CVD lab report snippets (F22) – on CVD graphene grown in VINSE by Sarah Driscoll on 9/29/22

Results/Discussion:

Optical Microscopy:

Optical microscope images were taken at 5x, 20x, 50x, and 100x magnification to visualize the graphene film produced. Images at 5x and 50x magnification are shown in figure 1 below. The areas of red are our substrate while the fainter blue is likely to be graphene.[3] The images are shown in figure 1 below.

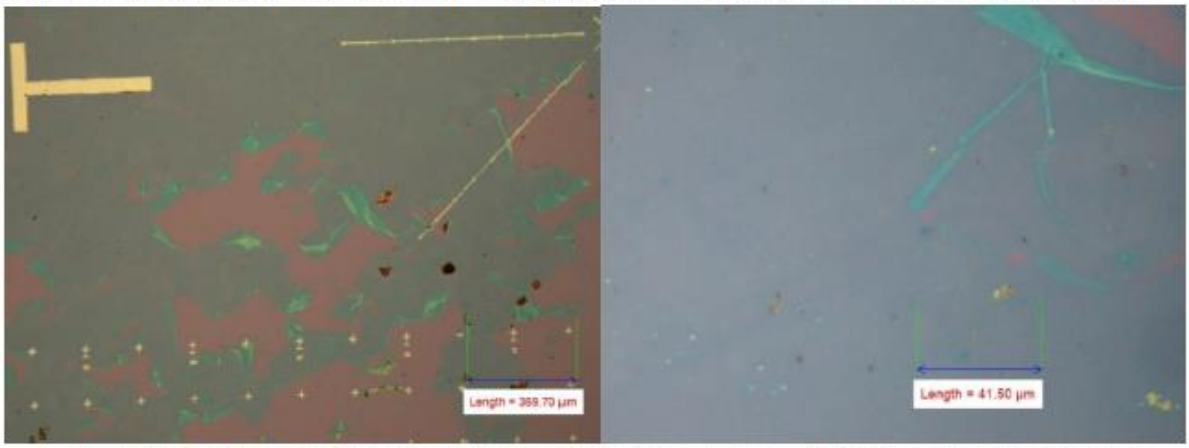


Figure 1: 5x (left) and 50x (right) images from an optical microscope. Areas of faint blue are most likely graphene.

Raman Spectroscopy:

The Raman spectrum produced is shown in figure 2. The 2D peak intensity in this spectrum is greater than the G peak, suggesting that there is monolayer graphene present in the sample.[4] Additionally, the 2D peak has a full width at half maximum of ~35 cm^{-1} and it can be fitted with a single Lorentzian curve, supporting monolayer.[4] Another notable feature of the spectrum is the presence of a D peak at ~1350 cm^{-1}. The relative intensity of I_D/I_G is large, meaning there are many defects present in the sample.[5]

