Growth 4

Copper: 046986 25micron 99.8%

Time (mins): 35 5 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 4 0

Pressure: 2.9x10-1 , 3.9x10-1

Temp: 1040 C

## 11/11/2022

Growth 1:

Copper: 046986 25micron 99.8%

Time (mins): 35 5 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 4 0

Pressure: 2.9x10-1 , 3.9x10-1

Temp: 1040 C

## 17/11/2022

Growth 1:

Copper: 046986 25micron 99.8%

Time (mins): 35 5 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 2.9x10-1 , 3.7x10-1

Temp: 1040 C

Growth 2:

Copper: 010950 25micron 99.999%

Time (mins): 35 5 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 3.0x10-1 , 3.7x10-1

Temp: 1040 C

Growth 3:

Copper:

%

Time (mins): 35 5 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 2.9x10-1 , 3.7x10-1

Temp: 1040 C

## 18/11/2022

Growth 1:

Copper: 046986 25micron 99.8%

Time (mins): 35 5 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 2.9x10-1 , 3.6x10-1

Temp: 1050 C

Line pressure: H2: 200kpa, CH4: 40kpa

Growth 2:

Copper: 046986 25micron 99.8%

Time (mins): 35 5 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 2.9x10-1 , 3.6x10-1

Temp: 1050 C

Line pressure: H2: 400kpa, CH4: 40kpa

## 22/11/2022

Growth 1:

Copper: 046986 25micron 99.8%

Time (mins): 30 4 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 3.0x10-1 , 3.6x10-1

Temp: 1050 C

Growth 3:

Copper: 046986 25micron 99.8%

Time (mins): 30 2 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 2.9x10-1 , 3.6x10-1

Temp: 1050 C

Growth 4:

Copper: 046986 25micron 99.8%

Time (mins): 30 1 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 2.9x10-1 , 3.6x10-1

Temp: 1050 C

## 23/11/2022

Growth 1:

Copper: 046986 25micron 99.8%

Time (mins): 30 30 inf

H2 (sccm): 15 15 15

CH4 (sccm): 0 0.3 0

Pressure: 2.0x10-1 , 2.1x10-1

Temp: 1060 C

## 24/11/2022

Growth 1:

Copper: 046986 25micron 99.8%

Time (mins): 30 5 inf

H2 (sccm): 15 15 15

CH4 (sccm): 0 0.3 0

Pressure: 2.0x10-1 , 2.1x10-1

Temp: 1060 C

Growth 2:

Copper: 046986 25micron 99.8%

Time (mins): 30 10 inf

H2 (sccm): 15 15 15

CH4 (sccm): 0 0.3 0

Pressure: 2.0x10-1 , 2.1x10-1

Temp: 1060 C

Growth 3:

Copper: 046986 25micron 99.8%

Time (mins): 30 25 inf

H2 (sccm): 15 15 15

CH4 (sccm): 0 0.3 0

Pressure: 2.0x10-1 , 2.1x10-1

Temp: 1060 C

Growth 4:

Copper: 046986 25micron 99.8%

Time (mins): 30 20 inf

H2 (sccm): 15 15 15

CH4 (sccm): 0 1 0

Pressure: 2.0x10-1 , 2.3x10-1

Temp: 1060 C

## 29/11/2022

Growth 1:

Copper: 046986 25micron 99.8%

Time (mins): 30 0.3 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 2.9x10-1 , 3.7x10-1

Temp: 1050 C

Growth 2:

Copper: 046986 25micron 99.8%

Time (mins): 30 0.6 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 2.9x10-1 , 3.7x10-1

Temp: 1050 C

Growth 3:

Copper: 046986 25micron 99.8%

Time (mins): 30 1.3 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 3.0x10-1 , 3.8x10-1

Temp: 1050 C

Growth 4:

Copper: 046986 25micron 99.8%

Time (mins): 30 1.6 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 3.0x10-1 , 3.7x10-1

Temp: 1050 C

## 02/12/2022

Growth 1:

Copper: 046986 25micron 99.8%

Time (mins): 30 1.6 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 3.0x10-1 , 3.6x10-1

Temp: 1060 C

Growth 2:

Copper: 046986 25micron 99.8%

Time (mins): 30 1.6 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 3.0x10-1 , 3.7x10-1

Temp: 1040 C

Growth 3:

Copper: 046986 25micron 99.8%

Time (mins): 30 1.6 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 3.0x10-1 , 3.7x10-1

Temp: 1030 C

Growth 4:

Copper: 046986 25micron 99.8%

Time (mins): 30 1.6 inf

H2 (sccm): 20 20 20

CH4 (sccm): 0 3 0

Pressure: 3.0x10-1 , 3.8x10-1

Temp: 1020 C