Growth of Graphene by Silicon Carbide Sublimation

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Abstract:

Graphene has become the material of choice for several investigators because of its desirable properties. This two-dimensional "super" material is hexagonally bonded in an sp^2 carbon arrangement. Successful methods for growing graphene include chemical vapor deposition (CVD) on metal surfaces like copper or nickel and by sublimation of silicon carbide (SiC). Graphene on SiC is of particular interest because it does not require transferal onto another substrate like graphene grown on copper does and the process is not as strenuous and damage-prone. This work investigates the conditions necessary for producing graphene on C-terminated 6H-SiC wafers by sublimation. Hydrogen (H_2) surface etching was performed at 1200°C, while sublimation was done between 1500°C-1700°C in the presence of argon (Ar) gas, at a pressure of 200 Torr. The growth times were varied from 15-60 minutes. Scanning electron microscopy (SEM) and Raman spectroscopy were used to characterize the results obtained for single and multilayer graphene.

Materials

Introduction:

Graphene, due to its specific aggregation of carbon atoms, forms a two-dimensional honeycomb crystal lattice. Graphene's first experimental discovery, via micromechanical cleavage using Scotch tape, catalyzed many researchers' interest. Since its discovery, unforeseen conclusions regarding the immense strength, thinness and durability of the material have spun into copious research topics within engineering and science. Since graphene's first experimental discovery, many techniques have been explored to increase its reproducibility. Core problems remain in regards to growing defect-free large area graphene.

Experimentation was designed to determine growth parameters for producing single, bi-layer and/or multi-layer graphene with large grain boundaries. Therefore, we chose to investigate the formation of graphene by sublimation of SiC substrates using a high temperature CVD system.

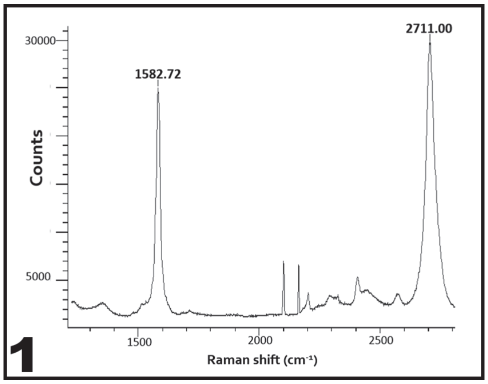
Experimental Procedure:

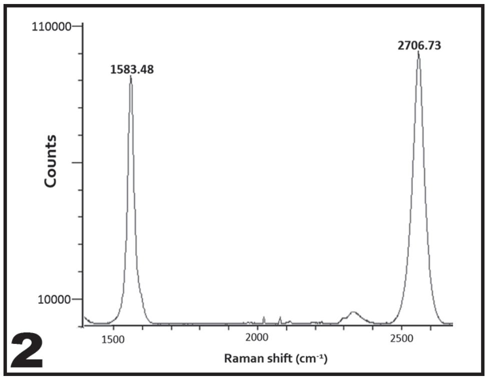
In this work, 4H and 6H SiC substrates were cut into smaller 1 × 1 cm pieces, which were then cleaned by acetone and methanol sonication, followed by a hydrofluoric acid dip. The samples were then loaded into the CVD system, where they were purged with H_2 for two cycles of five minutes at 200 Torr. The temperature was then increased from room temperature to the etch temperature of 1200°C in H_2, after which the temperature was again increased to the sublimation temperature of 1500 -1700°C in Ar. C-terminated 6H-SiC substrates were etched for 30 minutes at 1200°C in H_2 and sublimed for 30 minutes at 1700°C in Ar. Conversely, Si-terminated 6H-SiC substrates were etched for 60 minutes in H_2 at 1200°C and sublimed at 1500°C for 60 minutes in Ar. At the end of the growth cycle, the temperature was decreased to room temperature with the system being purged with Ar before removing the samples.

Results:

We concentrated on graphene by sublimation of 6H-SiC substrates relative to the other polytypes. Originally, it was observed that H_2 etch times contributed greatly to how efficiently silicon would sublime. Etch times ranged from 15-120 minutes and SEM was used to obtain surface imaging. There was expectancy for the surface to be smooth and consistent, but etch times longer than 60 minutes showed pits and scratches; depicting over-etching or high penetration. With this discovery, further etches were done for 30-60 minutes instead.

The sublimation growths under argon were then conducted, firstly at 1500°C and later increased to 1700°C. Increasing the growth temperature to 1700°C was the pinnacle modification for C-terminated samples.





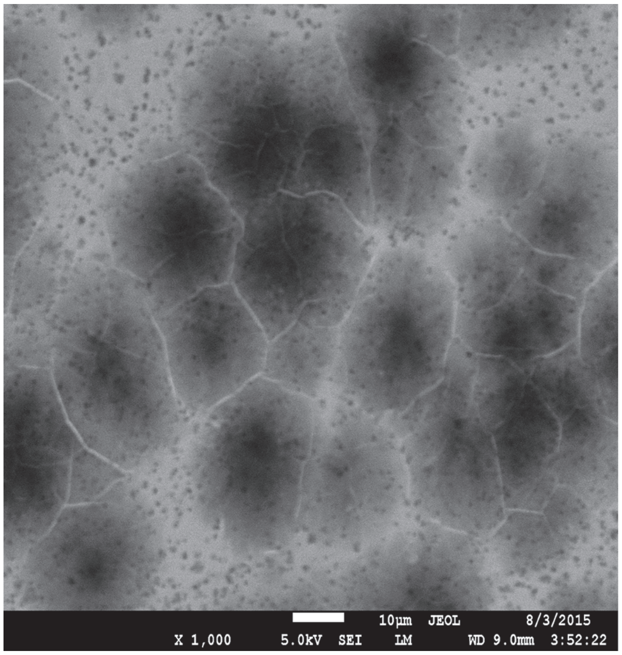


Figure 1, top left: Raman spectroscopy results of graphene on C-terminated 6H-SiC. ***Figure 2, bottom left:*** Raman spectroscopy results of graphene on Si-terminated 6H-SiC. ***Figure 3, above:*** SEM image of C-terminated 6H-SiC.

Using Raman spectroscopy, we characterized a G-band of 1587.82 cm^{-1} and 2D-band of 2711.00 cm^{-1} with a 2:1 ratio between the bands (Figure 1). Additionally, Si-terminated samples showed progress in growth when etch and growth times were increased to 60 minutes. Here the temperature remained at 1500°C with a G-band of 1583.48 cm^{-1} and 2D-band of 2706.73 cm^{-1} with a 3:1 ratio between bands (Figure 2).

Conclusions:

Small deviations in growth parameters caused significant variations in results. After numerous adjustments to the growth parameters and studying each result, patterns of epitaxial graphene growth arose for very specific conditions; noticeable for both the Si-terminated and C-terminated 6H-SiC substrates. Characterization by Raman spectroscopy, indicated bi-layer and multi-layer graphene growth by SiC sublimation. Si-terminated 6H-SiC grain sizes were 5.0-7.5 µm. In comparison, C-terminated 6H-SiC grain sizes were three times larger than those on Si-terminated, measuring 20-31 µm (Figure 3).

Future Work:

We intend to investigate the cause of grain boundary size deviations in C-terminated and Si-terminated 6H-SiC substrates. Also, we hope to further understand the parameter augmentations that affect graphene growth. Lastly, growth of graphene by sublimation on 3C-SiC grown on silicon may be useful in understanding and achieving high quality graphene growths.

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