Michael Hilke Group

Graphene Growth Guide

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This is a comprehensive guide to growing graphene using a CVD (**C**hemical **V**apor **D**eposition) system. It includes a methodology, a compilation of various growth parameters and some pitfalls to watch out for. Samples produced in this research group will be analyzed using raman spectroscopy with the end goal of studying the hydrodynamics of phonons in graphene.

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1 General Methodology

It's time efficient to start heating as soon as you enter the lab. The temperature of the furnace should be set within the $1030 - 1050°$ range. The pre-treatment can be started about $100°$ before the maximum temperature.

1. **Sample Pre-Treatment**

   You will need: 3 small beakers (Methanol, DI Water, Acetic Acid), a plastic petri dish, tweezers and scissors.

   - Dip in Methanol for 10-15s. Shake around a little to dislodge any dirt.
   - Rinse in DI water.
   - Bathe in acetic acid for 12-15 minutes.
   - Thoroughly rinse in DI Water to get rid of the acid.
   - Immediately Dry using N_2. The sample can be set upon a clean glass side for an easier time. Put in a petri dish once dry.

2. **Growth**

   You will need: Insulating Gloves and Heat Visor

   - Put clean sample in the quartz tube. This is our growth chamber.
   - Turn on the pump and seal the valves. Wait until near vacuum, 10 mTor is a good objective.
   - Turn on Hydrogen and Methane gas outlets.
   - Set the growth parameters on the matlab interface
   - Put the protective equipment on and slowly lower the quartz tube into the furnace.
   - Start the program timer as quickly as possible.
   - After all growth steps are over, put the protective equipment back on and gently pull the tube out to let it cool.

3. **Oxidization**

   You will need: Tweezers, Scissors and the hot plate.

   - Once the sample has cooled for a few minutes in vacuum, reintroduce an atmosphere to accelerate the cooling.
   - At this point, the hot plate can be set to around $250C$.
   - When the tube is no longer burning to touch, extract the sample from it. Place it in the petri dish.
   - Cut a thin strip of the sample lengthwise.
   - Place the freshly cut strip onto the hotplate. This will oxidize all regions of the copper where graphene is absent.
   - Bring the sample to the microscope once there is a noticeable change in hue. Note that in the case of full coverage, no oxygen is in contact with copper, and thus there will be no change in color.

4. **Observation**

   You will need: Microscope, tweezers and transparent green flattening film?

   - Place the oxidized strip onto the microscope tray and gently flatten it using the film.
   - Turn on the microscope and adjust the focus.
   - Look for graphene formations!

   Since the colorful copper oxides contrast with the graphene covered copper, it is easy to identify the presence of crystals.

2 Transfer

WIP -¿ check maya's paper

3 Growth Parameters

3.1 Full Coverage

$$\begin{bmatrix} t: & 30 & 2 & \infty \\ CH_4: & 0 & 4 & 0 \\ H_2: & 0 & 75 & 0 \end{bmatrix} \quad @\ \mathrm{T} = 1050°$$

3.2 Single Crystal, Single Layer

$$\begin{bmatrix} t: & 30 & 5 & \infty \\ CH_4: & 0 & 1 & 0 \\ H_2: & 0 & 30 & 0 \end{bmatrix} \quad @\ \mathrm{T} = 1050°$$

3.3 Bilayer

Could use some tweaks

$$\begin{bmatrix} t: & 30 & 1 & 3 & \infty \\ CH_4: & 0 & 2 & 0.9 & 0 \\ H_2: & 0 & 75 & 75 & 0 \end{bmatrix} \quad @\ \mathrm{T} = 1050°$$

3.4 Crucible Ring Fold

These weren't very good.

$$\begin{bmatrix} t: & 30 & 3 & 3 & \infty \\ CH_4: & 0 & 3 & 3 & 0 \\ H_2: & 0 & 75 & 40 & 0 \end{bmatrix} \quad @\ \mathrm{T} = 1030°$$

4 Git

Git is a popular version control system used for collaborative coding projects. Essentially, using Git allows for a centralized repository where all modifications are recorded and can be synchronized across multiple computers. If something breaks, it is easy to revert back to an instance of the repository where the code was working. This also simplifies collaborative work by combining changes from different team members onto the repo.

