Published in final edited form as:

J Cryst Growth. 2010 October 15; 312(21): 3219–3224. doi:10.1016/j.jcrysgro.2010.07.046.

Epitaxial growth of graphitic carbon on C-face SiC and Sapphire by chemical vapor deposition (CVD)

Jeonghyun Hwang^{1,*}, Virgil B. Shields¹, Christopher I. Thomas¹, Shriram Shivaraman¹, Dong Hao¹, Moonkyung Kim¹, Arthur R. Woll², Gary S. Tompa³, and Michael G. Spencer¹

¹School of Electrical and Computer Engineering, Cornell University, Ithaca, NY 14853, USA

²Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, NY 14853, USA

³Structured Materials Industries (SMI), Inc., 201 Circle Drive N., Piscataway, NJ 08854, USA

Abstract

Epitaxial, graphitic carbon thin films were directly grown on C-face/ (000 $\bar{1}$) SiC and (0001) sapphire by chemical vapor deposition (CVD), using propane as a carbon source and without any catalytic metal on the substrate surface. Raman spectroscopy shows the signature of multilayer graphene/graphite growth on both the SiC and sapphire. Raman 2D-peaks have Lorentzian lineshapes with FWHM of $\sim 60 \text{ cm}^{-1}$ and the ratio of the D-peak to G-peak intensity (I_D/I_G) linearly decreases (down to 0.06) as growth temperature is increased. The epitaxial relationship between film and substrates were determined by x-ray diffraction. On both substrates, graphitic layers are oriented parallel to the substrate, but exhibit significant rotational disorder about the surface normal, and predominantly rhombohedral stacking. Film thicknesses were determined to be a function of growth time, growth temperature, and propane flow rate.

Keywords

A1.X-ray diffraction; A3.Chemical vapor deposition processes; B1.Graphene; B1.Graphite

1. Introduction

Graphene is a single atomic layer of graphite and consists of sp^2 bonded carbon atoms arranged in 2-dimensional honeycomb lattice. Extremely high carrier mobility [1,2] and ballistic carrier transport [1] in graphene makes it an attractive candidate for high frequency electronic devices, and high electrical conductivity and optical transparency enables development of transparent conducting electrode [3]. Also, graphene's high Young's modulus and doping could be utilized to build efficient NEMS devices and sensors [4,5]. Mechanical exfoliation of graphite [1] provides high quality material but the unpredictable drawing results and limited size prevent practical applications. Large area, good quality graphene has been demonstrated by chemical vapor deposition (CVD) on transition metals such as Ni or Cu [3,6], but reliable methods of controlling graphene thickness at the grain boundaries and transferring graphene films to insulating substrates need to be developed. High quality graphene can also be directly formed on SiC surface as a result of Si

*Corresponding author. Tel: +1 607 351 9586; Fax: +1 607 257 1721; jh124@cornell.edu.

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evaporation at high temperature [7,8]. This thermal decomposition method is compatible with established semiconductor processing techniques, but the size and price of SiC substrates will limit commercialization. Graphene produced on SiC by supplying carbon atoms from a solid carbon source [9], graphitic carbon (randomly oriented polycrystalline films) on Si(111) by molecular beam epitaxy (MBE) [10], carbon nanowalls like graphene flakes by plasma enhanced chemical vapor deposition (PECVD) [11], and graphene formation on dielectrics using CVD on Cu/dielectrics and *in situ* Cu evaporation [12] have been also reported, but to date these techniques have not produced material competitive with either graphene grown on metal or SiC. Here, we demonstrate direct CVD growth of epitaxial, oriented graphitic carbon on C-face SiC and sapphire. Both substrate choices are insulating, stable at high growth temperature, and have hexagonal crystal structure. Sapphire is also one of the most widely used substrates available at low cost and large area. Growth on Si-face SiC was also tried, but it produced less ordered graphitic film under the same growth condition compared to C-face SiC or sapphire. More investigation will be needed to fully understand the effects of different starting surface and this paper concentrates on the growth on C-face SiC and sapphire. To our knowledge, this is the first report of epitaxial deposition of oriented, graphitic carbon films on a non-metallic substrate. The thinnest films reported here are 4 monolayers (ML) on C-face SiC and 9 ML on sapphire. This approach may provide a route to the growth of single-layer graphene films directly on insulating and/or semiconducting substrates.

