

Growth of carbon based nanostructures

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ABSTRACT

Carbon nanostructures such as carbon nanotubes (CNTs) and graphene are being applied to a wide variety of sensor applications. Both CNTs and graphene can be grown by chemical vapor deposition (CVD) from hydrocarbons using catalysts. Both materials require metallic catalysts. CNTs require small particles while graphene requires continuous films. Both materials can be grown by the thermal decomposition of SiC. Under the proper conditions either vertically aligned CNT arrays or planar graphene can be grown. Carbon source molecular beam epitaxy (CMBE) is also under development for growth of graphene. Like SiC decomposition, CMBE is catalyst free but it is not restricted to SiC substrates.

INTRODUCTION

Even though they have been known for decades, carbon nanostructures such as fullerenes¹, carbon nanotubes (CNTs)², and graphene³ are still in the forefront of materials research and development. CNTs and graphene in particular are finding a variety of applications in the sensor field. Due to their high sensitivity to surface contaminants CNTs^{4,5} and graphene^{6,7} are being developed for chemical and biological sensors. CNT based cathodes are finding their way into high power RF sources⁸ while both CNT and graphene have shown promise for RF transistors^{9,10}. CNTs have also been proposed as infrared detectors¹¹ but the possibility of electrically tuning the bandgap of bilayer graphene for use in tunable infrared detectors is eliciting significant interest¹² as well.

Many of these applications require different configurations. Both vertically and horizontally aligned CNTs are under development as are isolated nanotubes and clusters or arrays of tubes. Most graphene applications require horizontal sheets but clusters of vertically grown sheets have been demonstrated and are under investigation. All of this has led to a variety of growth and fabrication techniques for carbon nanostructures. Of particular interest here are chemical vapor deposition (CVD) and thermal decomposition of SiC. Each is being used for both CNTs and graphene. In this paper we will focus on growth of vertical CNTs and planar graphene. New advances in molecular beam epitaxy of graphene will also be discussed. The reader is referred to Liu et al.¹³ for a review of recent advances in CVD growth of horizontally aligned CNTs for electronic applications.

CVD GROWTH

Catalyst assisted CVD growth of CNTs is now well established. As seen in Fig. 1, carpet like dense vertically aligned arrays are now grown routinely¹³ and significant progress has been made in growth of horizontally aligned single walled CNTs for transistor applications¹⁴. In both approaches hydrocarbon gases are used as the carbon source and CNT growth initiates at nanometer size particles of metallic catalysts. The basic process for growth of vertically aligned CNTs is shown in Fig. 2. The presence of the metallic catalyst after growth is an issue for some applications. The metal can only be removed after growth with some difficulty. Single wall CNTs can be grown routinely but control of chirality remains an issue. Techniques have been developed to remove metallic CNTs from horizontal arrays¹⁵. A complete understanding of the growth process, however, is still lacking and significant research is still underway. For example, the role of ambient atmosphere on the size and density of catalysts and resulting CNTs is under active investigation¹⁶.

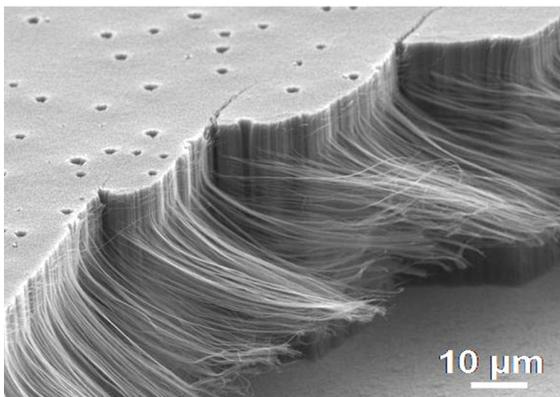


Fig. 1: Carpet of CVD grown single wall CNTs. (ref. 13)

Recent work on the growth process for CVD grown CNT carpets on insulating substrates has shown that much taller films are grown when H₂O is present in the chamber during growth. Amama et al.¹⁶ hypothesized that water impedes catalyst diffusion by temporarily complexing with the catalyst atoms. This reduces the Oswald ripening rate for the catalyst and keeps catalyst particles from disappearing, thus extending the life of the catalysts.