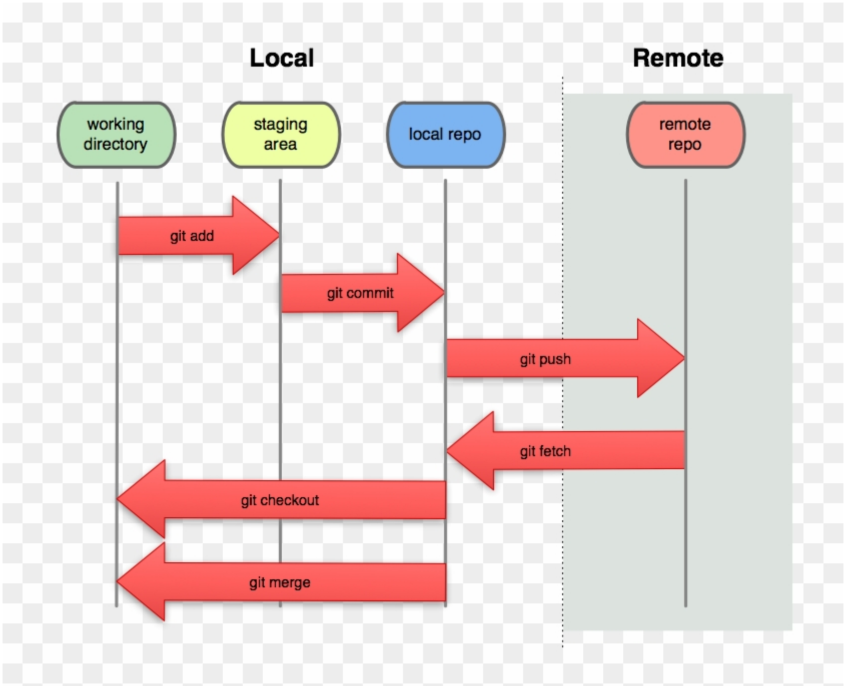
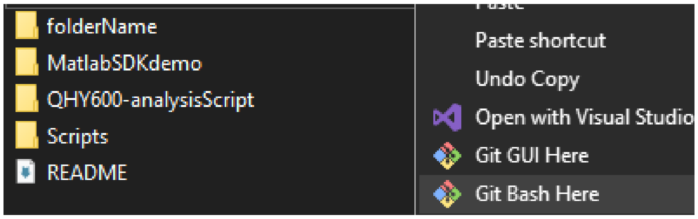


Figure 1: Git Workflow Diagram

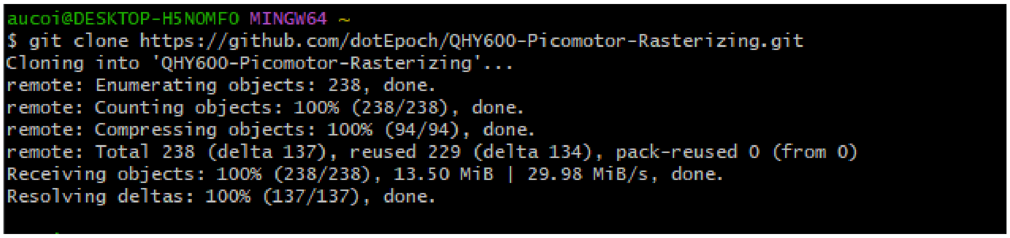
Github

Github is a free online repository platform. You can find the lab's repo at the following link: `https://github.com/dotEpoch/QHY600-Picomotor-Rasterizing.git`