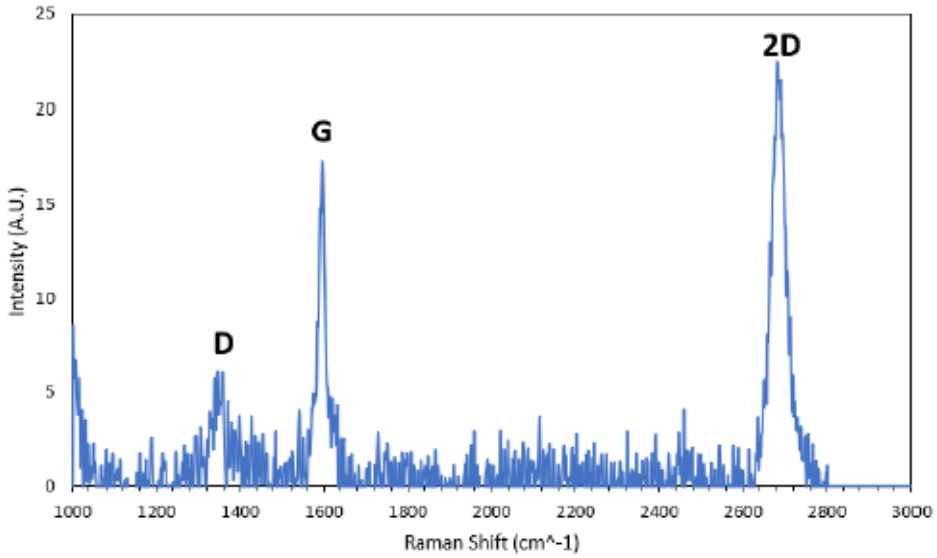


Figure 2: Raman spectrum of graphene produced via CVD. The D, G, and 2D peaks are labeled.

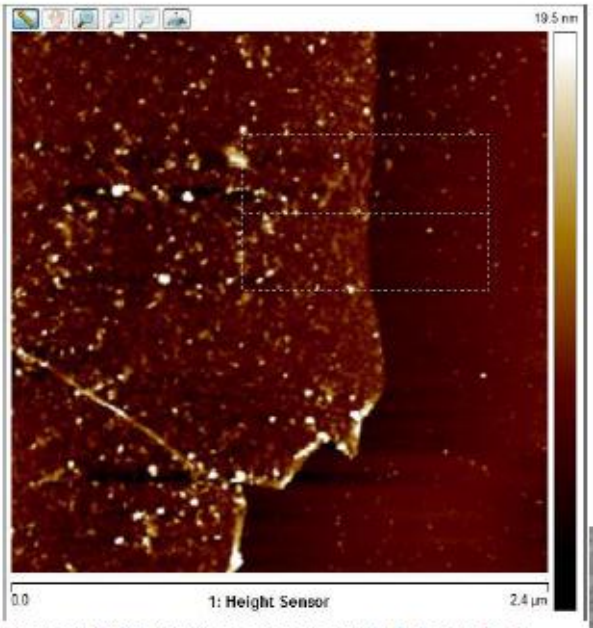


Figure 3: AFM analysis conducted on graphene produced using CVD.

Atomic Force Microscopy (AFM):

AFM analysis was used to determine the topology of the graphene produced. The analysis, shown in figure 3 on the left, determined a film height of 4.08 nm. This is much larger than the expected height of monolayer graphene from literature of <1 nm.[6] This suggests that while the film made using CVD is, at least in some parts, greater than a single layer of graphene. Additionally, the white spots on the sample are likely dust or other debris that give the appearance of a rough film when that isn't actually the case.

Scanning Electron Microscopy (SEM):

An SEM image of the graphene film produced on copper is shown in figure 4 to the right. The darker areas are where a large amount of graphene is present and as the image gets lighter, the amount of graphene and number of layers of graphene decreases.[3]

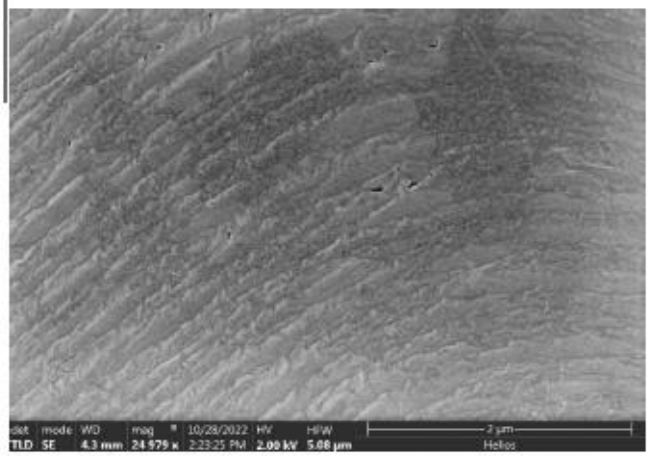


Figure 4: SEM image of graphene produced using CVD on copper

Conclusion:

While the characterization techniques showed conflicting information, it's clear CVD successfully produced "few" layers of graphene. While this method is cheap and scalable, the presence of impurities found with Raman spectroscopy as well as the polycrystalline nature of the graphene produced present challenges in CVDs outlook. Despite this, it's still the leading candidate for graphene synthesis.