As with catalyst assisted CVD growth of CNTs, CVD growth of graphene on metals has become one of the most widely used processes for growth of large area graphene.

However while the gaseous carbon sources are the same, the role of the metal is different for the two materials. The growth of graphene on transition metals like Ni has been known in metallurgy for a long time. Here graphene growth involves absorption of carbon from the hydrocarbon source into the Ni at elevated temperatures followed by precipitation as graphene as the temperature is lowered¹⁷. The temperature dependence of the solubility of carbon in the metal is the critical parameter. Recently graphene growth on Cu films has been demonstrated¹⁸. Copper has a very low solid solubility of carbon at growth temperatures and below so the process here is different from that on transition metals like Ni. It is believed that the hydrocarbons break up on the Cu surface and then form into graphene without absorption into the Cu. The Cu assists in the decomposition as well as the formation of the free carbon into graphene. This process has the benefit that graphene growth is usually self limited to a single atomic layer. Once a monolayer covers the substrate the role of the metal is diminished and higher temperatures are required to decompose the hydrocarbon source for growth of more graphene layers. Growth on Cu films is now the dominant process due to the ease of growing single layer graphene. However, bilayer graphene, of interest for electro-optic applications such as IR detectors, is more difficult due to the self limiting nature of growth on Cu. After growth with either transition metals or Cu the metal film is chemically etched to leave a bare graphene film that can be transferred to substrates of interest. The transfer process does degrade the graphene somewhat, as indicated by Raman spectroscopy before and after transfer. Continuous graphene films up to 30" wide have recently been demonstrated¹⁹. These are being developed for transparent conductors and touch screen applications for the commercial electronics industry. CVD graphene is polycrystalline but electron mobilities up to 4000 cm²/Vs after transfer have still been demonstrated¹⁸. The reason for polycrystalline growth is still under investigation but the graphene grain structure does not follow that of the metal film.

Somewhat vertical sheets of graphene can be grown on a variety of substrates, including Si, SiO₂ and Al₂O₃, by plasma enhanced CVD²⁰. These sheets are under development for applications in the energy field and have properties similar to vertical CNTs.

SiC DECOMPOSITION

It has been known for some time that heating SiC to temperatures above 1200°C results in decomposition of the SiC with selective evaporation of Si and graphitization of the surface²¹. In 2006 de Heer and coworkers at Georgia Tech demonstrated that this decomposition can be controlled to produce high quality graphene layers on oriented single crystal SiC substrates²², but well before that Kusunoki and coworkers²³ demonstrated growth of dense carpets of CNTs on SiC by annealing in vacuum at high temperatures. The processes for CNT and graphene growth on SiC are clearly related. Fig. 3 shows transmission electron microscopy (TEM) images of both forms of carbon on SiC as well as simultaneous growth of both CNTs and graphene on the same substrate. The general process consists of the removal of Si from the SiC, yielding a carbon rich surface that over time organizes into sp² bonded carbon in either the hexagonal honeycomb lattice of graphene or vertically aligned CNTs. Unlike in CVD processes described above, both CNTs and graphene on SiC grow from the bottom up with the top being the first to

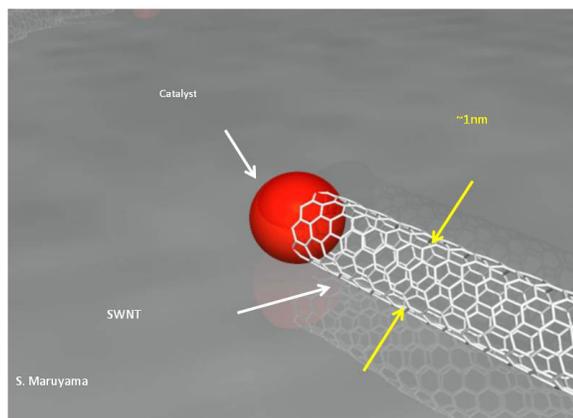


Fig. 2: Growth process for catalytic growth of CNTs, after B. Murayama.