2. Experimental details

On-axis 6H-SiC and C-plane (0001) sapphire were prepared for graphitic carbon growth as follows. The SiC was semi-insulating and CMP polished to remove surface scratches and other defects. All the samples were thoroughly cleaned using acetone and methanol before loading, but no chemical etching was employed. Growth was carried out in a conventional vertical cold wall CVD system which has been used for SiC epitaxy. The samples were placed on a graphite carrier, loaded into the CVD chamber, and then baked at ~600 °C for 30 min for outgassing. Sample heating was by a DC resistance heater with graphite filaments located below the wafer carrier, and temperature was monitored by pyrometer. The temperature was raised to 1200 °C at a rate of 120 °C/min, and then to the final growth point (1350 °C to 1650 °C) at a faster rate (250 °C/min). The argon (Ar) flow during the growth was ~10000 sccm and chamber pressure was controlled between 100 Torr and 600 Torr. Propane (C₃H₈) was supplied as a carbon source. It was delivered from a separate gas tank as a mixture (10% propane in Ar) and thermally cracked at the growth temperature. The flow rate of (propane + Ar) mixture was between 2 sccm and 40 sccm. The typical growth time was 1 min to 5 min for the higher growth temperatures (1550 °C and 1650 °C) and 5 min to 15 min for the lower growth temperatures (1350 °C and 1450 °C). Samples were cooled down (at a rate of 150 °C/min) right after growth, under Ar but without propane flow. Grown samples were characterized by Raman spectroscopy utilizing 488 nm Ar ion laser. X-ray data were obtained at the G2 station at Cornell High Energy Synchrotron Source (CHESS) using a beam energy of 8.64 ± 0.01 keV ($\lambda = 0.1435$ nm), selected using a single-crystal Be crystal monochromator. Motorized slits were used to define a 0.2×3 (V×H) mm² beam, with a typical flux of 2×10^{10} photons/s. Data was collected using a 640-element 1D diode-array, each element of which incorporates its own pulse counting electronics, and is capable of count rates of $\sim 10^5$ photons/s. For grazing incidence diffraction, a set of 0.1° Soller slits were used on the detector arm to define the in-plane resolution. For the analysis below, the following lattice parameters were used; graphite: $a = 2.461$ Å, $c = 6.708$ Å; 6H-SiC: $a = 3.073$ Å, $c = 15.117$ Å; and sapphire: $a = 4.759$ Å, $c = 12.991$ Å [13,14].

3. Results and discussion

The presence of graphitic carbon on both C-face SiC and sapphire was determined by characteristic features in Raman spectra [15-20], two examples of which are shown in Figure 1(a) and 1(b). The in-plane vibration associated G-peak ($\sim 1580\text{ cm}^{-1}$) and 2D-peak ($\sim 2700\text{ cm}^{-1}$) from double resonance of two-phonon are clearly observed. The disorder induced D-peak ($\sim 1350\text{ cm}^{-1}$) was also detected with the ratio of the D-peak to G-peak intensity (I_D/I_G) varying depending on growth conditions. Film thicknesses, as estimated from the attenuation of substrate Raman signal [21], varied from 4 ML up to ~ 100 ML. These estimates were found to agree well with film thicknesses determined by X-ray reflectivity (see below), which was performed on a subset of films. To confirm that the graphitic film formation on SiC was not induced by thermal decomposition, SiC was heated up under the same condition but without propane flow, which resulted in no signature of graphitic carbon by Raman spectroscopy. This indicates that graphitization at the pressures used here would require significantly higher temperature ($1600\text{ }^\circ\text{C} \sim 2000\text{ }^\circ\text{C}$) and longer growth time [8].