References:

1) P. Kidambi, *Brightspace*, Class 3, Slide 21
2) P. Kidambi, *Brightspace*, Class 11, Slide 10
3) H. Hiura *et al* 2010 *Appl. Phys. Express* **3** 095101
4) N. O. Weiss et. al, *Advanced Materials* **24**, 43 (2012)
5) A. C. Ferrari et. al, *Phys. Rev. Lett.* **97**, 18 (2006)
6) Pang, Shuping & Englert, et al. Extrinsic Corrugation-Assisted Mechanical Exfoliation of Monolayer Graphene. *Advanced materials*. **22**. 5374-7. (2010)
7) P. Kidambi, *Brightspace,* Chemical Vapor Deposition of Graphene

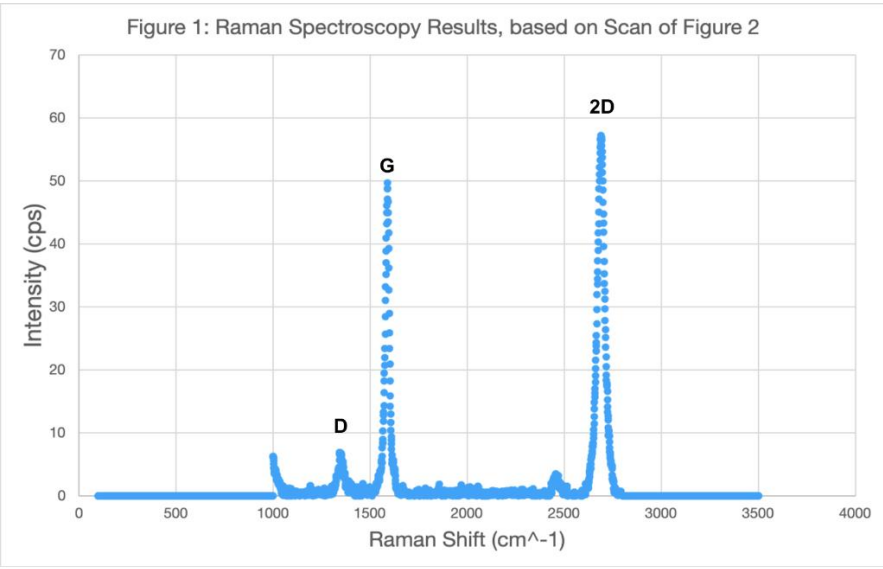
Chemical Vapor Deposition of Graphene

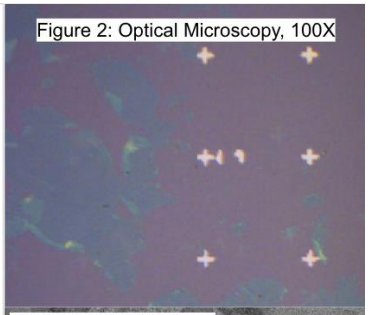
Abstract Optical microscopy imaged light blue colors, suggesting monolayer results. Raman indicated ID/IG ratio of 0.16, a I2D/IG ratio of 1.14, and FWHM of about 43 cm^{-1}, meaning there were samples of monolayer graphene, but the specific points chosen were likely turbostratic graphene, where monolayers overlap. SEM and AFM supported this.