grow and the material closest to the SiC being the last to grow. The principal factor in determining whether graphene or CNTs will be formed is the furnace ambient²⁴. In general, graphene forms in ultra high vacuum (UHV, $P < 10^{-7}$ Torr)²⁵ or in an inert gas such as argon at or near atmospheric pressure²⁶. In high vacuum (HV, $10^{-7} < P <$

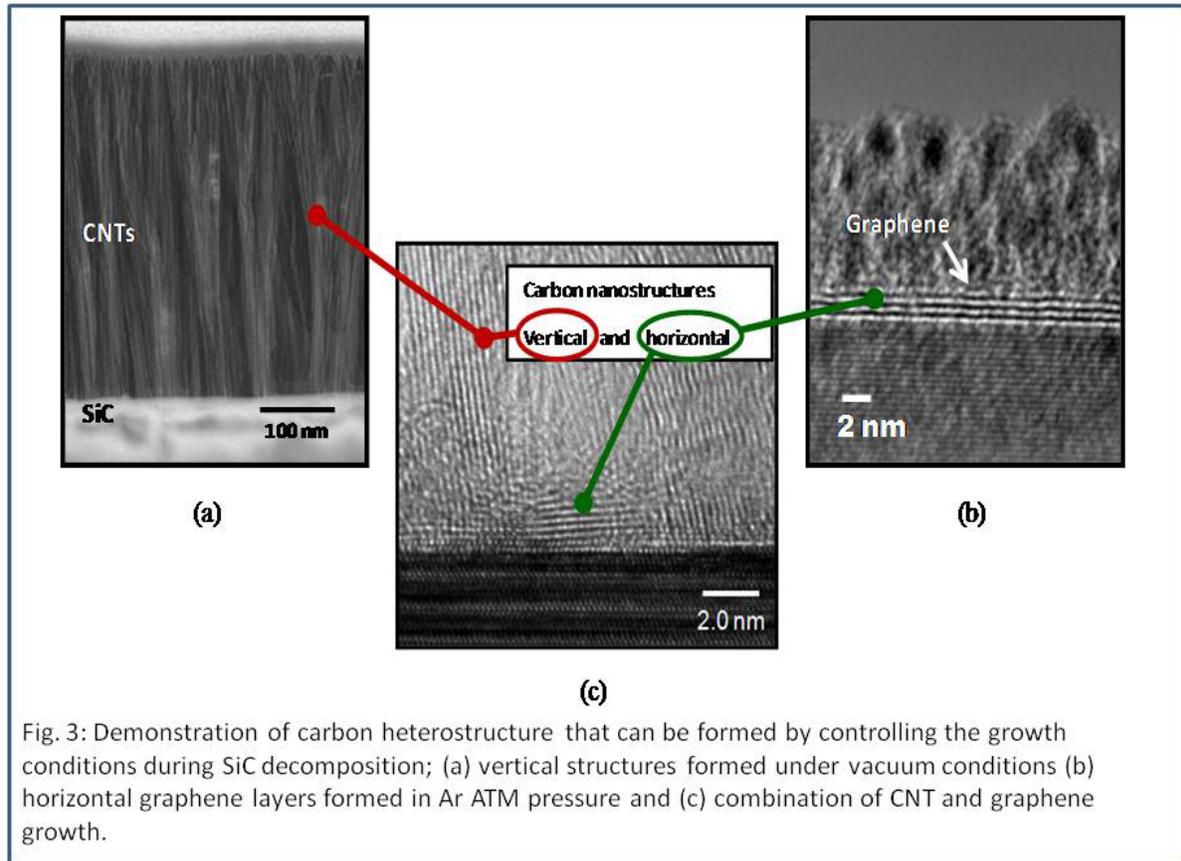


Fig. 3: Demonstration of carbon heterostructure that can be formed by controlling the growth conditions during SiC decomposition; (a) vertical structures formed under vacuum conditions (b) horizontal graphene layers formed in Ar ATM pressure and (c) combination of CNT and graphene growth.