The spectra in Figures 1(a) and 1(b) were obtained from films grown at same propane flow rate (40 sccm) and chamber pressure (600 Torr), but with different growth times in order to obtain similar thicknesses (10 $\sim$ 15 monolayer). Note that the Raman spectra shown here were corrected by subtracting the Raman signal of bare SiC. The Raman I_D/I_G ratio is thought to be inversely proportional to crystallite or grain size (L_a): $10^3/L_a(\text{\AA}) = 24 \times (I_D/I_G)$ [15], and is a widely used measure of film quality in graphitic materials. Figure 1(c) shows the I_D/I_G ratio as a function of growth temperature when propane flow rate and chamber pressure were fixed at 40 sccm and 600 Torr. At this pressure, I_D/I_G ranges from 0.15 to 0.7, corresponding to domain sizes ranging from 278 $\text{\AA}$ to 60 $\text{\AA}$, respectively. The ratio decreased almost linearly as the temperature increased. When the chamber pressure was low at 100 Torr, I_D/I_G was systematically higher, ranging from 1.0 (at $1350\text{ }^\circ\text{C}$) to 0.4 (at $1650\text{ }^\circ\text{C}$). It is inferred from this that crystallization at high temperature with reduced surface decomposition is important to achieve high quality films. The samples grown at $1650\text{ }^\circ\text{C}$ show that 2D-peaks are single Lorentzian observed in multilayer graphene, rather than the asymmetric and convoluted shape of highly oriented pyrolytic graphite (HOPG) [16-19]. The FWHM of 2D-peak is 60 cm^{-1} and 64 cm^{-1} for graphitic film on SiC and sapphire, respectively. These values are slightly larger than the typical 2D-peak width ($45 - 50\text{ cm}^{-1}$) of our few layer graphene prepared on C-face 6H-SiC by thermal decomposition but comparable to reported value ($60 - 70\text{ cm}^{-1}$) of few to multi-layer epitaxial graphene on 6H-SiC [18]. As compared to free standing epitaxial graphene (3 $-$ 4 ML) which had the 2D-peaks at $\sim 2707\text{ cm}^{-1}$ [22], the CVD graphitic films showed slightly blue-shifted 2D-peak. For example, the Raman 2D-peaks were observed at $\sim 2720\text{ cm}^{-1}$ for ~ 10 ML films on C-face SiC or sapphire and at 2735 cm^{-1} for 4 ML on C-face SiC. These upshifts of 2D-peak have been attributed to hole-doping or compressive strain [19, 20]. Hall-effect measurements showed that these graphitic films are doped with electrons, so the main reason for the upshift could be compressive strains in the films [19, 20]. Since the CVD graphitic films have smaller domains, and are relatively thicker than few layer graphene, more strain relaxation is expected. No significant difference was observed in the 2D-peak position between SiC and sapphire substrate, if the growth condition was the same.

The relation between thickness and growth time is shown in Figure 2(a) with the I_D/I_G values on the second axis. The samples were grown at $1650\text{ }^\circ\text{C}$, 20 sccm propane, and 600 Torr chamber pressure. The thickness increased linearly after the first 2 $\sim$ 3 min, but there was almost no growth during the first few minutes. The Raman I_D/I_G ratio remained the same once the linear growth started, but it increased suddenly as the growth time was reduced below the t_0 described in Figure 2(a). This initial t_0 is believed to be nucleation time

and low growth rate and incomplete surface coverage are expected during this period. Sapphire needed more time than SiC to reach the linear regime. The t_0 was also a function of growth temperature and propane flow rate (longer t_0 at lower temperature and propane flow), since cracking efficiency of propane drops at lower temperatures resulting in lower growth rate. The detailed growth mechanism during this nucleation period has not been fully understood and more investigation is underway. In the linear growth regime of Figure 2(a), the C-face SiC sample has a slightly higher growth rate than the sapphire sample. However, more growth data from many samples showed that the growth rates are almost the same on the two substrates, once the samples are fully covered by good quality continuous graphitic film.

