Graphene Growth on Ge(110) Substrates

ENGR 241 Final Report
Michelle Chen, Risa Hocking
Mentors: Hye Ryoung Lee, Swaroop Kommera, Michelle Rincon

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2 Introduction

2.1 Motivation

The importance of graphene was emphasized in 2018 with the discovery of unconventional super-conductivity in magic-angle twisted bilayer graphene [1]. In that seminal work, the authors used exfoliated graphene. However, exfoliating graphene is a bespoke process - the quality, size, and shape are limited by those of the bulk crystal. Bottom-up synthesis processes such as chemical vapor deposition (CVD) allow for continuous, large-scale growth. This increases the yield of device fabrication but may result in poorer performance due to higher defect concentrations.

This issue is apparent in CVD growth of graphene on copper foil, a common substrate. Although copper foil allows for easy transfer through spin-coating of a protective polymer membrane before etching the entire substrate, the polycrstalline nature of the film imparts a polycrystalline nature to the graphene monolayer as well [3]. This is evident in the previous E 241 graphene growth project by Ning Wang and Chris Neumann - their work resulted in continuous monolayer growth of graphene on Cu foil with the caveat that it was polycrystalline with grains on the size of 1 µm. When they worked with Cu thin films instead, they noted that the quality had likely improved due to a more planar substrate (and single crystal Cu thin films are possible, allowing for single crystal graphene growth), but the transfer yield had dramatically decreased due to difficulty in etching the copper. The strong graphene-copper interactions require a wet transfer (e.g. a transfer requiring the use of solvents, etchants, or a salt solution to delaminate a 2D material from its growth substrate), which introduces many potential contaminants.

Single crystal germanium substrates offer another solution. Similarly to copper, graphene will match with the structure of the germanium surface in a preferred orientation. In the case of Ge(110), there is only one preferred orientation, allowing several nucleated seeds to stitch themselves into a continuous, single-crystal sheet (Figure 1) [3]. Moreover, the graphene-germanium interactions are much weaker than the graphene-copper interactions to the point that a dry transfer is easily completed [3]. The dry transfer (e.g. a "tear-and-stack" method where a monolayer can be mechanically ripped from the substrate and then placed on the desired substrate) introduces fewer potential contaminants and allows for reuse of the substrate material.

2.2 Project Concept and Vision

We intended to grow wafer-scale, single crystal monolayer graphene on a Ge(110) substrate using the Aixtron Black Magic 4 inch CVD furnace. Two papers in literature used the exact same instrument [4][5], giving us a starting point for development.
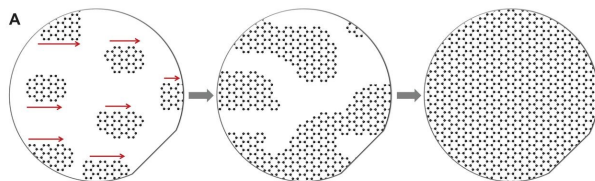
Figure 1: Schematic showing the coalescence of several unidirectional grains into a single crystal monolayer on the Ge(110) substrate as adapted from [3].

2.3 Benefits to SNF Community

Previous graphene projects in SNF have resulted in polycrystalline, monolayer graphene growth on copper and nickel substrates that must be dissolved to release the 2D material. The growth of graphene on Ge(110) would offer three primary benefits: 1) single crystal, wafer-scale growth of monolayer graphene; 2) metal-free processing; and 3) reusable substrates, which lower the cost of each run.

3 Experimental Methods

3.1 Materials

Two different germanium wafers were used in these experiments. Six 2" undoped Ge(110) wafers were ordered from WaferPro. Their sheet resistance was 40-60 ohm-cm, and their thickness was 500 +/- 20 microns. They were single side polished (SSP) with a surface roughness of less than or equal to 20 Å. As the shipping on these wafers was significantly delayed, we also used 4" Ge(100) wafers with a 6°miscut from MTI Korea. These were also SSP with a surface roughness less than or equal to 8 Å.

3.2 Substrate Preparation

The purpose of the substrate preparation is to clean the wafer for growth and remove the native germanium oxide on the surface. The cleaning methods in literature can be divided into two primary categories: solvent-based solutions and acid-based solutions.

Solvent-based cleaning is more user-friendly and safer, so we started with that method. We cleaved the Ge substrates using a diamond scribe similarly to how one would cleave single crystal Si, although the cleavage planes are oriented closer to 45°or 60°from the flat rather than perpendicular. After removing large particles using a N_2 gun, individual pieces were sonicated in acetone followed by isopropanol for 15 minutes each at wbflexsolv-1. After each solvent rinse, they were sprayed with isopropanol as they were being lifted out of the beaker to remove any debris that may have been agitated during sonication. The specimens were thoroughly dried with N_2 before being dropped into a beaker of standing DI water at wbflexcorr for 15 minutes. This final step is meant to remove much of the native germanium oxide, which will reform after being removed from water. Therefore, during this step, the Aixtron BM (aixtron-graphene) chamber was vented and opened just before the piece was removed from the water to expedite transfer to vacuum and minimize oxide formation. After the sample had finished etching in the water, it was removed from the beaker with tweezers,

rinsed again with DI water, and blown dry with N_2. Care was taken to ensure all water droplets were removed, which would negatively affect the vacuum of the Aixtron BM.

Acid-based cleaning was utilized by several groups in literature. In particular, the seminal paper that we are referencing in this project used a standard RCA clean, an oxygen plasma treatment, and finally a dilute HF dip to remove the native oxide and terminate the surface with hydrogen [3]. This was supplemented by deposition of a fresh germanium layer using GeH_4 in the growth chamber, though the pre-chamber clean should not be neglected. We tested a similar clean to this as well. In our procedure, the individual pieces were dipped into hydrogen peroxide (H_2O_2) for 60 s at wbflexcorr. They were dipped into water to rinse of residue, and then dipped into 2% HF for 30 s. The water bath was rinsed and refilled during this time. The piece was transferred to the DI water bath for 30 s and then returned to the HF dip. This process occurred three times (3 dips in HF and 3 dips in DI water). As with the solvent-based clean, the chamber was vented and opened as the clean was being finished to expedite transfer to vacuum and minimize oxide formation.

An anneal at the same temperature as the growth completes the substrate preparation. Because the growth is longer than the anneal, any change in the material that occurs during annealing will be overridden if the annealing is performed at a lower temperature than the growth. The annealing atmosphere is a mixture of argon and hydrogen gas to reduce the oxide and promote hydrogen termination, although these claims were not experimentally verified with chemical characterization during this project.

