Vacuum Technology in the study of Graphene

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Abstract. Graphene, an allotrope of carbon is a two-dimensional sheet of covalently bonded carbon atoms that has been attracting great attention in the field of electronics. In a recent review graphene is defined as a flat monolayer of carbon atoms tightly packed into a 2-D honeycomb lattice. A survey has been made of the production processes and instrumentation for characterization of graphene. In the production of graphene, the methods mainly used are Epitaxial growth, oxide reduction, growth from metal-carbon melts, growth from sugar. In the characterization of graphene, the instruments that are mainly used to study the atomic properties, electronic properties, optical properties, spin properties are Scanning Electron Microscopy, Transmission Electron Microscopy, Raman Spectroscopy. In all these instruments high or ultra-high vacuum is required. This paper attempts to correlate vacuum technology in the production and characterization of graphene.

1. Introduction.

Graphene, a carbon allotrope with a two-dimensional honeycomb structure, has become an important player at the forefront of condensed matter physics, drawing the attention of theorists and experimentalists alike due to its challenging nature as a many-body problem, its unusual electronic properties and possible technological applications (see Refs. [1] and references therein). Graphene also belongs to a large class of planar condensed-matter systems, which includes other graphite-related materials as well as high-Tc superconductors. The mobility of carriers in graphene has been reported as high as 15,000 cm2V-1s-1 with the potential to reach 100,000 cm2V-1s-1 with the reduction of impurities [1]. The increase of charge carriers does not significantly reduce the mobility, unlike 3-dimensional semiconductors where dopants and phonons act as scattering centers and reduce mobility. From Lattice Monte Carlo simulations of the phase diagram of graphene as a function of the Coulomb coupling between quasiparticles, it was shown that the graphene in vacuum is likely to be an insulator([1]).

An important property of graphene is optical transparency. This somewhat limits observation and detection of the material, however Raman spectroscopy and electron microscopy are viable techniques to identify single-layer graphene [1]. The optical transparency of graphene attracts attention because the conductivity is not adversely impacted by the thinness of the material. The single-atom layer is not depleted of charge carriers (in contrast to conventional semiconductors) and may offer solutions to the opto-electronics industry.

Graphene can be fabricated in many forms: few-layer sheets vs. free-standing sheet, nano-scale vs. micro-scale. However, to be industrially viable the method needs to be scalable and relatively low cost. The application or end-use of the product usually dictates the method of fabrication. In particular, a
method to fabricate large-area free-standing sheets of single-layer graphene needs to be obtained. This requires an approach that is not limited in size to the starting material. For graphene to be competitive with current or other next-generation products it needs to be affordable. This requires a low-to-moderate fabrication expense. The next three sections will describe some of the patented and patentpending methods to fabricate graphene.

The inherent properties of graphene appeal to many industries, including the electronics industry. The high mobility of charge carriers and the high thermal conductivity offer the industry a potential alternative to silicon and diamond. The nature of the carriers has the potential to create next generation solid state devices (ballistic transistors, spin transistors, etc.). The optical transparency of graphene coupled with the electronic properties may provide the optoelectronics industry with photovoltaic solutions such as transparent electrodes. Other industries also have the opportunity to use graphene’s inherent properties. The carbon base of graphene offers compatibility with organic-based materials. High strength, lightweight materials may be formed with the addition of graphene to conventional plastics.

This paper attempts to correlate vacuum technology in the production and characterization of graphene.

2. Production Processes.

Three primary synthesis methods have emerged for the production of graphene: (i) micromechanical cleavage (Giem 2007, Park 2009), (ii) chemical vapor deposition (CVD) (O’biren, 2010), and (iii) chemical exfoliation (Srinivason 2007, Park 2009).[1]

Micromechanical exfoliation of graphite or the 'scotch tape' method is relatively easy and can yield high quality, large area (~ 1 mm) sheets; however, this technique is low yield and only useful for experimental purposes. In the CVD or epitaxial approach, graphene is grown on a metal, generally Cu, substrate. Single layer and bi-layer graphene sheets, measuring up to approximately 1 cm square have been produced successfully by this method. However, neither method is currently capable of producing bulk quantities of graphene. The chemical methods of synthesizing graphene (Srinivason 2007, Park 2009) have emerged as the main approach for large quantity production. This can be done through the chemical exfoliation of graphite oxide (GO). The chemical exfoliation starts with natural graphite and reacts with a mixture of strong acids, such as nitric and sulfuric, and an oxygen donating compound. This reaction induces stress within the graphite layers by intercalating the graphite sheets with oxygen atoms and expanding their separation distance (Srinivason, 2007). The end result is graphitic oxide.