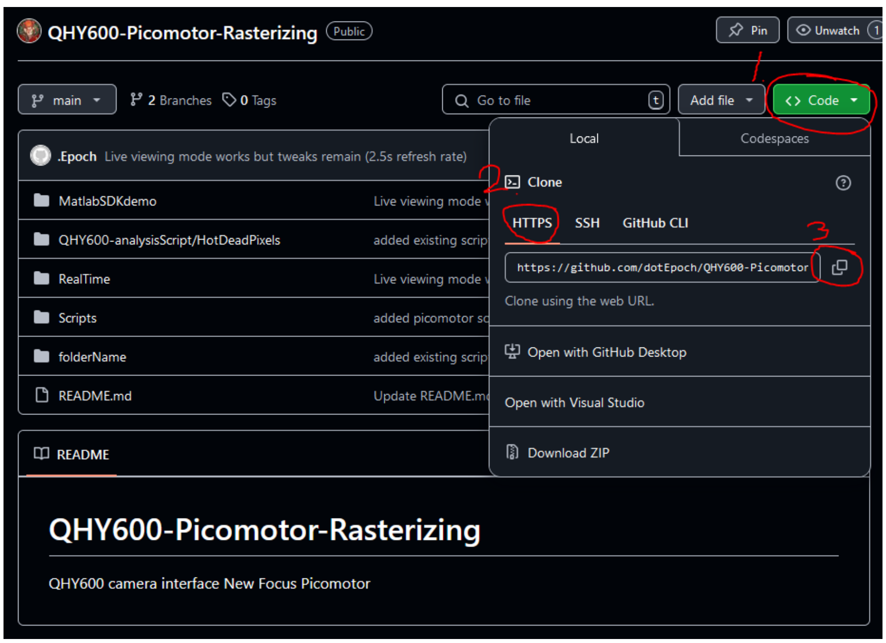
Let's see how to interface with this repository. You will need to install git bash here. Navigate to a new project folder and right click to open git bash.



Step 1: Clone

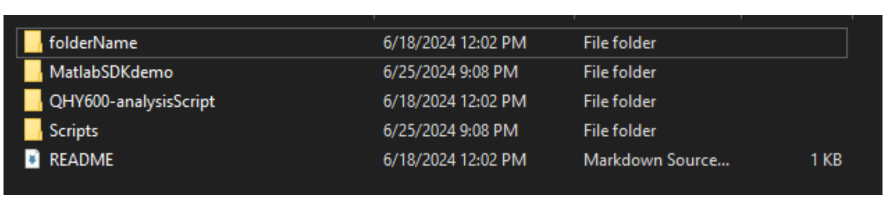


First, we want to use the `git clone [REPO-LINK]` command to create local "fork" of our repository. A fork is simply a copy of the original repository which is still linked to it. This effectively counts as the first pull and must only be done once. You can use the provided link above, or find it on github by following these steps:



Step 2: Modifying

You can now modify the code locally. It is good practice to create a README.md file which will be displayed on the public github page.



Step 3: Add

To add files to the repository, we can use the `git add [FILES]` command. I suggest using `git add .` where the dot indicates all files in the current directory.

```
aucoi@DESKTOP-H5NOMFO MINGW64 /c/zZ.Projects/Picomotor (main)
$ git add .
```

Step 4: Commit

The commit command stages every change you've made locally and readies it to be uploaded to the online repository. Its syntax is `git commit -m "commit message"`

```
aucoi@DESKTOP-H5NOMFO MINGW64 /c/zZ.Projects/Picomotor (main)
$ git commit -m "Pertinent message of what was changed"
On branch main
Your branch is up to date with 'origin/master'.
```

Step 5: Push

Push will upload all staged modifications to the online repo. This will allow all team members to pull your changes and work on their own machine with your code. Now, you can log off.

```
aucoi@DESKTOP-H5NOMFO MINGW64 /c/zZ.Projects/Picomotor (main)
$ git push
```

Step 6: Pull

Pulling allows you to be up to date with the online repository and integrate changes that have been pushed from other computers. Use `git pull`. Do note that conflicts may arise and must be solved before doing anything. Whenever you start working on something, it is important to pull any changes that were pushed while you were away.

```
aucoi@DESKTOP-H5NOMFO MINGW64 /c/zZ.Projects/Picomotor (main)
$ git pull
remote: Enumerating objects: 109, done.
remote: Counting objects: 100% (109/109), done.
remote: Compressing objects: 100% (18/18), done.
remote: Total 68 (delta 51), reused 66 (delta 49), pack-reused 0 (from 0)
Unpacking objects: 100% (68/68), 11.37 MiB | 13.78 MiB/s, done.
From https://github.com/dotEpoch/QHY600-Picomotor-Rasterizing
   be89f05..d9164e0  main       -> origin/main
Already up to date.
```