3.3 Growth

Methane and hydrogen carried in argon were used as the gaseous precursors during this growth. The basic recipe and steps are given below:

1. Purge chamber with Ar twice.

2. Start flowing H_2 and Ar, purging for 60 s.

3. Close pump valve and start ramping to 930°C.

4. Once 930°C has been reached, hold for 30 min for the anneal.

5. Introduce 2 sccm of CH_4 to initiate growth. Hold for 60 minutes.

6. Cease H_2 and CH_4 flow, allowing Ar to continue flowing. Turn off the heater.

7. At 175°C, turn on the pump valve and allow user to vent the chamber.

The complete script for the recipe is in Appendix 7.3.

In the case of growths with pressures above 100 mbar, a high pressure test had to be run before the instruments interlocks would allow those pressures. Otherwise, the growth would shut down as soon as the chamber reached 100 mbar.

3.4 Characterization

Graphene's Raman fingerpint is characterized by the D, G, and 2D (or G') bands (Figure 3.4) [6]. The quality can be determined by taking the ratios of the I_D/I_G peaks and the I_{2D}/I_G. The former correlates with defect density of the material and should be minimized. The latter correlates with

the number of monolayers and should be as close to 1 as possible. The measurements were taken with the 532 nm laser on the Horiba Labram HR Evolution in SNSF. This included a grating of 1800 gr/mm, a spectral range of 1000-3000, and a laser power of 5-10%.
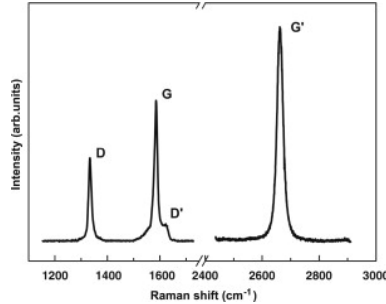

Figure 2: Characteristic Raman spectrum of few layer graphene showing the D, G, and 2D (G') peaks as adapted from [6].

3.5   Design of Experiment

Several Design of Experiments (DoE) were considered for this project. The primary iteration was based on several papers in literature that can be seen in 7.2.

	Anneal Time (min)	Methane (sccm)	Growth Temp (C)	Growth Time (min)	ID/IG Ratio	I2D/IG Ratio
1	15	2	930	60	•	•
2	5	2	910	120	•	•
3	15	2	930	120	•	•
4	15	5	930	120	•	•
5	5	5	930	120	•	•
6	5	2	930	60	•	•
7	15	2	910	120	•	•
8	15	2	910	120	•	•
9	5	2	910	60	•	•
10	5	2	930	120	•	•
11	15	5	910	60	•	•
12	15	5	910	60	•	•
13	5	2	910	60	•	•
14	5	5	910	120	•	•
15	5	5	930	60	•	•
16	5	5	910	120	•	•

Figure 3: Initial DoE considering the influence temperature, time, and precursor ratio.

After several exploratory runs, the DoE was revised to consider precursor flow as a combination of the chamber pressure and methane flow rate.

As neither of these DoEs produced graphene, they were not completed to be mindful of the budget. The hope is that future experiments will allow for a complete DoE to be executed.

	Pressure (mbar)	Methane (sccm)	ID/IG Ratio	I2D/IG Ratio
1	500	5	•	•
2	750	5	•	•
3	750	2	•	•
4	655	3.5	•	•
5	655	3.5	•	•
6	625	2	•	•
7	500	3.5	•	•
8	500	3.5	•	•

Figure 4: Final DoE considering the influence of the precursor flow.

4   Results and Discussion

We sought out several edge cases in the pursuit of graphene. The samples and their parameters are listed in Table 1. As mentioned earlier, a non-ideal Ge(100) substrate was used for the first several runs due to a major shipping delay with the Ge(110) wafers.

We started with the two extremes of our first DoE: the higher methane flow, longer time, and higher temperature (Trial 2) as well as the lowest methane flow, shorter time, and lower temperature

Table 1: Variations in runs from base recipe detailed in experimental methods section.

Trial	Base pressure (mbar)	Substrate	Annealing time (min)	Methane flow (sccm)	Other comments
1	10	Ge(100)	5	2	907C
2	10	Ge(100)	15	5	120 min growth
3	95	Ge(100)	15	2	-
4	95	Ge(100)	15	2	Cleaned with HF
5	130	Ge(100)	15	2	300 sccm H2 + 400 sccm Ar during anneal, 50 sccm H2 + 600 sccm Ar during growth
6	750	Ge(100)	15	2	Cleaned with HF, 600 sccm H_2 + 400 sccm Ar during anneal
7	750	Ge(100)	30	2	600 sccm H_2 + 400 sccm Ar during anneal
8	750	Ge(110)	30	2	600 sccm H_2 + 400 sccm Ar during anneal
9	750	Ge(110)	30	2	-
10	655	Ge(110)	30	2.5	-
11	625	Ge(110)	30	2	-
12	500	Ge(110)	30	5	-
13	750	Ge(110)	30	40	-

(Trial 1). Neither produced graphene (Appendix 7.4). Notably, however, there were many pyramidal pits that formed, particularly around the edges.

Next, a cleaning comparison was made. The growth was taken up to 95 mbar as many points in literature were clustered around 100 mbar (Appendix 7.2). The ceiling was determined by the Aixtron BM; a high pressure test has to be run to go above 100 mbar, which wasn't known at the time. One sample was cleaned using acetone, IPA, and water (Trial 3) whereas the other was primarily cleaned using HF (Trial 4).
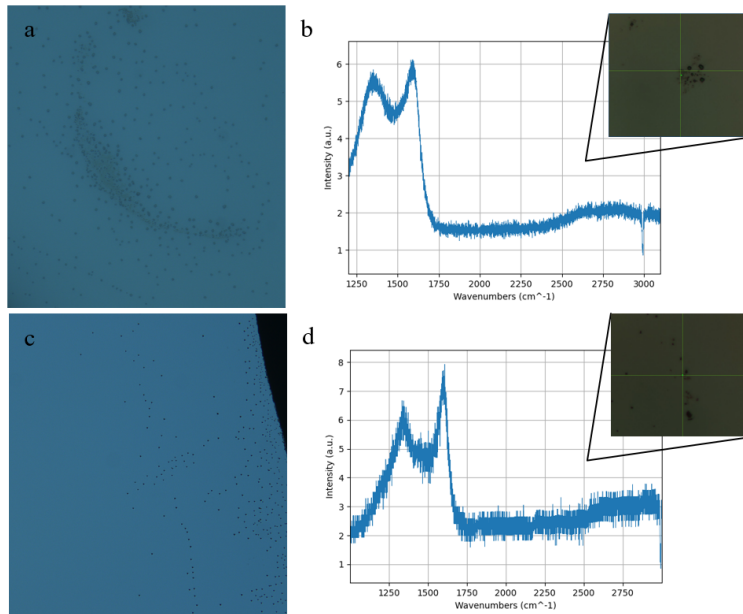
Figure 5: Optical images of (a) Trial 3 and (c) Trial 4 along with Raman spectra from (b) Trial 3 and (d) Trial 4.