The level of oxidation varies based on the method and initial type of graphite used (Park, 2009). Each method leaves different functional groups at the edge, or sometimes also on the surface of the graphene sheet that influence the chemical and physical properties of the GO. Prior experimental results show that often, chemical exfoliation method can create irreversible defects in the graphene sheets, which can decrease the conductance by 3 orders magnitude compared to a defect-free graphene-sheet (Park, 2009). Therefore, our efforts have been focused on optimizing the oxidation and exfoliation processes to gain finer control on surface defects and edge/surface functional groups.[1]

3. Characterization Instruments

3.1 Scanning Electron Microscope (SEM).

ll electron beam instruments are built around an electron column, which produces a stable electron beam, controls beam current, beam size and beam shape, and raster the beam. Electron optics are a very close analog to light optics, and most of the principles of an electron beam column can be understood by thinking of the electrons as rays of light and the electron optical components as simply their optical counterparts.
3.1.1. Vacuum system of a SEM.
The pump-down sequences for a microprobe and scanning electron microscope are very similar. Initially, a mechanical pump is used to evacuate the column and sample chamber. Pressure is monitored using a thermocouple gauge. Thermocouple gauges work down to a pressure of about $10^{-3}$ torr. Once the vacuum is sufficiently good, the "gate" valve that isolates an oil diffusion pump from the column is opened. This allows the diffusion pump to evacuate the column further. There is a water-cooled baffle located above the pump to prevent oil vapor from entering the electron column. A cold-cathode (ion) vacuum gauge, which operates at pressures down to $10^{-6}$ torr, is used to monitor the pressure at higher vacuums. A cold-cathode gauge gets dirty with time and reads a better vacuum than actually exists.

During initial pumping (green and blue) the column is evacuated using mechanical pump 1. Once a vacuum of about 1 torr is achieved the gate valve opens to access the oil diffusion pump (green and red), isolating mechanical pump 1. The diffusion pump is kept at operating vacuum by mechanical pump 2. The ballast tank serves as a vacuum reservoir and allows the diffusion pump to function for short intervals with pumps 1 and 2 turned off. This minimizes mechanical vibration and permits high magnification operation.

3.2. Transmission Electron Microscope (TEM)
Due to strong interactions of electron with matter, gas particles must be absent in the column. The required high vacuum is maintained by a vacuum system typically comprising a rotary pump (pre-vacuum pump), a diffusion pump and one or more ion getter pumps.

There are three main types of vacuum pump: rough pumps, high vacuum pumps which need backing, and high vacuum pumps which don’t need backing.

A rough pump can pump down from atmospheric pressure, but can only reach a rather modest vacuum, at best 0.01 mbar (0.00001 of an atmosphere). High vacuum pumps can reach good or ultra-high vacuum (UHV), between $\log(-6)$ - $\log(-10-11)$ mbar. A high vacuum pump that needs backing means that it needs another pump (a rough pump) to work on the 'back end of it' (the high-pressure end), to take away from it air that it has pumped out of the vacuum chamber. Examples of such pumps are diffusion pumps and some types of high-vacuum turbo pumps.
Some UHV pumps, like ion pumps, do not need backing: the vacuum they deal with has such a low pressure that the pump can dispose of residual gas atoms simply by accelerating them into the solid walls of the pumping chamber (this seems improbable, but it does work).

3.3. Raman Spectroscopy

Raman spectroscopy is a useful technique for the identification of a wide range of substances - solids, liquids, and gases. It is a straightforward, non-destructive technique requiring no sample preparation. Raman spectroscopy involves illuminating a sample with monochromatic light and using a spectrometer to examine light scattered by the sample.

At the molecular level photons can interact with matter by absorption or scattering processes. Scattering may occur either elastically, or inelastically. The elastic process is termed Rayleigh scattering, whilst the inelastic process is termed Raman scattering. The electric field component of the scattering photon perturbs the electron cloud of the molecule and may be regarded as exciting the system to a ‘virtual’ state. Raman scattering occurs when the system exchanges energy with the photon, and the system subsequently decays to vibrational energy levels above or below that of the initial state. The frequency shift corresponding to the energy difference between the incident and scattered photon is termed the Raman shift. Depending on whether the system has lost or gained vibrational energy, the Raman shift occurs either as an up- or down-shift of the scattered photon...
frequency relative to that of the incident photon. The down-shifted and up-shifted components are called respectively the Stokes and anti-Stokes lines. A plot of detected number of photons versus Raman shift from the incident laser energy gives a Raman spectrum. Different materials have different vibrational modes, and therefore characteristic Raman spectra. This makes Raman spectroscopy a useful technique for material identification. There is one important distinction to make between the Raman spectra of gases and liquids, and those taken from solids - in particular, crystals. For gases and liquids it is meaningful to speak of the vibrational energy levels of the individual molecules which make up the material. Crystals do not behave as if composed of molecules with specific vibrational energy levels, instead the crystal lattice undergoes vibration. These macroscopic vibrational modes are called phonons.