10^{-4} Torr) multiwalled CNTs (MWCNT) are more likely to form. The presence of residual oxygen in the HV environment appears to be the critical factor in the growth of MWNTs^{27,28}. Low pressures of O_2 over SiC are known to produce volatile SiO as opposed to SiO_2 . The oxygen also catalyzes nanotube growth. These MWCNTs are metal-free with minimal structural defects. Recently our group has shown that SWCNTs can also be grown on SiC by thermal decomposition.

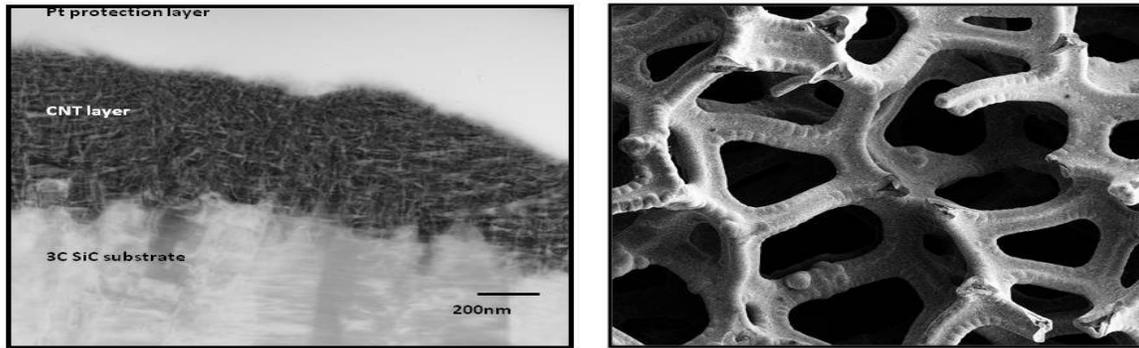


Fig. 4: TEM image of CNTs grown on polycrystalline SiC foam.

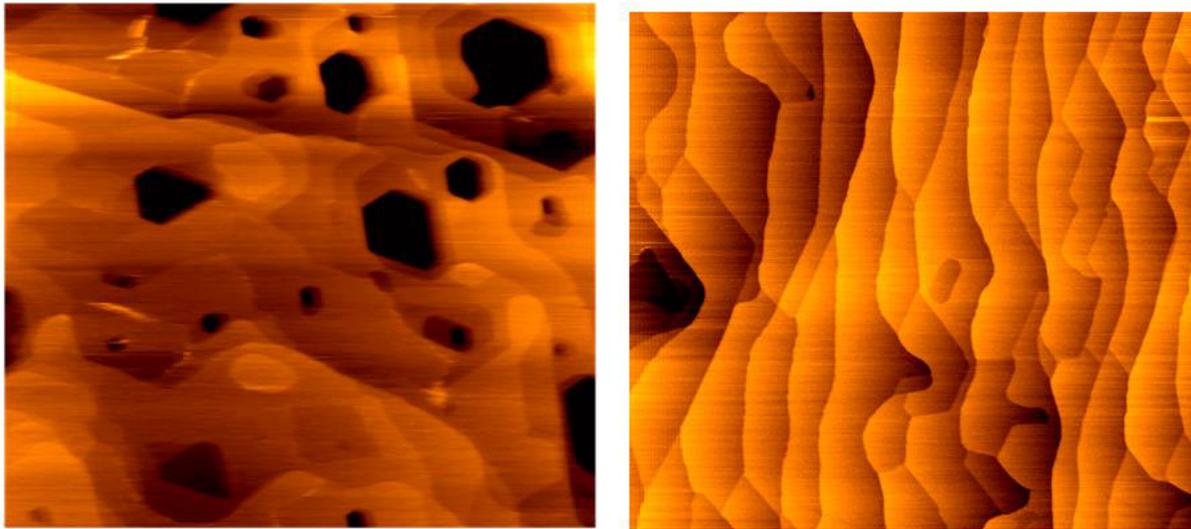


Fig 5: AFM images of graphene grown at UHV (left) and under Ar pressure (right).