Qualitatively, the HF-cleaned sample showed fewer pyramidal pits and carbon contamination spots as seen in Figure 5(c). However, the absence of graphene was confirmed using Raman. Therefore, for safety reasons, we switched to primarily using the solvent-based clean. In both of these samples, the Raman spectra of the carbon contamination was similar to amorphous carbon (Figure 5).

Similarly, a higher hydrogen ratio during the anneal and a lower hydrogen ratio during the growth was investigated (Trial 5). The intention was to increase hydrogen passivation during the anneal and lower the rate of hydrogen etching during growth. Again, no graphene was produced.

The pressure was increased all the way up to 750 mbar in the next few trials as several papers in literature had used a similar chamber pressure. The Raman spectra of the carbon contamination was different at these higher pressures as seen in Figure 6. It appears that the advantageous carbon was annealed and reduced to a higher sp^2 character compared to germanium processed at lower pressures, becoming more graphitic in nature. Moreover, the number of pyramidal pits dropped significantly.

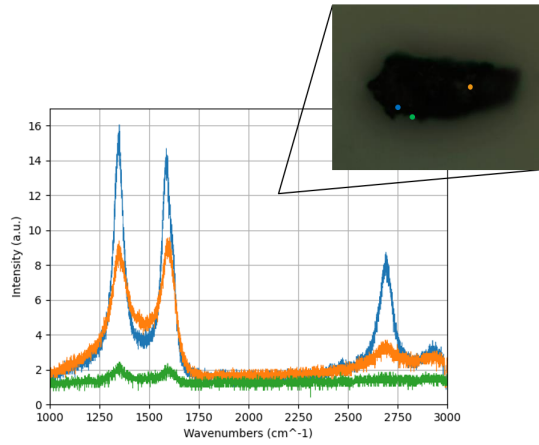The figure below (Figure 6) shows the isolated nature of the carbon annealing. As one gets

Figure 6: Comparison of spectra across a carbon particle on Trial 7.

further away from the interior of the particle, the intensity of the signal drops. This was true for all carbon contamination on the samples after Trial 6 (inclusive).
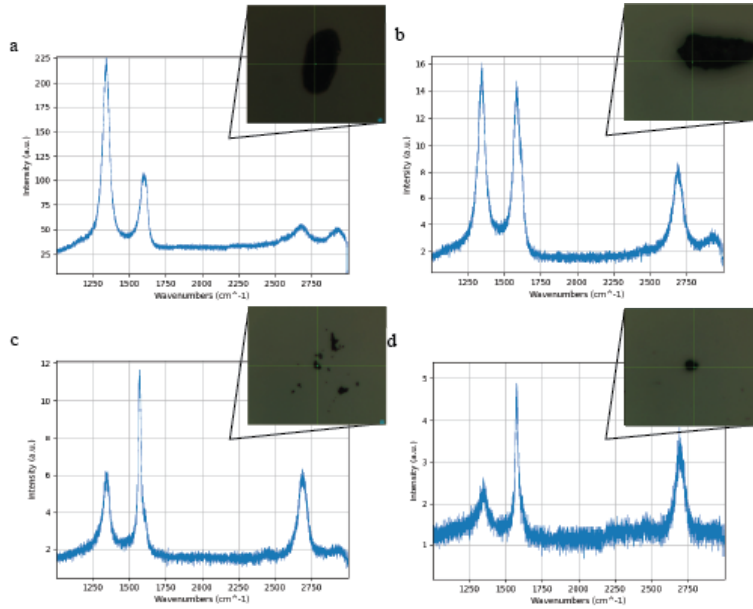

Figure 7: Comparison of Raman spectra from (a) Trial 6, (b) Trial 7, (c) Trial 8, and (d) Trial 9.

The effect of cleaning was investigated again at these higher pressures with no graphene produced. Similarly, the annealing atmosphere ratio was investigated. The higher hydrogen ratio that we had been using previously (Trial 8) performed equivalently to the common 1:4 H_2:Ar ratio seen

in literature (Trial 9) (Appendix 7.2). The transition from Ge(100) (Trial 7) to the Ge(110) (Trial 8) substrate did seem to indicate a slightly higher quality, shown by the higher intensity I_{2D} peak and lower intensity I_D peak (Figure 7).

Finally, a purposeful overpressure of methane (Trial 13) was run to determine if anything was depositing onto the samples. The relative amounts of methane were computing by determing the methane partial pressure during growth and multiplying by the chamber pressure, seen in Table 2. Two studies from the literature that also used the Aixtron BM were examined for comparison. Trial 13 was designed to have an entire order of magnitude more methane than previous trials. Even then, no graphene was detected using Raman (Appendix 7.4).

Table 2: Relative amounts of methane for all processes run in Aixtron BM.

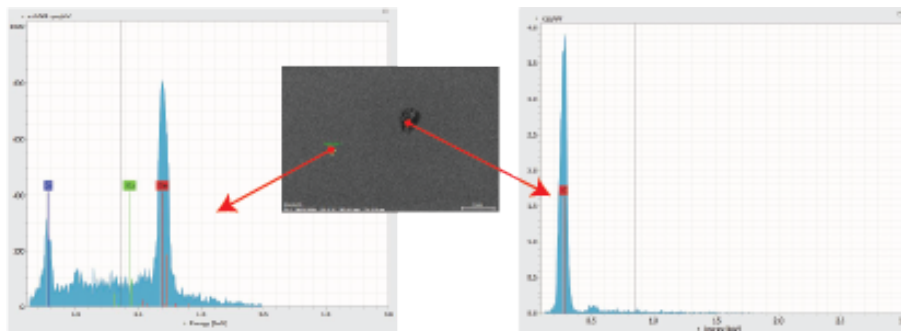| Trial	Ar (sccm)	H_2 (sccm)	CH_4	Chamber pressure (mbar)	Relative amount of CH_4 (a.u.)
[4]	800	200	2	100	0.20
[5]	450	100	2	750	2.72
Trial 1	800	200	2	10	0.02
Trial 3	800	200	2	95	0.19
Trial 5	600	50	2	130	0.99
Trial 6	800	200	2	750	1.50
Trial 13	800	200	40	750	28.85

Figure 8: EDS spectra from two points on the Trial 3 specimen indicating no appreciable copper contamination on the surface.

