Large-Area Chemical Vapor Deposition of Graphene over Thin Films of Cobalt

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Abstract:

The synthesis of graphene over thin films of cobalt was demonstrated by chemical vapor deposition, using methane as a precursor. At sufficiently high temperatures, decomposition of methane led to dissolution of carbon in the cobalt film. Upon subsequent cooling of the metal film to room temperature, the solubility of carbon in cobalt is reduced, leading to segregation of some carbon atoms to the surface in the form of graphene. Subsequently, etching away the underlying cobalt made it possible to transfer the graphene film to arbitrary substrates, including insulator substrates such as silicon dioxide. Further analysis of the graphene films revealed that they generally consisted of a large continuous region of thin few-layer graphene, with many patches of thicker multi-layer graphene present throughout the film. Raman spectroscopy confirmed the presence of single-layer regions, as well as the presence of defects pervasive throughout the films.

Introduction:

Graphene, first identified in 2004, is a one-atom thick sheet of carbon atoms, wherein the carbon atoms are arranged in a 2-dimensional hexagonal lattice. The common material graphite can be viewed as a large number of graphene sheets stacked together.

Single-layer graphene has many favorable electronic properties, such as a high electron mobility, that may lead to transistors that operate much faster than conventional silicon devices. However, these properties are substantially degraded when graphene is present in multiple layers.

Unfortunately, it is very difficult to produce large, continuous layers of single-layer or even few-layer graphene. Most graphene used in research is obtained by "mechanical exfoliation," a process that is inefficient, labor-intensive, and non-scalable. For this project, we sought to develop a practical method to synthesize large graphene films using chemical vapor deposition.

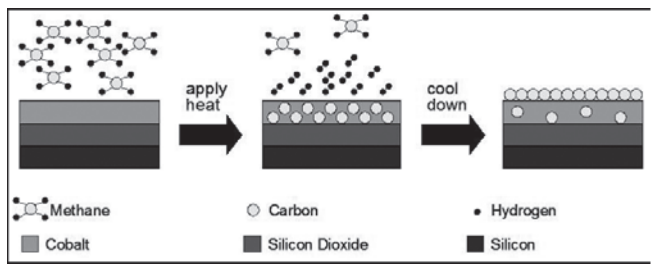


Figure 1: Graphene synthesis mechanism.

Experimental Procedure:

For this project, we began by depositing a 100 nm film of polycrystalline cobalt on a silicon dioxide substrate using electron-beam evaporation. We then exposed this cobalt to methane and hydrogen at approximately 850°C for a few seconds. Methane molecules (CH_4) were adsorbed at the cobalt surface and hydrogen was then desorbed from the surface, leaving the remaining carbon atoms to dissolve in the cobalt film. The methane had thus decomposed into carbon and hydrogen according to the reaction:

$$CH_4 \rightarrow C + 2H_2$$

Any amorphous carbon on the surface was etched away by the high-temperature hydrogen gas. Afterwards, as the cobalt cools to room temperature, the solubility of carbon in the cobalt decreases. This causes some of the dissolved carbon to segregate out to the surface, forming a continuous film of graphene, as shown in Figure 1.

The cobalt was subsequently etched away, and the graphene was transferred to a new silicon dioxide substrate. Further analysis was then performed using optical microscopy, scanning electron microscopy, atomic force microscopy, and Raman spectroscopy.