We have demonstrated that CNT carpets such as those in Fig. 1a are not limited to oriented single crystal SiC substrates. CNT carpets can be grown on any material onto which a film of SiC can be grown, usually CVD processed, and can withstand the temperatures of 1250°C or higher required to decompose the SiC. Fig. 4 shows a TEM of CNTs grown on polycrystalline SiC foam. We have also grown CNT on nanoscale SiC powders. These dense carpets of nanotubes on both SiC and other substrates are under investigation for application as electron emitters and chemical sensors.

Graphene grown by decomposition of SiC, also called epitaxial graphene, has attracted particular attention because, unlike in CVD grown graphene, the graphene is grown directly on a useable substrate in large areas and transfer is not required. The mobilities of epitaxial graphene are similar to CVD graphene, on the order of a few thousand at room temperature, which is significantly below those of exfoliated graphene. This process does require higher temperatures than CVD growth, which is usually performed between 900° and 1000°C. UHV growth of epitaxial graphene requires temperatures above 1250°C while argon growth requires temperatures about 200°C higher. The higher temperatures for argon growth are, in fact, the reason it is becoming the dominant technique for epitaxial graphene on SiC. The atmospheric pressure reduces the Si evaporation at a given temperature so higher temperatures can be used which enhances the surface mobility of carbon atoms, resulting in smoother films. UHV graphene is often pitted while this is significantly reduced in argon grown material. Fig. 5 shows atomic force microscopy images of UHV and argon grown material.

The properties of epitaxial graphene are different depending on whether it is grown on the Si- or C-face of the SiC substrate. This should be expected since it is well known that the two faces of SiC oxidize at different rates and have different chemical reactivities. Graphene grows more slowly on the silicon face than on the carbon face. It is very difficult to control the thickness of graphene on carbon face due the more rapid growth but the Georgia Tech group has recently demonstrate significant improvements in thickness control²⁹. Even though it consists of multiple layers of graphene, C-face material in general has higher Hall mobilities than Si-face material but mobilities up to several thousand at room temperature have recently been reported for Si-face material, comparable