Aside from Raman, Trial 3 was inspected using a Scanning Electron Microscope (SEM). No graphene grains were seen on the specimen. EDS was performed on some parts of the sample, on the bulk and on a carbon spot (Figure 8). The spectra from the bulk showed primarily germanium with some carbon, whereas the dark spot was almost entirely carbon. Neither showed any appreciable amount of copper, which was a concern with the chamber as it had not been cleaned from previous copper growths. This indicates that copper was not evaporating onto the germanium substrates from the chamber liners. It does not rule out copper playing another role - for example, the methane

may be preferentially reacting at the copper surfaces on the top heater ring rather than reacting on the germanium.

5 Conclusions

Many edge cases have been tested within this experiment (methane concentration, chamber pressure, substrate cleaning, hydrogen concentration, long time) without evidence of graphene growth. Clearly, however, some edge cases have had more of an effect than others. Namely, the chamber pressure has had the greatest effect. From 10 mbar to 750 mbar, there is evidence of advantageous carbon modification to increase sp^2 character. Although not graphene itself, this is promising for future work.

6 Future Work

There is still one more edge case left: a clean chamber. That run will be done in the future using a high pressure (750 mbar), low methane concentration case (2 sccm CH_4). Five full 2" Ge(110) wafers are left to continue experimentation, and this report will be updated with those results.

If that does not work, there is another option that we could try. Based on the positive results of the growth on copper foil from April 29, it's clear that something is not mechanically wrong with the system (e.g. gases are still flowing as expected, thermocouple is not wildly off). The remaining idea is that we could transfer a successful graphene growth from the copper foil onto the Ge(110) substrate and run it through the chamber with and without precursors flowing. Although this may act as a seed for growth, this is not expected due to the distinct epitaxial relationship that graphene has with Ge(110) - the transferred polycrystalline graphene may not be in the exact preferred arrangement on the surface. Instead, we would look to see how the graphene quality may have changed during the session or whether it is even still on the substrate (completely etched). This would inform future recipe iterations.

7 Appendix

7.1 Transfer Project

While waiting for the Ge(110) wafers to arrive, we tried to improve the yield of graphene grown on Cu thin films using the established recipe for the Aixtron BM. The objective of this study was to oxidize the copper film underneath the graphene such that the surface interactions between the graphene and copper oxide would be weak enough for mechanical delamination. We were also looking to compare the effect of PMMA against poly(bisphenol-A carbonate) (PC), the latter of which has been suggested to leave less residue on the 2D material. The DoE is shown below in Figure 9. The experimental setup is shown in Figure 10.

	Water	Temp (C)	Time (hr)	Polymer	Surface Yield
1	Y	25	3	PMMA	•
2	N	25	3	PC	•
3	N	50	24	PMMA	•
4	Y	50	3	PC	•
5	Y	50	3	PC	•
6	Y	25	3	PMMA	•
7	N	50	24	PMMA	•
8	N	25	3	PC	•
9	Y	25	24	PC	•
10	Y	25	24	PC	•

Figure 9: Interim DoE considering the influence of oxidation parameters and polymer chemistry for transferring graphene from Cu thin film substrate.

A premixed solution of 495k A4 PMMA in ansiole was spin-coated onto each piece at 3000 rpm for 60 s. A homemade solution of 6wt% PC in chloroform was spin-coated onto each piece at 3000 rpm for 60 s as well.
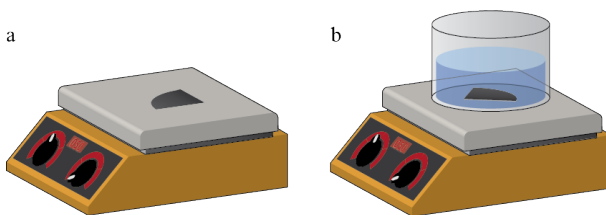
Figure 10: Experimental setup. Wafers were either directly put onto hotplates or submerged in a beaker of DI water heated to the appropriate temperature (confirmed with thermocouple).

For the copper substrate, we used the AJA evaporator to deposit 500 nm of Cu onto Si wafers from the SNF stockroom at a rate of 1 Å/s. Unfortunately, a mistake was made with the substrate: the copper film should have been deposited onto an oxidized Si wafer with more than a native oxide. As a result, our copper surface was only roughened by the growth temperatures in the Cu thin film recipe, and no graphene was grown on the surface. This was confirmed using Raman,

shown in Figure 11. This was confirmed with an unrelated copper foil growth performed in April of the same quarter as this project; there was graphene as determined by Raman, indicating that there is nothing inherently wrong with the Aixtron BM or its current recipe.
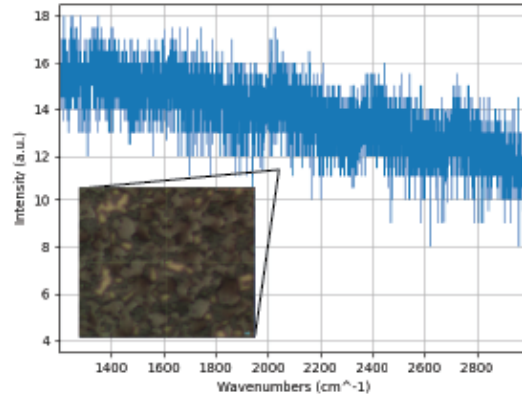

Figure 11: Raman spectra of roughened Cu film after running through Aixtron BM.

Notably, though, the PC films qualitatively seemed easier to remove than the traditional PMMA films. We were able to rip some of the film off in a clean sheet if an edge was started, whereas we were not able to rip any of the PMMA film from the wafers. This may be a good sign for future transfer experiments, although the weaker adhesion of the PC may also not lend itself to delaminating the graphene.

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7.2 Literature Review

Table 3: Literature review of graphene growth primarily on Ge(110) surfaces but also extending towards other surface constructions.