Figure 2(b) shows the thickness and I_D/I_G ratio for a series of samples grown for five minutes at fixed growth temperature and chamber pressure of 1650 °C and 600 Torr, but with varying propane flow rate (40, 20, 10, 5, and 2 sccm). Evidently, I_D/I_G shows a slight improvement (decrease) as the flow is decreased, except for the film grown at 5 sccm on SiC. On SiC, the I_D/I_G was reduced to 0.06 (at 10 sccm) from 0.15 (at 40 sccm). On sapphire, the smallest I_D/I_G was 0.11 at 20 sccm. The estimated grain size was 70 nm on SiC and 38 nm on sapphire for the best I_D/I_G samples [15]. However, the I_D/I_G increased suddenly to 0.45 at 5 sccm on SiC, and no signature of graphitic materials was detected by Raman when propane flow was even lower. Raman peaks completely disappeared at 2 sccm on SiC, and at 5 and 10 sccm on sapphire. At that low propane flow, there was no evidence of graphitic film growth, even with prolonged growth time up to 30 min. It is inferred that different nucleation dynamics occurred with the low carbon supply and such films cannot nucleate below a critical propane flow level. More growth optimization could provide precise thickness control which is crucial to achieve mono or bilayer graphene and to fully exploit their excellent properties.

The variation of thickness and grain size was measured across 12 mm × 12 mm size samples using Raman spectroscopy. The Raman setup had a ~2 μm focused light spot and the measurement was at every 500 μm. The samples used for this uniformity study were grown at 1650°C, 600 Torr, and 40 sccm propane flow rate. The mean and standard deviation of thickness were 9.5 ML ± 1.2 ML on C-face SiC and 11.2 ML ± 1.7 ML on sapphire, except at a few points where obvious defects originating from substrate were present. The variation of grain size estimated by the Raman I_D/I_G ratio was ~4 % on both the substrates. More investigation is going on to see the relation between uniformity and growth condition.

Two of the grown films representing each of the two substrate types, were further characterized using synchrotron-based x-ray diffraction. The samples were grown at 1650 °C and 40 sccm propane flow but with different growth times (3 min on SiC and 4 min on sapphire). Figure 3 shows specular X-ray data obtained for these samples. Peaks near $Q = 1.9 \text{ \AA}^{-1}$ and $Q = 3.7 \text{ \AA}^{-1}$ in both scans arise from the films, and coincide almost perfectly with the $[002]_{\text{gr}}$ ($Q = 1.873 \text{ \AA}^{-1}$) and $[004]_{\text{gr}}$ ($Q = 3.747 \text{ \AA}^{-1}$) positions of bulk graphite ($c_{\text{gr}} = 6.708 \text{ \AA}$). From the position of these peaks, average layer spacings of 3.376 Å and 3.386 Å ($\pm .003 \text{ \AA}$ for each) are obtained for the films grown on SiC and sapphire, respectively. These values are slightly larger than that of bulk graphite (3.354 Å Bernal graphite, 3.348 Å rhombohedral graphite) [23], possibly resulting from rotational stacking faults between adjacent layers [24]. The peak-widths in Figure 3 are inversely proportional to the correlation length of grown layers along the growth direction, and constitute a lower bound on the film thickness. These widths are $0.057 \text{ \AA}^{-1}$ and $0.051 \text{ \AA}^{-1}$ ($\pm .001 \text{ \AA}^{-1}$ for each) for the graphitic film on SiC and sapphire, respectively. Using the Scherrer formula ($D = 2\pi \times 0.93 / \Delta q$) [25], correlation lengths of 10.3 nm (~31 ML) and 11.5 nm (~34 ML) were obtained. These values agree well with the thicknesses for the same two samples, 33 ML on SiC and 35 ML on sapphire, estimated by Raman. The inset in Figure 3 is a *transverse* scan through

the $[002]_{\text{gr}}$ peak of the film on sapphire, obtained by rotating the sample while keeping the detector fixed. If the graphitic film were a randomly oriented powder, this scan would show nearly constant intensity. Instead, the intensity is sharply peaked along the surface normal, demonstrating that the graphitic layers are oriented parallel to the substrate surface.