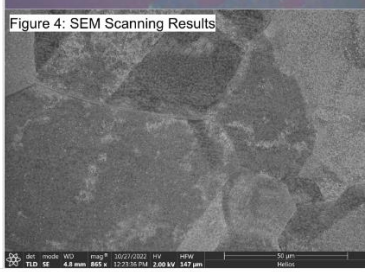
Introduction

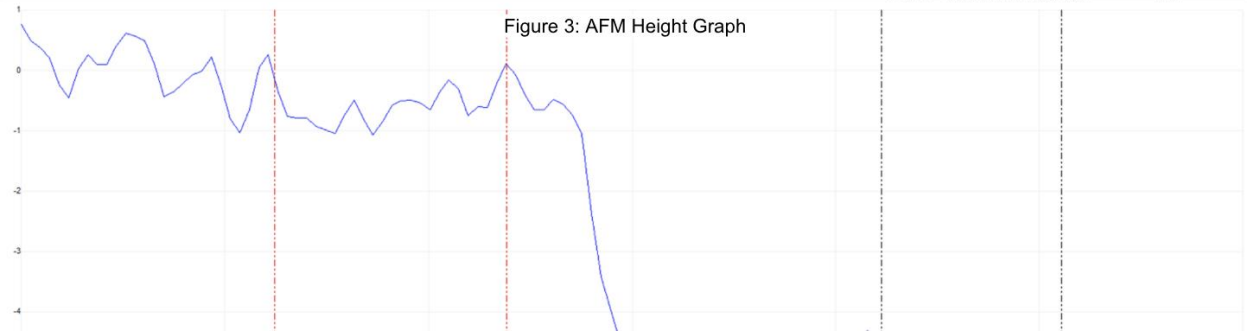
Optical microscopy a method of visually assessing whether a sample is one of monolayer graphene by color. A dark, almost black color is an indication of a bulk sample, a yellow-orange color suggests less layers, but still a bulk sample; a blue with high transparency is likely to be a monolayer graphene sample.[1] To verify this visual analysis, Raman spectroscopy can be used.[4,5] A Raman spectrum for graphene often has three peaks: the D, 2D, and G. The ratios of peak sizes and the full width at half maximum (FWHM) of the 2D peak give insights into the number of layers: a 25-35 cm^{-1} FWMH matched with a 2D/G ratio of >2 is likely to be monolayer. This is because with additional layers, there are increased splits on the 2D peak, making it wider, caused by the interference.[4] Anything fitted with a single Lorentian is a good indication of monolayer. Ideally, the D/G ratio should be < 0.1, because bond stretching of sp2 atoms will be clean. Atomic Force Microscopy (AFM) scans the topography of a sample by probing the surface, creating highly precise scanning images. Graphene has a thickness around 0.35 nm. Scanning Electron Microscopes (SEM) also provide information about the topography of the image, specifically about the quality of the sample and location of grain boundaries.[1]

Results and Discussion









As seen in Figure 1, the Raman spectroscopy yielded three peaks: the D peak had an intensity of 8 cm^{-1}, the G peak had an intensity of 50 cm^{-1}, and the 2D peak had one of 57 cm^{-1}. Thus, the ID/IG ratio was 0.16,

and the I2D/IG ratio was 1.14, a sign that this was not just one layer of graphene. For the 2D peak, the FWHM was about 43cm^{-1}, as it ranged from 2668 cm^{-1} – 2711 cm^{-1}. These values are an indication that the sample viewed was likely overlapping monolayers of graphene. In monolayer graphene, the 2D peak should have a FWHM within the range of 25-35 cm^{-1}, but the value from the graph is slightly higher than this, meaning it is unlikely there are many layers. The I2D/IG ratio should be > 2, but the actual value is 1.14, meaning that it is not meeting the standards set for monolayer graphene. The ratio of the ID/IG is only 0.16, where the ideal for monolayer graphene would be 0.10, so this further suggests that the sample is one of turbostratic graphene. The 2D peak has a higher intensity than the G peak, meaning that this is a medium-quality graphene and the sample is probably intrinsic. Optical microscopy at 100X supports these findings, as the light blue color of samples in Figure 2 denotes. Additionally, the size of the sample from AFM scans shows a thickness comparable to monolayer graphene, as seen in Figure 3.