doi	Substrate			Graphene Growth					Characterization		Comments
	Material	Prep (outside chamber)	Prep (inside chamber)	Gas ratio	Base pressure	Temperature (°C)	Time (min)	Cooling	I_D/I_G	I_{2D}/I_G	
10.1126/science.1252268	single crystal Ge(110) wafer	RCA clean followed by oxygen plasma treatment followed by dip into 10% HF	Deposited fresh epi layer of Ge using CH_4 (40 sccm, 10-30 Torr) at 500-900°C for 30 min, pre-baked chamber under H_2 flow	1-2% CH_4 in H_2	100 Torr	900-930	5-120	Rapid under vacuum	0.03		Monolayer coverage. Mobility of 7250 +/- 1390 cm² V⁻¹ s⁻¹
10.1063/5.0003234			Heated up to 930°C within 5 min under high vacuum. Filled with 80 mbar H_2 to clean sample surface for 15 min.	3-8 sccm CH_4, 25 sccm H_2	10-30 mbar	850-930	60	Slow under vacuum			Submonolayer coverage.
10.1021/acs.nanolett.5b02836	Single crystal Ge(110)	Sonicated in acetone and IPA for 15 min each, then etched in DI water at 90°C for 15 min.	Annealed at 910°C for 30 min under 200 sccm of Ar and 100 sccm of H_2	3.6-4.6 sccm CH_4, 100 sccm H_2, 200 sccm Ar	10e-6 Torr			Rapid under vacuum		0-4	Heated to 700°C in ultra-high vacuum for 1-2 hr after growth.
10.1021/acsami.9b18448	Epi Ge(110) on Si			10 sccm CH_4, 200 sccm H_2		885			0.05		
10.1016/j.apsusc.2019.143823	Single crystal Ge(110), n-type	Multiple rinsing and drying cycles, alternating IPA and DI water.	In Ar/H_2 atmosphere: Heated from RT to 800°C at 4°C/s, then to 850°C at 1°C/s, then up to final annealing temp at 0.125°C/s and kept there for 5 min.	2 sccm CH_4, 200 sccm H_2, 800 sccm Ar	100 mbar	910-930	60	Slow under Ar and H_2 atmosphere	0.3-2.0	1.7-3.0	Used Aixtron BM. Authors suggest slower growth rate or higher hydrogen fraction (could etch away defective carbon regions) for higher quality graphene.
10.1038/s41598-020-68846-7	Single crystal Ge(110)	Cleaved to 1 sq cm, boiled in acetone and ethanol for 2 min. Flushed with IPA and dried with N_2.		3 sccm CH_4, 100 sccm H_2, 450 sccm Ar	750 mbar	907	90		1.2	¿3.9	Used Aixtron BM. Submonolayer growth.
10.1016/j.apsusc.2018.04.039	Ge(100)	Acetone and IPA for 15 min each followed by 15 min rinse in DI water	Ramped up to temp with 100 sccm Ar, 50 sccm H_2.	05-5 sccm CH_4, 50 sccm H_2, 100 sccm Ar	500 mbar	910	120	Rapid (300°C/min) under same atmosphere as synthesis	0.01		Best performance was 1% methane in hydrogen.
10.1021/acsami.6b11701	Ge(100)	Sonicate in IPA, rinse in DI water	Heat up chamber with Ar/H_2 mixture	1-10 sccm CH_4, 200 sccm H_2, 800 sccm Ar	100 mbar	930	60				
10.1021/acsami.0c10725	Epi Ge(100) on Si				700 mbar	885	60				
10.1016/j.carbon.2020.12.024	Ge(100)	Clean in HF or HCl or HBr for 1 min, rinse with DI water for 5 min		5.3 sccm CH_4, 102 sccm H_2, 888 sccm Ar	atmospheric	910	100	Rapid under 888 sccm Ar and 102 sccm H_2	0.2		Thermal pits form from residual Ge suboxides. HBr shows best performance in removing suboxides (and reducing pitting).

7.3   Recipe

```
 COMM Ar Ar CH4 CH4 H2
COMM furnademode off
COMM topheatertemperaturecontrol
COMM Turn on pump
VALV 1 OPEN
TUNE PCON Graphene 750 mbar
PCON ON 750.0 20.0
COMM Close pump
VALV 1 CLOSE
COMM INTERLOCK- CHECK GAS OPEN
FLOW 2 ON 0
WAIT TIME > 10
COMM Purge chamber with Ar
FLOW 2 ON 500
WAIT TIME > 40
WAIT PRES > 0.50
FLOW 2 OFF
COMM Pump out Ar
VALV 1 OPEN
WAIT PRES < 0.10
VALV 1 CLOSE
COMM Purge chamber with Ar
FLOW 2 ON 1000
WAIT TIME > 60
FLOW 2 OFF
COMM Pump out Ar
VALV 1 OPEN
WAIT PRES < 0.20
COMM Season chamber with H2 and Ar
FLOW 2 ON 800
FLOW 6 ON 200
WAIT TIME > 60
COMM Close pump
VALV 1 CLOSE
COMM Tune heaters to zero power
TUNE HTTC zero power
TUNE TOPH zero power
COMM Start substrate anneal
HEAT ON 550.0 240.0
TOPH ON 550.0 240.0
COMM Tune heaters to next setpoint
TUNE HTTC Graphene 750C
TUNE TOPH Graphene 650C
COMM Wait until substrate reaches temp and stabilizes
WAIT TEMP > 535.0
```

```
WAIT TIME > 20
COMM Tune heaters to next setpoint
TUNE HTTC Graphene 1000C Stable
TUNE TOPH top heater 950C
COMM Ramp to next point in substrate anneal
HEAT ON 800.0 240.0
TOPH ON 800.0 240.0
COMM Wait until substrate reaches temp and stabilizes
WAIT TEMP > 795.0
WAIT TIME > 20
COMM Ramp to next point in substrate anneal
HEAT ON 860.0 60.0
TOPH ON 860.0 60.0
COMM Wait until substrate reaches temp and stabilizes
WAIT TEMP > 850.0
WAIT TIME > 20
COMM Ramp to next point in substrate anneal
HEAT ON 930.0 7.5
TOPH ON 930.0 7.5
COMM Wait for 30 min anneal
WAIT TEMP > 925.0
WAIT TIME > 1800
COMM Turn on process gases for deposition
FLOW 5 ON 2
COMM Length of deposition
WAIT TIME > 3600
COMM Turn off methane and hydrogen
FLOW 5 OFF
FLOW 6 OFF
COMM Start ramping down temp with Ar flowing
HEAT ON 750.0 150.0
TOPH ON 750.0 150.0
WAIT TEMP < 800.0
COMM Start pumping out Ar
VALV 1 OPEN
WAIT TIME > 30
COMM Continue ramping down temp, increase Ar flow
HEAT ON 450.0 300.0
TOPH ON 450.0 300.0
FLOW 2 ON 500
WAIT TEMP < 700.0
COMM Turn off heaters
HEAT OFF
TOPH OFF
COMM Reduce pressure to vacuum and increase Ar flow
TUNE PCON Fully open
```
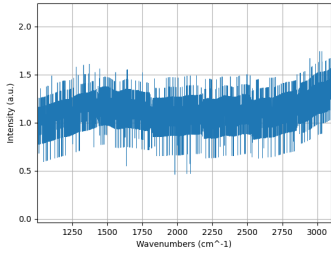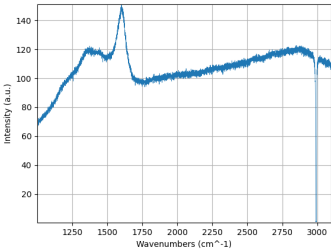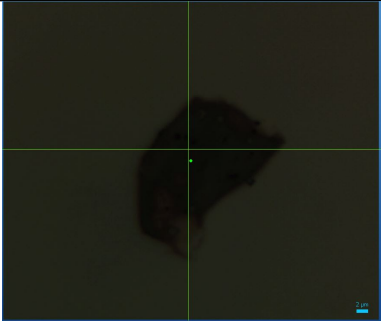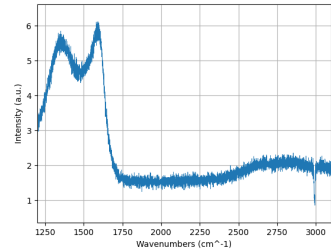
```
PCON ON 1.0 1.0
FLOW 1 ON 1000
FLOW 2 ON 1000
COMM Wait until temp below 200 to turn off pressure config
WAIT TEMP < 200.0
PCON OFF
COMM Wait until temp below 175 to turn Ar off
WAIT TEMP < 175.0
FLOW 1 OFF
FLOW 2 OFF
WAIT PRES < 0.50
```
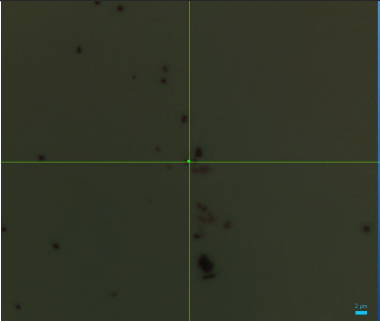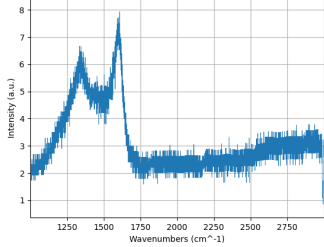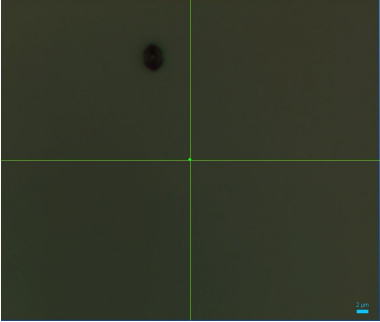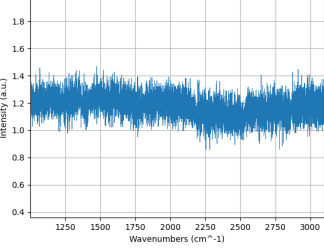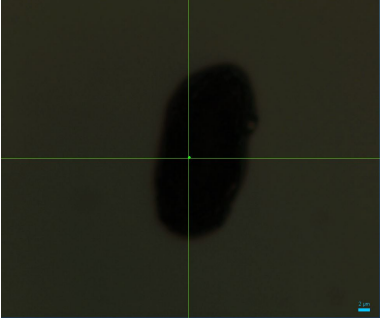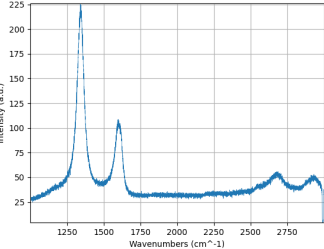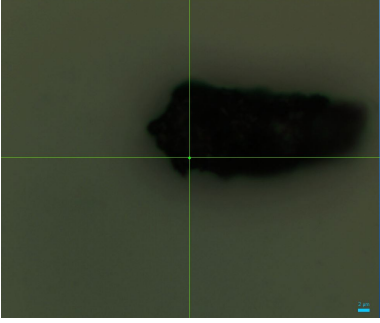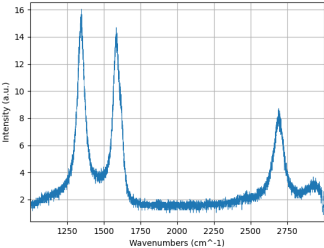
7.4 Raman Data