Further scans were performed to determine the rotational orientation and stacking order of the graphitic films. Figure 4 shows scans along the off-specular, graphite $[10L]$ crystal truncation rod of the films represented in Figure 3. These scans were obtained with a fixed, grazing angle of incidence between the incident beam and substrate of $\sim 0.2^\circ$. In contrast to Figure 3, the intensity distribution in this scan is sensitive to the stacking arrangement of graphitic layers. For reference, vertical bars in the plot represent expected intensity distributions for ideal “AA”, “ABA” (Bernal), and “ABC” (rhombohedral) stacking. For rhombohedral stacking, ABC and ACB domains are assumed to be equally probable. By inspection, the most prominent peaks in both scans correspond to rhombohedral stacking, although both scans also show diffuse intensity in the vicinity of position expected for Bernal stacking (the $[101]_{\text{gr}}$ position). This is in contrast to natural bulk graphite which contains $\sim 80\%$ Bernal and $\sim 14\%$ rhombohedral stacking [26]. The coexistence of Bernal and rhombohedral stacking in few layer epitaxial graphene on Si-face SiC was also reported, which was prepared by typical thermal decomposition method [27]. However, a recent study showed that “ABC” stacked graphene layers were selectively formed on Si-face SiC by the same thermal decomposition but with an oxidized surface layer [28]. This may indicate that the stacking order sensitively depends on growth conditions, such as temperature or pressure. This will be a subject of future investigation whether the stacking order can be controlled by changing growth conditions or substrates. The inset of Figure 4 is a schematic representation of the scan in reciprocal space, and is indexed using rhombohedral indices

(Note, $[002]_{\text{gr}} = [003]_{\text{rh}}$ and $[101]_{\text{rh}} = [10\frac{2}{3}]_{\text{gr}}$).

The widths of the $[101]_{\text{rh}}$ and $[102]_{\text{rh}}$ peaks in both scans of Figure 4 are significantly larger than those in Figure 3, indicating the presence of stacking faults. Scherrer analysis of these peaks results in correlation lengths of ~ 6 nm for the film on C-face SiC, and ~ 4 nm for the film on sapphire. These correspond to approximate vertical domain sizes of 17 ML and 12 ML, respectively, compared to the film thicknesses of ~ 31 and ~ 34 ML as determined above. Finally, we note that additional scans through the $[101]_{\text{rh}}$ Bragg peaks of each film, and perpendicular to the scans in Figure 4 were performed to estimate the domain size parallel to the graphitic planes. For these films, grain sizes of 25.1 nm for the film on C-face SiC and 21.4 nm on sapphire were obtained, which are in good agreement with the estimates of 26 nm (C-face SiC) and 24.5 nm (sapphire) for the same films obtained from the Raman, described above.

Figure 5 shows data obtained by rotating the sample about its surface normal, while measuring intensity at a detector position corresponding to the rhombohedral graphite $[101]_{\text{rh}}$. This scan serves to determine the rotational orientation of graphitic planes in the film. The inset illustrates the scan geometry (where h and k correspond to in-plane basis vector directions in hexagonal reciprocal space) and also the positions of the SiC $\langle 100 \rangle$ ($a = 3.08 \text{ \AA}$) and sapphire $\langle 110 \rangle$ ($a = 4.763 \text{ \AA}$) Bragg peaks. The data reveal several structural features of the films. First, the intensity distribution of the graphitic film on C-face SiC is highly structured, consisting of strong, sharp peaks rotated 30 degrees from the SiC $[100]$ direction ($[100]_{\text{gr}} \parallel [110]_{\text{SiC}} \pm 0.7^\circ$) in addition to several other features at other rotations, mostly conspicuously a sharp, weak peak parallel to $[100]_{\text{SiC}}$ and two diffuse peaks rotated $\pm 9.7^\circ$ from this peak. Qualitatively, these results are similar, but not identical to results previously observed for graphene films formed on C-face SiC by thermal desorption of silicon [29]. As in Figure 5, films in Ref. [29] also exhibited domains for which $[100]_{\text{gr}} \parallel$