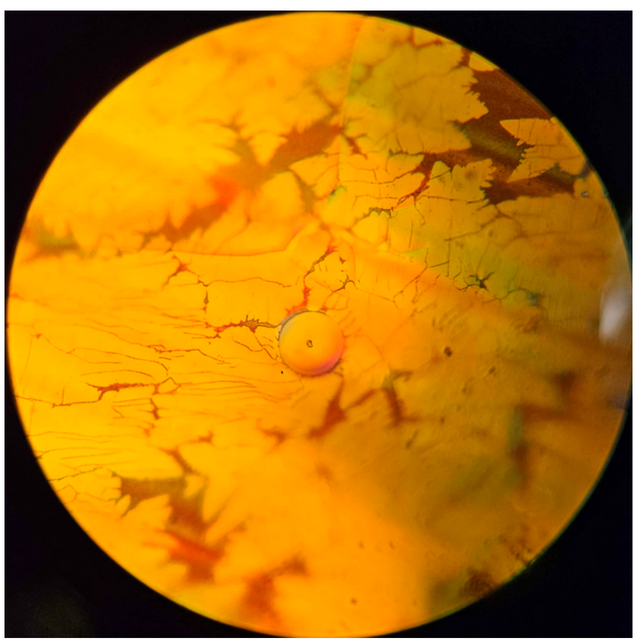
5 Issues/Tips

- Growing anything but graphene

  ↪ Make sure to vigorously stir the DI water with the etched sample in it before drying it **fully** with N_2. Traces of acid on the substrate will lead to unwanted vapors inside the growth chamber. The green deposit in the tube is potentially due to a chemical reaction with the copper and the acid. Always check that the pressure reaches a low enough point before dropping the tube in the furnace. A pressure plateau above the usual amount could indicate partial pressures of acid vapor → rinse and dry again !! Ex: Some samples with traces of acid generated structures that were similar to carbon-nanotubes. Unfortunately, we're trying to grow graphene...

- Debris on the surface

  ↪ The main impurities that arise from this system come from the diffusion of Cu atoms at the mouth of the furnace. This intermediary zone is at a lower temperature than the inside of the furnace (600-800°C), which enables the *devitrification* of the quartz tube[1]. This is the red-ish residue seen on the inside of the tube. Essentially, these conditions are conducive to α/β quartz phase transformations, forming SiO vapor which deposits as nanoparticles onto the growth substrate, contaminating the sample.



- Irregular growth formations
  ↪ Ideally, we aim to grow either clean full coverage or snowflake-like crystals. A general trend I noticed was that bad graphene, or lack thereof, was often due to faulty heat control. Indeed, once gas flow stops, the sample **must** be in the cooling stage, some studies even suggesting preemptive removal from the furnace $^{Source?}$. Overheating the sample under pure vacuum will destroy the graphene, causing irregularities and ruining the sample. The crucible growths also featured interesting patterns relative to the color, or polarization, of the underlying regions in the copper. Due to its thermal conductivity, the graphite crucible affected the cooling stage of the process resulting in regular deformations in the sample. There may be some interesting properties to study here.

- Twisted Bilayers
  ↪ Twisted bilayers are the reason Depending on their angle and configuration, dfferent properties emerge. are due to these interactions. BLG can be made either naturally through CVD or artificially by physically layering two samples. Finding better growth recipes that produce large bilayer flakes is crucial to better understanding graphene.

6 Checklist

☐ Furnace is at 90°C

☐ Pump is off

☐ Gas valves are sealed

☐ Hot plate is off

☐ Chemicals are properly disposed of

☐ Glassware is washed

☐ Fume hood is clean

References

[1] N. Lisi, T. Dikonimos, *et al. Contamination-free graphene by chemical vapor deposition in quartz furnaces*, Sci Rep. 2017; 7: 9927 https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5577164/ 7