Some trials are missing Raman data as similar parameters did not result in graphene, so we tried to be conscientious of the budget (1, 10-11). In the locations where nothing is visible, we focused using the size of the laser spot on the surface.
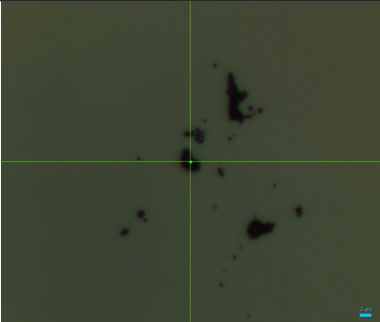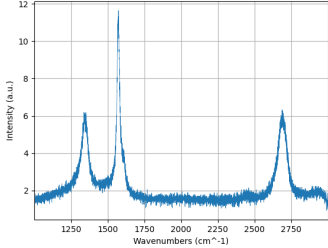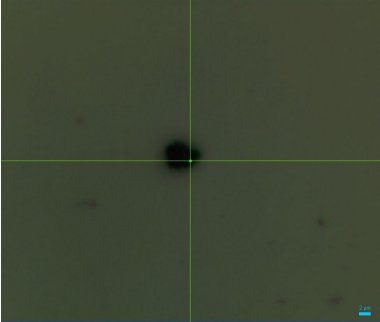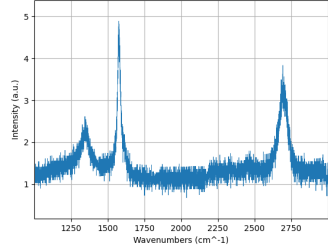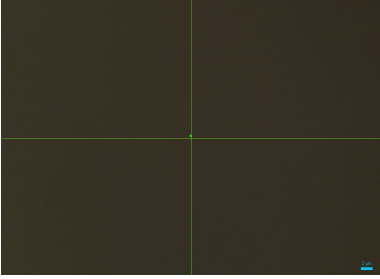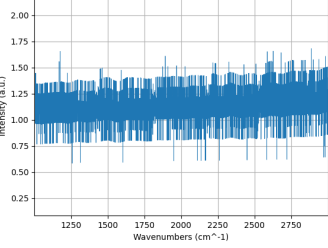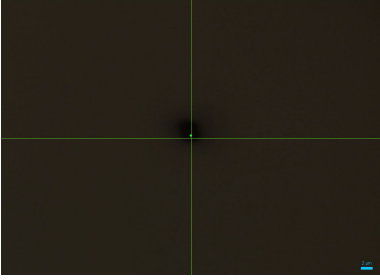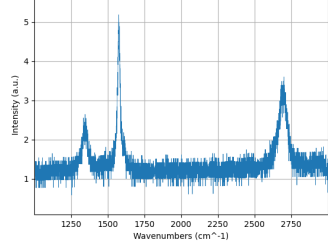
Table 4: Complete Raman data for trials.