Raman spectroscopy is a purely optical experiment. The sample is cooled to cryogenic temperatures under a vacuum and exposed to radiation, usually in the visible spectrum. This radiation causes the atoms in the sample to enter an excited state. When the atoms return to a lower energy state, they emit radiation, which is measured by a detector. This luminescence yields a great amount of information about the electronic structure of the sample.

4. Study of graphene by Scanning Electron Microscopy, Transmission Electron Microscopy, Raman Spectroscopy.

The SEM micrograph of graphene samples can examine the nature of structure of growth of the on the substrate. at 80 kV acceleration voltage. Example:

Fig. 7: TEM images of few-layer graphene (a) single layer graphene (S) and bilayer graphene (B) supported by multi-layer graphene (M) (scale bar : 250 nm), (b) Atomic resolution image of the single layer in (a) (scale bar : 1 nm), inset: electron diffraction pattern corresponding to a single layer graphene (left) and higher magnification image (right) (c) bilayer graphene having a mismatch of crystal orientation (scale bar : 2 nm), inset : electron diffraction pattern corresponding to a turbostructurally arranged bilayer (right) and (d) chemically bonded few-layer graphene having different orientations (scale bar : 2 nm).[ Growth and properties of few-layer graphene prepared by chemical vapour deposition[2].

TEM micrograph can detect the types of layer in a graphene i.e. single layer,multilayer,bi-layer. Atomic resolution imaging of graphene has been achieved in TEM using an aberration-correction technique in combination with a monochromator;point defects, formation and annealing of Stone-Wales defects, and multiple pentagons/heptagons combinations were observed in situ. The stability and dynamics of the edge of a hole in a suspended graphene platelet has been studied; TEM images with a stated sub-Ångstrom resolution showed that both ‘armchair’ and ‘zigzag’ configurations could be formed during the edge reconstruction and ‘zigzag’ edges were observed to be particularly stable under electron irradiation.
4.1 Raman Spectroscopy.
Raman spectroscopy has been used to characterize graphene and several review articles have been published discussing the optical phonon spectrum and Raman spectrum of graphene. The Raman spectra of graphene includes the G peak located at ~ 1580 cm$^{-1}$ and 2D peak at ~ 2700 cm$^{-1}$, caused by the in-plane optical vibration (degenerate zone center $E_2g$ mode) and second-order zone boundary phonons, respectively. The D peak, located at ~ 1350 cm$^{-1}$ due to first-order zone boundary phonons, is absent from defect-free graphene, but exists in defected graphene. It was proposed that Raman could be used to distinguish the ‘quality’ of graphene and to determine the number of layers for n-layer graphene (for $n \leq 5$) by the shape, width, and position of the 2D peak. As shown in Figure 5, the 2D peak shifts to higher wavenumber values and becomes broader for an increasing number of layers. The shifting and splitting of Raman modes can be used to analyze mechanical strain in graphene. For example, Raman spectra of epitaxial graphene grown on SiC show a significant phonon ‘hardening’ (blue shift of the G and 2D peaks), mainly due to the compressive strain that occurs when the sample is cooled down after growth. It has been stated that the substrates play a negligible role in the Raman spectrum of micromechanically cleaved graphene transferred onto them, indicating the weak interactions between the transferred graphene and such substrates. The frequency of the G and 2D peaks can also be tuned by charge doping through electron-phonon coupling changes. The Raman spectral signatures of epitaxial graphene grown on SiC, especially the width of the 2D peak, have been correlated to the carrier mobility of the graphene. The intensity ratio of the D and G peak has been used as a metric of disorder in graphene, such as arising from ripples, edges, charged impurities, presence of domain boundaries, and others. For edges, the intensity of the D peak depends on the edge structure; it is weak at the zigzag edge and strong at the armchair edge.

Fig. 8. (a) Comparison of Raman spectra at 514 nm for bulk graphite and graphene. They are scaled to have similar height of the 2D peak at 2700 cm$^{-1}$; (b) Evolution of the spectra at 514 nm with the number of layers; (c) Evolution of the Raman spectra at 633 nm with the number of layers.

4. Conclusion.
This paper attempts to correlate vacuum technology in the production and characterization of graphene.

References.

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