References

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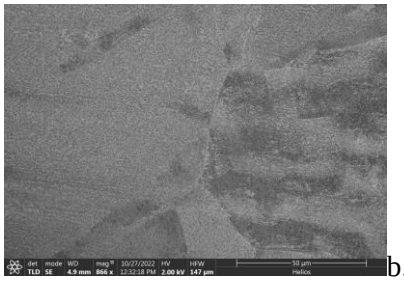
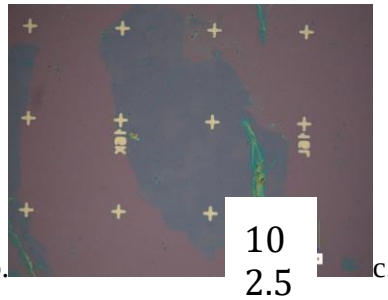
4. CVD Graphene - Creating Graphene Via Chemical Vapour Deposition – Graphenea. https://www.graphenea.com/pages/cvd-graphene#.Y3b4V-zMJzQ.
5. Discovery of graphene - Graphene - The University of Manchester. https://www.graphene.manchester.ac.uk/learn/discovery-of-graphene/.

Chemical Vapor Deposition Synthesis and Characterization of Graphene

Optical microscopy and Raman Spectroscopy provide valuable insight into the nature of our sample of graphene through details such as flake size and thickness. Scanning Electron Microscopy (SEM) is often used to determine the surface morphology of materials as it involves a detector for secondary electrons being emitted from the sample. Similar to optical microscopy, it shows contrast differences between the graphene sample and the substrate (in this case, the Cu foil or Si/SiO_2 wafer). This lab also used AFM which provided information about the sample surface morphology and thickness. These characterization techniques are all unique in that they are each able to provide a different piece of information regarding the sample in a way that will hopefully allow us to have a better overall understanding when combined.

Results

a. 
b. 

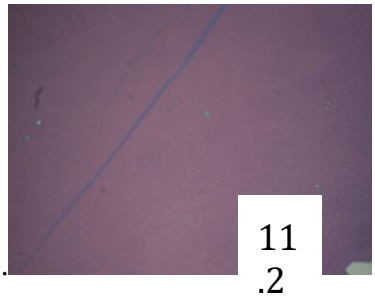
c. 

Figure 1: (a) SEM of CVD Graphene on Copper Foil; (b) 20x Optical Mi f CVD Graphene; (c) 100x Optica copy of CVD graphen

Figure 1(a) shows the SEM of graphene on copper and its subsequent folding lines and wrinkles. Furthermore, as shown in Figure 1(b), indicated by the dull blue color and grid, our CVD produced a rather large flake of graphene. Figure 1(c) at 100x zoom reflects flake characteristics as it causes a hazy blue over the entirety of the visual portion.

After having transferred the graphene from the copper foil to the silicon wafer, we were able to better image the sample with the Optical Microscope and subsequently use Raman Spectroscopy to better quantify the number of layers of graphene present in the sample.

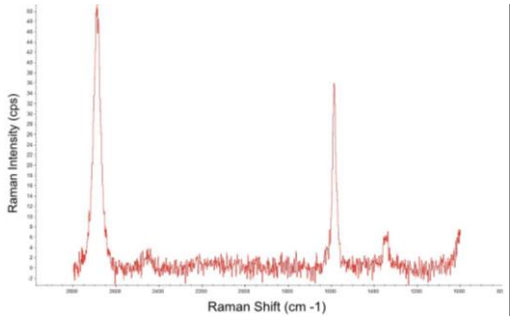


Figure 2: Raman Spectroscopy of Graphene on Si wafer

The Raman Spectra suggests this sample may be monolayer graphene. This is supported by the fact that the G peak (at about 1600 cm-1) is much smaller than the 2D peak (at about 2700 cm-1). The 2D peak can likely be fit with a single Lorentian curve with a FWHM of greater than 40 cm-1 which suggests the possibility of turbostratic graphene (overlapping monolayers). On the right, the low intensity of the D peak (at about 1300 cm-1), suggests there are fewer out of plane sp2 bonded carbons which indicates the sample collected is of high quality.