Trial	Location	Spectrum
Trial 2	Image not taken.	
Trial 3	Image not taken.	
Trial 4		

Continued on next page

Trial	Location	Spectrum
Trial 5		
Trial 5		
Trial 6		
Trial 7		

Trial	Location	Spectrum
Trial 8		
Trial 9		
Trial 12		
Trial 12		

Trial	Location	Spectrum
Trial 13		

7.5 Cleaning the Aixtron BM

The Aixtron BM should be cleaned on an annual or biannual basis depending on tool usage. Ideally, there should be separate sets of quartzware for all substrates to prevent contamination and decrease downtime, but this clean may be conducted between substrate types as well. Pages 214-223 and 254-265 in the Aixtron BM manual should be consulted during disassembly and reassembly for valuable pictures and diagram.
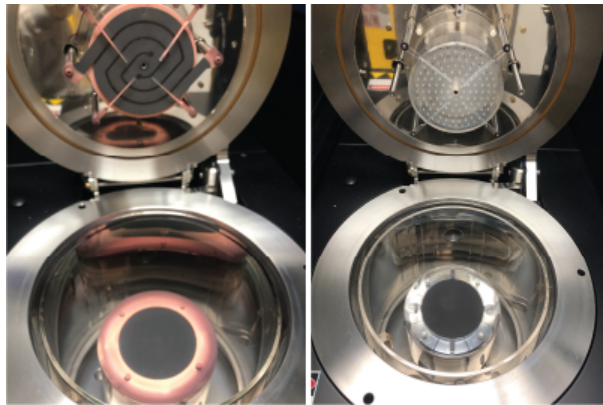
Figure 12: Photos of the chamber before (left) and after (right) cleaning. The right image is missing the top heater, which will be added later.

1. With the chillers and gases off, vent and open the chamber.

   (a) Open the pecvd software and login. The password for the GUEST account is "graphene," case-sensitive. The keys are sticky, so watch to make sure all the letters are entered.

   (b) Click on the close pump valve button.

   (c) Click on the vent valve button, and wait for the green LED near the enclosure to turn on after a minute.

   (d) Carefully open the enclosure. Unscrew the clamp and lift the chamber door fully open. Push back the door to ensure that it is fully open before proceeding.

2. Put on a second pair of gloves. Disassemble the bottom heater.

   (a) Using just your hands, unscrew the four ceramic bolts on the top of the bottom heater. They should be fairly loose. As you remove the pieces, you should wrap each set (or large piece) in its own cleanroom wipe and separate into plastic bags.

   (b) Lift the quartz heater top ring off.

   (c) *Carefully* lift the graphite cathode up. Wrap this piece in a cleanroom wipe and place separate from all the other pieces due to its fragility.

   (d) Slowly lift the quartz heater dome. The thermocouple on the north end of the dome may be sticking to the tube, so watch it as you lift.

(e) Remove the loose ceramic washers (8).

(f) Use the provided torque screw (0.4 N*m) with the 2.5 mm head to remove the bottom heater. Wrap this piece in a cleanroom wipe and place separate from all other pieces due to its fragility. Keep the metal screws (4) separate.

    i. Put your fingers on the heater near the screws while you remove them to minimize forces on the heater.

    ii. Remove the rectangular heat spreader as well and place with the fragile graphite pieces.

(g) Lift off the steel heater reflector shield. This will not be cleaned in aqua regia or SC2, so it may be good to put it in a separate location.

(h) Lift off the quartz reflector cover.

(i) Carefully lift off the three quartz tubes (one on the thermocouple, two on the Mo rods).

3. Change your gloves. Disassemble the top heater.

(a) Holding your hand under each part, unscrew the twisted quartz legs (4). Keep the screws and washers separate.

(b) Remove the thermocouple by pulling it out from the base.

(c) Use the provided torque screw (0.4 N*m) with the 2.5 mm to remove the top heater. Wrap this piece in a cleanroom wipe and place separate from all other pieces due to its fragility. Keep the metal screws (4) separate.

    i. Put your fingers on the heater near the screws while you remove them to minimize forces on the heater.

    ii. As this graphite heater is vertical rather than horizontal, it may be useful to have a second person to hold the heater as you unscrew it.

    iii. *Carefully* lift the heater out.

(d) Remove the quartz tubes from the four anode rods and the two Mo rods.

(e) While holding the quartz showerhead fixture, use your hands to remove the ceramic screws (4) holding it vertically. It may be useful to have a second person to hold the fixture while the first removes the screws. Lift the showerhead fixture away.

4. Wipe all metal, quartz, and ceramic parts down with an IPA-soaked cleanroom wipe. This will remove some of the carbon contamination, but evaporated metal may remain.

5. Clean the quartz and ceramic components with dilute aqua regia in an exhausted wetbench to remove metal deposits. Stainless steel tweezers or teflon tweezers can be used with aqua regia.

(a) Put on normal corrosive PPE (blue chemical apron, inner latex gloves, chemical-resistant gloves, a second pair of vinyl gloves, safety glasses, face shield).

(b) Turn on the DI water faucet and leave running while working with aqua regia.

(c) Fill a large pyrex beaker with DI water and set next to your work station. This water will be used to quench a reaction if it starts going wrong.

(d) Pour 2 parts DI water : 3 parts 37% HCl : 1 part 70% HNO_3 by volume into a large pyrex beaker in that order. Slowly add the acids to the water as mixing aqua regia is an exothermic reaction.

(e) Slowly submerge the parts into the beaker. This will need to be done in several batches. For many of the small parts, it may be necessary to use a teflon piece holder to dip them in and out. The quartz showerhead may also serve as a colander of sorts for smaller pieces.

(f) After 10 minutes, all of the copper or nickel should be removed. Very carefully transfer the parts to the water bath using tweezers, piece holders, or gloved hands (in the case of the quartz showerhead, which does not fit entirely into a large pyrex beaker and hangs over the edge). Soak the pieces (and tweezers or piece holders) in DI water for at least 5 minutes.

(g) Carefully pour aqua regia mixture into a separate hazardous waste container as it contains dissolved metals. Also pour the first rinse bath from the cleaned pieces into the same waste container.

(h) Rinse the pieces with the DI water gun.

6. Clean the quartz and ceramic components in SC2 in an exhausted wetbench to clean any particles left behind from the aqua regia mixture. Teflon or delrin tweezers can be used with SC2.

   (a) Put on normal corrosive PPE (blue chemical apron, inner latex gloves, chemical-resistant gloves, a second pair of vinyl gloves, safety glasses, face shield).

   (b) Fill a large pyrex beaker with DI water and set next to your work station.

   (c) Pour 5 parts DI water : 1 part H_2O_2 : 1 part 37% HCl by volume into a large pyrex beaker in that order. Add the acid carefully as this is an exothermic mixture.