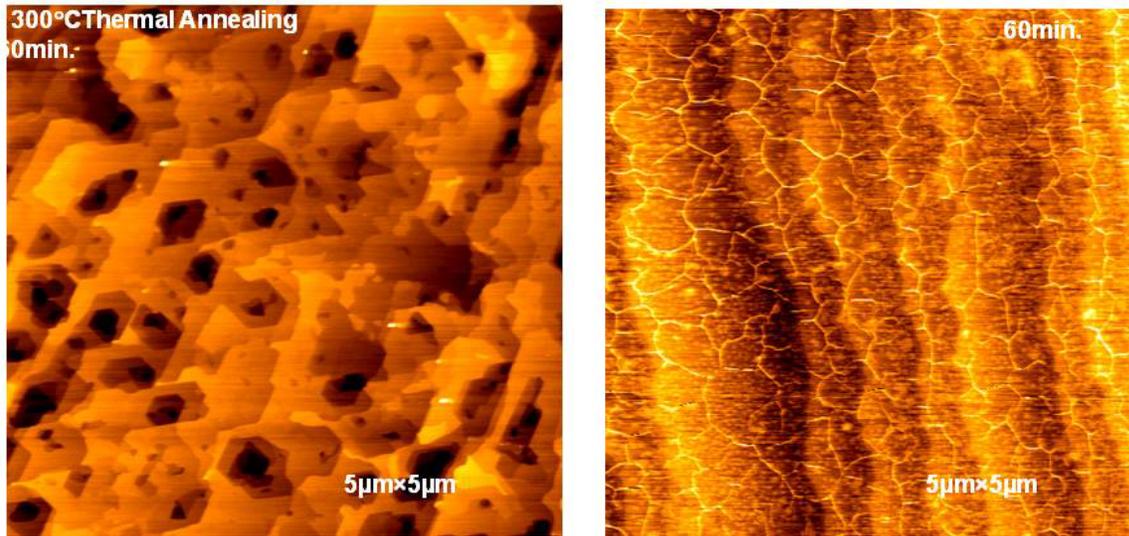


Fig. 6: AFM images of graphene grown by thermal decomposition (left) and carbon source MBE (right) in the same chamber at the same temperatures and time.

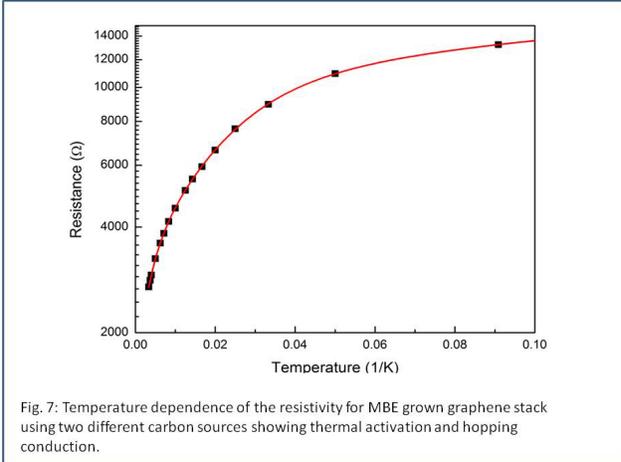
to the best CVD material. The first layer to grow on the Si-face is not graphene. Structurally similar to graphene this buffer or zero layer is chemically bonded to the SiC and is electrically insulating. It isolates the subsequent graphene layers from the SiC somewhat. This layer is not present on the carbon face. Another difference between graphene grown on the two faces is the stacking order. Graphene on Si-face SiC generally shows Bernal stacking typical of natural graphite while that grown on C-face lacks order in the stacking. The random stacking of graphene layers on C-face SiC has been used to explain why multilayer films on this form of graphene behaves more like single layer graphene even though it is usually up to ten layers thick. The Georgia Tech group has argued that only the layer closest to the SiC is doped. In their model the upper layers are insulating and all conduction occurs in the bottom layer.

Several groups are developing RF field effect transistors based on epitaxial graphene. These devices do not require complete pinch off as do digital transistors of ambipolar, zero gap graphene can be used. RF field effect transistors with f_{\max} of 100 GHz have been demonstrated on Si-face epitaxial graphene³⁰ and this material shows significant promise for analog RF applications. Our group is investigating bilayer graphene on SiC for electric field tunable mid to long wave IR detectors but the fundamental absorption of graphene is low and needs to be enhanced by external means before practical sensors can be fabricated.

MBE GROWTH OF GRAPHENE

While significant progress has been made, both epitaxial graphene on SiC and CVD growth on metals have limitations. Many applications require direct deposition of high quality films on different materials, such as Si/SiO₂, sapphire or GaN. These issues are being addressed by molecular beam epitaxy (MBE) growth of graphene from elemental carbon sources or hydrocarbons. Unlike CVD growth, metal catalysts are not required so the graphene is ready for immediate use after growth without transfer or etching of the metal. Heterostructures such as