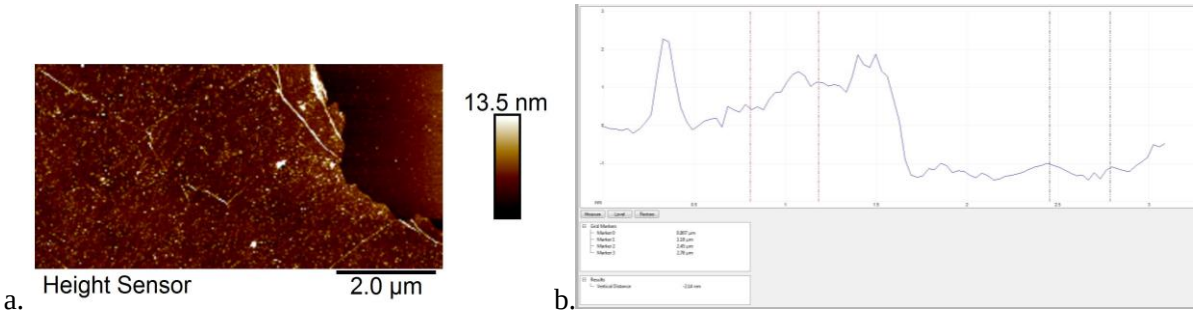


Figure 3: AFM (a) image and (b) spectra

The AFM analysis shows detail about the graphene thickness. The sample seems to be about 2.14 nm in height as seen in the graph of Figure 3(b). Figure 3(a) is greatly indicative of the surface morphology of our graphene sample as it shows areas of greater and lower heights to an incredibly small resolution. It also shows relatively uniform contrast, indicative of height, throughout which would support the Raman data suggesting high quality (and consistent) graphene.

various characterization techniques.

Results

SEM was used to observe the graphene on the Cu foil prior to PMMA transfer. Fig.1 shows the SEM images obtained. At a lower magnification, distinct domains of Cu can been identified, as well as Cu grain boundaries. With higher resolution imaging, patches of varying contrast can be seen.

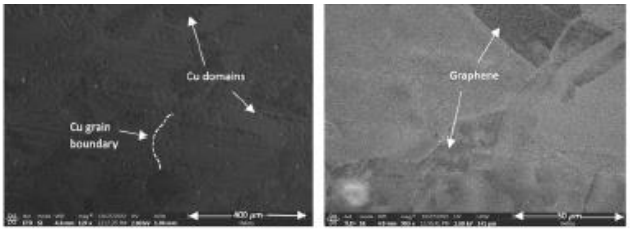


Figure 1: (A) Low magnification, and (B) higher resolution SEM images of graphene on Cu foil

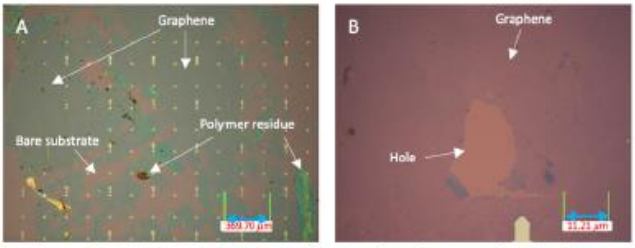


Figure 2: (A) 100X, and (B) 5X optical images of graphene transferred on SiO_2

Optical microscopy was used to observe the graphene after PMMA transfer onto SiO_2. The 100X magnification optical image shows relatively large coverage of uniform dull blue contrast (>500 μm islands). There are also smaller areas of brighter blue contrast, as well as patches of light purple. There are smears of blue and black residue, ranging in size from ~50 μm to >400 μm in length (Fig.2A). A higher magnification optical image (Fig.2B) confirms mostly uniform contrast throughout the sample, with a small (~15 μm) hole seen in the sample.