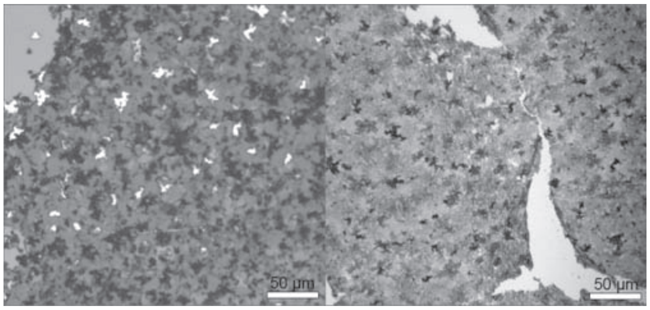


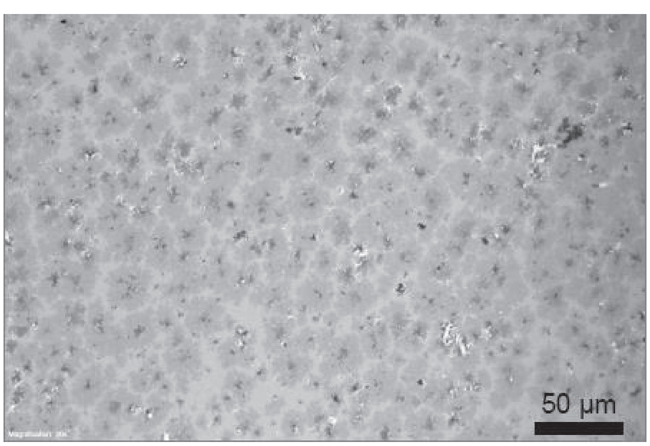
Figure 2: Optical comparison of nickel-grown graphene (left) and cobalt-grown graphene (right). Bright white indicates the thickest, most undesirable graphitic regions. All scale bars 50 µm.

Results and Conclusions:

Researchers have already successfully grown graphene over thin films of nickel [1]. We therefore began by growing graphene both over nickel and over cobalt, and compared the results as shown in Figure 2. From this comparison, we found that using cobalt instead of nickel virtually eliminated the thickest, most undesirable regions.

Ultimately, we found that drastically shorter growth processes, on the order of minutes instead of hours, yielded significantly better results, as shown in Figure 3. Unfortunately, thicker patches were still present throughout, which we believed to be due to the polycrystalline nature of the original cobalt surface. Scanning electron microscopy revealed microscopic cracks in the graphene, while atomic force microscopy revealed small growths over the graphene.

We also analyzed our films using Raman spectroscopy over a region that we thought might be single-layer graphene, with the Raman spectrum shown in Figure 4. The relative strength of the 2D peak (~ 2700 cm^{-1}) to the G peak (~ 1581 cm^{-1}) suggests the presence of single-layer or bilayer graphene. Further analysis of the 2D peak revealed that it could be fit to a single Lorentzian curve, which strongly suggests the presence of single-layer graphene. However, the strength of the D peak (~ 1350 cm^{-1}) indicates a substantial presence of microscopic defects throughout our film. This is in addition to the thicker multilayer patches previously mentioned.



Future Work:

Most crucially, the electronic properties of these films must be measured by fabricating devices. As well, continued Raman studies may allow us to estimate what percentage of the total graphene films is single-layer, bilayer, multilayer, etc. Furthermore, since Raman spectroscopy indicates a strong presence of defects, the source of these defects must be determined so as to minimize them. It is likely that these defects arise during the transfer process, however this is not yet confirmed.

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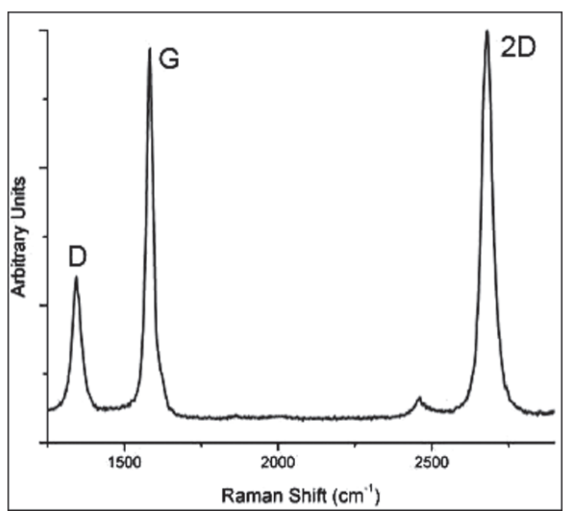

Figure 3, left: Graphene synthesized after shortening the growth process. Note the greater uniformity of the film compared to those shown in Fig. 2.

Figure 4, above: Raman spectrum of a region of monolayer graphene.