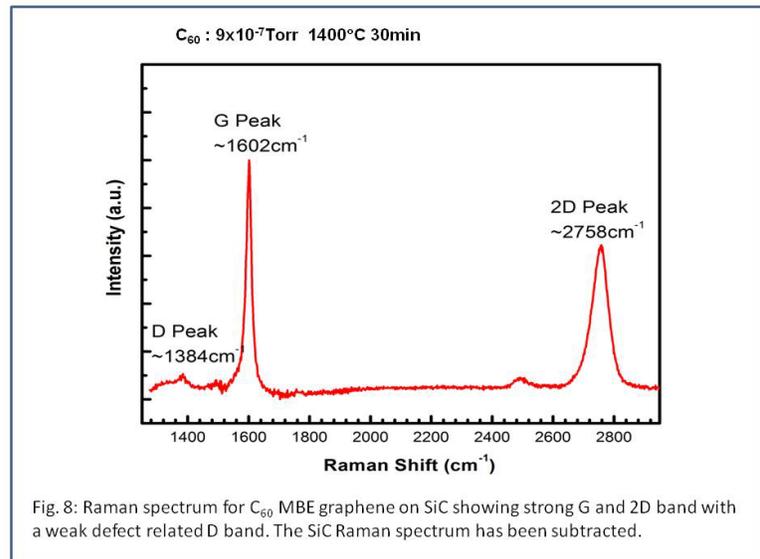
graphene/BN are difficult or impossible to grow by the methods discussed above but the flexibility of MBE offers the potential for growth of heterostructures.



but with acetylene Usachov et al. recently reported direct growth of graphene on BN films³⁵. The present authors³⁷ reported graphene growth on Si-face SiC in a UHV MBE chamber using both thermally evaporated C₆₀ and a resistively heated graphite filament carbon source. The MBE growth process significantly improved the smoothness of the graphene compared to decomposition grown material using the same chamber. Fig. 6 shows an AFM image of C₆₀ MBE grown graphene compared with thermal decomposition growth for the same time and temperature. The MBE graphene is significantly thicker as evidenced by the presence of the wrinkle network. However, no pits are present in the MBE material. Using analysis of the Raman spectra, we have shown that the two sources result in different stacking for multilayer graphene. C₆₀ gives Bernal stacking, similar to thermal decomposition grown material, but multilayer films grown from the graphite filament source random stacking even though they were grown on Si-face SiC. Other groups reporting MBE growth from graphite filaments (refs. 33 and 34) did not report stacking order. The two carbon sources also give different carrier types. As grown graphite filament source material is usually p-type, as is exfoliated graphene, while C₆₀ grown material is mostly n-type, as is standard epitaxial graphene grown by thermal decomposition. We have used this difference in doping to create internal fields by growing C₆₀ material on top of graphite filament material. These structures have thermally activated conduction that may be due to bandgap formation in bilayer graphene due to large internal fields. Fig. 7 shows a plot of resistivity versus inverse temperature for one of these stacks. The data are best fit by assuming thermal activation at high temperatures and a combination of nearest neighbor hopping conduction and variable range hopping conduction at low temperatures. It should be noted that only Park et al. and Hwang et al. reported resistivity and Hall effect measurements of carbon source grown graphene.

The structural quality of MBE grown graphene on SiC is comparable to that grown by thermal decomposition. The Raman D band, due to disorder, is weak or nonexistent in both materials. Fig. 8 shows the Raman spectra for C₆₀ MBE graphene grown in our laboratory. However, so far the

Hackley et al.³¹ reported growth of graphitic films directly on Si(111) in an MBE chamber using electron beam evaporated graphite as the carbon source. Al-Temimy et al.³² and Moreau et al.³³ used a resistively heated graphite filament as their carbon source to grow graphene on SiC. Hwang et al.³⁴ reported graphene growth on SiC and sapphire substrates by chemical vapor deposition growth using propane at temperatures from 1350 to 1650°C in the same chamber used for thermal decomposition growth. Raman measurements showed strong G and 2D bands and a weak D band for both substrates. Synchrotron X-ray measurements indicated that the stacking sequence in multilayer graphene depended on the substrate and non-Bernal on both substrates. Also using CVD



mobility of MBE material on SiC is low while the carrier concentration is high. The highest room temperature mobility we have achieved is about $300 \text{ cm}^2/\text{Vs}$.