Raman spectroscopy was used to confirm the composition of the sample. A large uniformly blue area of the sample was chosen to analyze. The raw data collected from Raman spectroscopy was plotted using Excel, and the peak features were identified (Fig.3). There was a tall and narrow peak ~2688 cm^{-1} corresponding to the 2D peak, with I_{2D}=506 and $FWHM_{2D}$=38 cm^{-1}. There was a peak ~1589 cm^{-1} corresponding to the G peak, with I_G=289 and $FWHM_G$=19 cm^{-1}. The D peaks occurs ~1344 cm^{-1}. The small peak at ~1626 cm^{-1} corresponds to the D' peak ($I_{D'}$=41.4). There was a peak ~2457 cm^{-1} (intensity=28). There was also a peak ~3250 cm^{-1}(intensity=29).

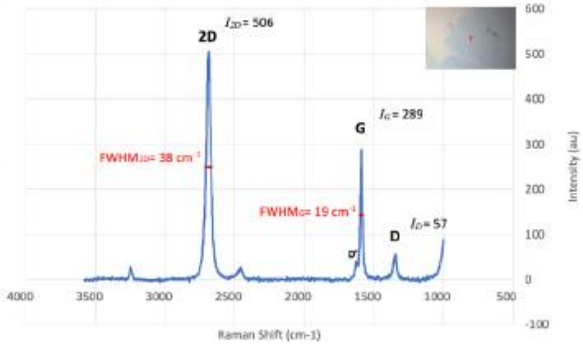


Figure 3: Labeled Excel plot of raw Raman data with corresponding optical image

AFM was used to measure the thickness of the graphene. The AFM tip was tapped across a graphene/SiO_2 edge. Figure 4 shows the raw data plotted using Excel (Fig.4A), and corresponding AFM topography map (Fig.4B). The red dashed lines in Fig.4A represent the area of the plot chosen for averaging height values for graphene; the black dashed lines represent the area of the plot chosen for averaging height values for SiO_2. The difference in the two average values was determined by the software to be 4.08 nm. The AFM height map provides topographical information and confirms a distinct difference in height of graphene and SiO_2.

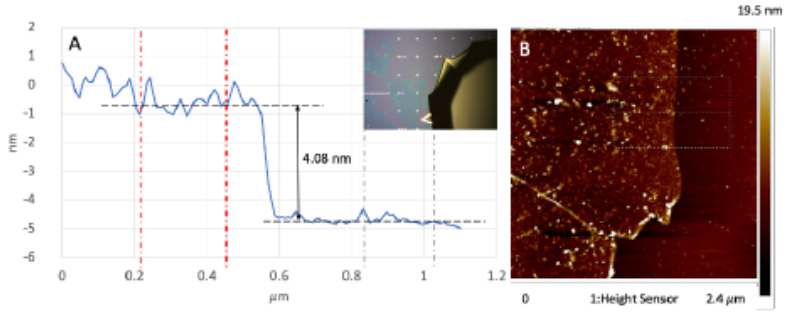


Figure 4: (A) Labeled Excel plot of raw AFM data with corresponding optical image, and (B) AFM height map

Discussion

The SEM images of the sample were analyzed. At a lower magnification, distinct domains of Cu are distinguished by varying levels of contrast in the image corresponding to different crystal orientations of the Cu. With higher resolution imaging, patches of graphene can be identified as the areas of the image with darker contrast (graphene will conduct more electrons). It should be noted that the magnification must be increased (typically >2k) to see wrinkles in the sample; wrinkles arise from the difference in thermal expansion coefficients for graphene and Cu. SEM images can provide information about the coverage of flakes, but definite identification of graphene is hard using SEM. Contrast in SEM images is hard to predict, as contrast depends on a material's efficiency for generating secondary electrons (provides no chemical contrast). Therefore, further SEM images were not useful to confirm the composition of the sample.

The optical microscopy images of the sample were analyzed. The sample contained large (>500 μm) areas of dull uniformly blue contrast suggesting monolayer graphene. The smaller areas of brighter blue contrast indicate multiple layers of graphene. The patches of dull purple throughout the 100X optical image represent bare SiO_2, indicating holes in the transferred film. These conclusions are supported by Deshmukh and Singh's work with optical microscopy of graphene on 300 nm SiO_2/Si[1], but Raman spectroscopy is needed to confirm monolayer graphene. The various residue patches are a result of the PMMA transfer process. The yellow scratch in the bottom left corner of the 100X optical image is likely scratching from the process of depositing gold onto the Si/SiO_2 wafer to create the markers on the substrate.