   (d) Slowly submerge the parts into the beaker. This will need to be done in several batches. For many of the small parts, it may be necessary to use a teflon piece holder to dip them in and out. The quartz showerhead may also serve as a colander of sorts for smaller pieces.

   (e) Carefully transfer the parts to the water bath using tweeers, piece holders, or gloved hands (in the case of the quartz showerhead, which does not entirely fit into a large pyrex beaker and instead hangs slightly over the edge). Soak the pieces (and tweezers or piece holders) in DI water for at least 5 minutes.

   (f) The SC2 mixture and any rinse baths can be poured into the AWN drain.

   (g) Rinse the pieces with the DI water gun.

7. Dry the items at 80C in an oven for an hour to remove excess water. You will want to put down fresh aluminum foil to protect the quartzware from the bottom of the oven.

8. Wipe everything down with an IPA-soaked cleanroom wipe. Take care to wear fresh gloves to avoid getting fingerprints on the quartzware.

9. Bake the quartzware and ceramic pieces in the Vulcan 3-1750 furnace located next to the Aixtron BM to remove carbon deposits. There is enough quartzware that it will take at least 3 days to finish baking everything.

(a) Open the exhaust flue to 0.06 inches of water.

(b) Flip the green switch on.

(c) Open the door to the oven, which should automatically stay open. It may not stay open, in which case you should work with a second person to keep it open.

(d) Load the quartzware into the oven and close the door. As a precautionary measure, do not let the quartzware touch other pieces or the sides of the oven when loaded into the oven.

(e) Using the numberpad, press 2 and then press enter. Press the green start button. This will start program 2, which ramps up to 950°C at a rate of 4°C/min and holds for one hour.

(f) The program will begin ramping down but will not ramp fully down. After several hours, the furnace will be stalled around 850°C. Press the red stop button to escape program 2. Quickly press 3 using the numberpad, then hit enter. Press the green start button. This will start program 3, which will carefully bring the quartzware and ceramic pieces down to 50°C at 4°C/min.The program does not need to run for the full six hours as three of the hours are holding steps at 50°C; it can be stopped early at that point using the red stop button.

(g) Once the furnace is at 50°C, press the stop button the end the program. Unload the oven. It may be necessary to wipe some pieces with an IPA-soaked wipe if there is visible ceramic dust on them.

(h) Repeat two or three times to accomodate baking all the quartzware.

(i) Switch off the power switch and close the exhaust flue.

10. Reassemble the top heater.

(a) Having a second person hold the quartz showerhead fixture to the instrument, gently screw and hand tighten the ceramic bolts to fix it in place. Loosen the ceramic bolts by one turn. This will prevent them from breaking as the neighboring materials expand during heating.

(b) Slip the quartz tubes over the four anode rods.

(c) Using graphite washers and the small metal screws, put the four twisted quartz legs back onto the anode rods of the top heater. The legs should be loose enough to allow you to move them around with unscrewing further but tight enough to stay in place once moved. Face them away from the heater.

(d) Slip the two quartz tubes over the Mo rods.

(e) Have a second person *carefully* hold the graphite top heater in place. Note that the legs should be clockwise instead of counterclockwise. Using the provided torque screw (0.4 N*m), screw the heater in with the graphite washer and screw. Hold the edge of the heater to minimize the forces put onto it.

(f) Attach the thermocouple. Bend the thermocouple so it touches the edge of the graphite top heater.

11. Reassemble the bottom heater.

(a) Put two quartz tubes onto the Mo rods and one quartz tube onto the top thermocouple.

(b) Carefully set the quartz reflector cover onto the bottom heater, lining the edges up with the rods.

(c) Screw the four metal studs into the four corners to help with alignment.

(d) Set the stainless steel heat reflector down, aligning its four holes over the edges. Make sure that the bottom and top thermocouples are able to poke through the holes.

(e) Fit the quartz heater stage over the heat reflector such that the rectangular divot is facing up.

(f) Place the rectangular heat spreader into the divot.

(g) *Carefully* screw the graphite heater into the Mo rods using the provided torque screw (0.4 N*m). Hold the edge of the heater to minimize the forces put onto it.

(h) Place two ceramic washers over each metal stud (8 washers total). This will prevent the quartz heater dome from placing pressure on the graphite heater.

(i) Carefully lower the quartz heater dome over the assembly, watching the position of the top thermocouple.

(j) Place the graphite cathode onto the quarter heater dome with its tabs rotated 45°from the metal studs.

(k) Place the quartz heater top ring over the cathode such that the cathode's tabs sit in the slotted grooves.

(l) Remove the metal studs from the setup and replace with ceramic screws. Hand tighten and then loosen by one turn. This will prevent the screws from breaking when the materials expand.

12. Run a growth that has been known to work. Confirm the presence and quality of graphene using the Horiba Labram.
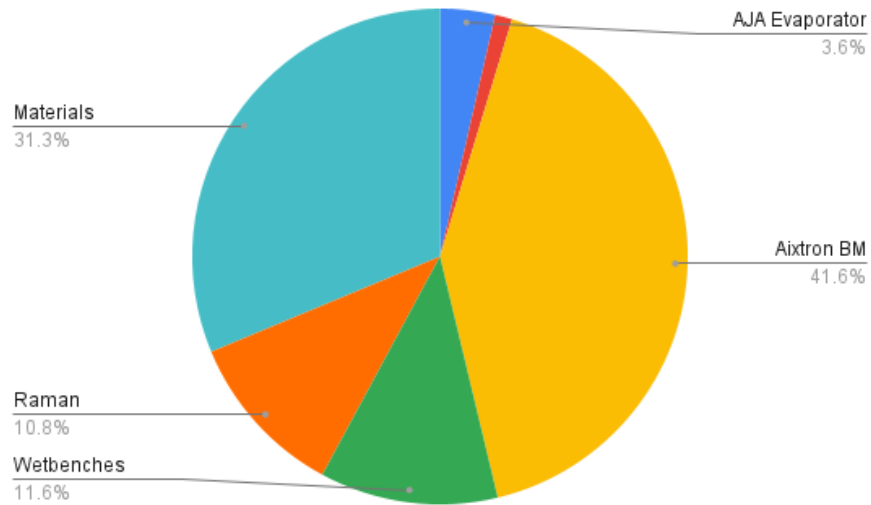
7.6   Budget

Figure 13: Budget distribution for this project.

Tool	Time (hr)	Cost ($)
AJA Evaporator	4.1	146
Samco P3000	0.9	46
' Aixtron BM	48	1693
Wetbenches	9.5	473
Raman	12.6	442

Material	Amount	Cost ($)
Si wafers	5	85
Ge wafers	6	1152
Carriers	many	38
	Total	$4075

Table 5: Detailed breakdown for budget items.

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