MBE as well as CVD without catalysts have been used to grow graphene on substrates other than SiC. Hackley et al.³¹ used an MBE like process to grow graphitic carbon on (111) Si but this was very poor material compared to other growth processes. Hwang et al.³⁴ reported growth on sapphire as well as C-face SiC. They noted a difference in the stacking order for the two substrates. Our group has also demonstrated MBE growth of graphene on GaN and sapphire but of lower quality than that grown on Si-face SiC. Fig. 9 shows the Raman spectrum for a graphene film grown on a thick GaN film grown on sapphire. MBE grown graphene on alternate substrates such as

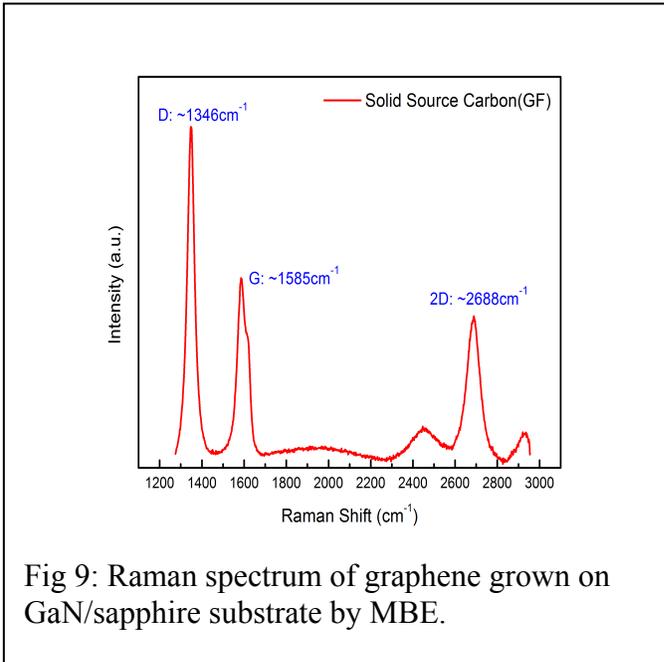


Fig 9: Raman spectrum of graphene grown on GaN/sapphire substrate by MBE.

Si/SiO₂, sapphire and GaN in general shows strong D bands with very low mobilities. The strong D band suggests that the material is polycrystalline. However, this material has not been optimized yet and significant improvements are expected once improved surface preparation techniques are developed and the growth process is optimized.

We have also observed graphene growth on the back sides of our SiC samples which are coated with a Ta film for thermal management during growth. Tantalum has a low but finite solubility of carbon at our growth temperatures so we believe this graphene growth is similar to CVD growth on Ni films.

It should also be noted that Michon et al.³⁷ used a CVD process without catalysts to grow graphene directly on 3C-SiC on Si in addition to bulk 6H-SiC using propane. They reported growth at temperatures significantly lower than those for thermal decomposition. Even though the material was grown on Si face SiC they observed rotational disorder in the

stacking of their few layer graphene similar to our graphite filament MBE grown material. The observation by multiple laboratories of stacking irregularities in carbon source grown graphene suggests that the Bernal stacking observed in thermal decomposition grown epitaxial graphene is related to the decomposition process rather than an intrinsic effect of graphene. Growth by Michon et al. on 3C-SiC on Si opens the possibility of incorporating graphene electronics and sensors directly with silicon electrons.

CONCLUSIONS

CVD growth with metal catalysts has been shown to be very effective for both CNT and graphene growth. Both CNTs and graphene can be grown by thermal decomposition of SiC. This process has advantages over CVD growth of graphene in that the material is grown directly on an electronic grade substrate and removal from the metal film and transfer is not required. MBE is a new process for growth of graphene that is currently under development in several laboratories. It is potentially useful for direct growth on alternate substrates and may permit growth on SiC at lower temperatures than those required for thermal decomposition growth.

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