Raman spectroscopy was used to confirm the composition of the sample. The peak features are not necessarily all characteristic of monolayer graphene. The 2D peak occurs ~2688 cm^{-1} ($FWHM_{2D}$=38 cm^{-1}), and can be fitted with a single Lorentian curve. The typical accepted valued for $FWHM_{2D}$ is ~25-35 cm^{-1} for monolayer graphene The I_{2D}/I_G peak ratio ≈1.75. Typically for monolayer graphene, I_{2D}/I_G >2. Yao et al. found I_G/I_{2D} =0.44 for bilayer graphene, and I_G/I_{2D} =0.63 for 4L graphene[2], suggesting the area of the sample is somewhere in between that (I_G/I_{2D} ≈0.57 for sample). It is possible that the sample contained areas of monolayer graphene folded onto itself, which would lead to these deviations from the expected values for monolayer graphene. The D' peak ~1626 cm^{-1} corresponds strain in the lattice. The ratio of I_D/I_G ≈ 5, implying very poor quality of graphene. The peak ~3250 cm^{-1} is considered to be the D+D' peak, and arises from defects[3]. The peak ~2457 cm^{-1} is also characteristic of graphene (but its significance will not be discussed).

AFM was used to determine the height of the sample. The height difference between graphene and SiO_2 determined by AFM analysis was 4.08 nm. This is significantly larger than the height difference Yao et al. observed between monolayer graphene and substrate (1.52 nm)[3]. This confirms Raman analysis indicating the possibility of monolayer graphene folded onto itself.

The CVD grown graphene was compared to the mechanically exfoliated and liquid-phase exfoliated samples previously synthesized in lab. The CVD graphene domains were much larger than flakes obtained

by mechanical or liquid-phase exfoliation. The CVD graphene has a significant decrease in number of layers of graphene as evident by the I_{2D}/I_G peak ratios. The quality of the mechanically exfoliated graphene was by far the best (with $I_D/I_G \approx 0.013$) compared with liquid phase exfoliation (with $I_D/I_G \approx 0.113$) and CVD growth ($I_D/I_G \approx 5$). The decrease in quality and large amount of defects present in the CVD graphene likely predominately arose as a result of the PMMA transfer process. CVD graphene is the most scalable synthesis method, but requires precision at every step to obtain high quality monolayer graphene.

Conclusion

CVD synthesized graphene was characterized by SEM, optical microscopy, Raman spectroscopy, and AFM. SEM images of the sample show the polycrystalline nature of the Cu substrate used for CVD growth. At higher resolutions, patches of graphene can be identified by darker contrast. Optical microscopy shows fair coverage of uniform contrast indicating large domains of graphene (>500 μm). PMMA residue can be seen in the optical images, which leads to a decrease in overall quality of the sample. Raman spectroscopy was used to identify the composition of the sample. The 2D, G, and D peak positions are all characteristic of graphene, but the I_{2D}/I_G peak ratio (1.75), and the height difference between graphene and SiO_2 obtained by AFM (4.08 nm) suggest something other than strictly monolayer graphene. It was hypothesized the areas of the sample analyzed contained layers of monolayer graphene stacked on top of each other. The I_D/I_G peak ratio obtained by Raman suggested poor overall quality of the sample. CVD synthesis (compared to mechanical or liquid-phase exfoliation synthesis methods) is a much more scalable way to produce graphene, but can come with a sacrifice in sample quality if each step (particularly PMMA transfer) is not very precisely performed.

References

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[1] Deshmukh, M.M. and Singh, V. Graphene – An exciting two-dimensional material for science and technology. *Reson.* 16, 238-253 (2011).

[2]Yao, Y. et al. Histogram method for reliable thickness measurements of graphene films using atomic force microscopy (AFM). *Journal of Materials Science & Technology* 33, 8 (2017)