[110]_{SiC}. However, the other prominent domains were oriented with [100]_{gr} parallel to $\pm 2.2^\circ$ from [100]_{SiC} rather than $\pm 9.7^\circ$ in the present case. The data suggest that graphitic planes nucleate with several different rotational orientations relative to the substrate. A similar conclusion is drawn from the scan of the film deposited onto sapphire. In this case, graphitic domains evidently grow, with roughly equal probability, with their [100]_{gr} directions aligned to within ± 7 degrees of both the [100] and [110] sapphire crystallographic directions. Together with Figure 3, Figure 5 shows that the deposited, graphitic films on both C-face SiC and sapphire have their c-axes well aligned with the surface normal, but have in-plane orientations that are only weakly constrained to the crystalline substrate.

4. Conclusion

Direct CVD growth of epitaxial graphitic film on C-face SiC and sapphire substrates was demonstrated by supplying hydrocarbon gas at elevated temperature. Raman spectroscopy and x-ray diffraction showed the presence of good quality thin graphitic film and the epitaxial nature of growth. Grazing incidence x-ray measurements found that stacking order of the grown films is predominantly rhombohedral (ABC) on both the substrates. Although more growth optimization and characterization are needed to precisely control thickness and to improve film quality such as grain size, this technique could open pathways to achieve uniform large area graphene at low cost. Also, rhombohedral stacking of this film could be utilized for electric field induced band-gap opening in few layer graphene [30].

Acknowledgments

This research was supported by Air Force MURI/SBIR monitored by Dr. Harold Weinstock and NSF through the Center for Nanoscale Systems (CNS). CHESS was supported by the NSF & NIH/NIGMS via NSF award DMR-0225180.

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FIG. 1.

Raman spectra of samples grown on (a) C-face SiC and (b) sapphire at 1350 °C (dotted line) and 1650 °C (solid line), with fixed propane flow and chamber pressure at 40 sccm and 600 Torr. (c) The ratio of the D-peak to G-peak intensity (I_D/I_G) vs. growth temperature, when other growth conditions were same (40 sccm propane and 600 Torr).

FIG. 2.

(a) Thickness and Raman I_D/I_G as a function of (a) growth time and (b) propane flow rate. These samples were grown with other parameters fixed: (a) 1650 °C, 20 sccm propane, and 600 Torr chamber pressure and (b) 1650 °C, 600 Torr, and 5 min.

FIG. 3.

X-ray specular reflectivity vs. Q ($|Q|=4\pi/\lambda \times \sin\theta$, and Q is perpendicular to the surface) obtained for graphitic films grown on C-face SiC (bottom) and sapphire (top). Sapphire data are offset by a factor of 500 for visual clarity. Vertical lines indicate the positions of the bulk Bragg peak positions: (dotted lines) graphite [002] and [004] ($c = 0.6708$ nm), (dash-dot) 6H-SiC [006] ($c = 1.5117$ nm), (dashed) sapphire [006] ($c = 1.2991$ nm). Additional sharp spikes in the bottom curve result from stacking variation in the 6H-SiC substrate. Inset is a rocking curve or transverse scan on the sapphire sample through the [002] peak. The same scan through the [002] peak on SiC exhibits a similar width.

FIG. 4.

Grazing incidence diffraction scans of the graphite [10L] crystal truncation rods for the two films represented in Figure 3 on C-face SiC (bottom) and sapphire (top). Vertical bars on the lower portion of the plot indicate the position and relative intensity of peaks expected from differently stacked carbon films: (black bars) the [101] and [102] peaks for rhombohedral graphite assuming both ABC and ACB domains, (gray bars) the [101] and [102] peaks for hexagonal graphite, and (open bar) the [101] for “AA” stacked graphite. Dashed lines extend the positions of rhombohedral peaks for visual clarity. Inset is a schematic representation of reciprocal space. The scan in the figure is represented by the dashed arrow.

FIG. 5.

Azimuthal scans of the $[101]_{rh}$ Bragg peak of the two graphite films on C-face SiC (bottom) and sapphire (top). The scan is obtained by aligning the $[101]_{rh}$ and rotating the sample about its surface normal, leaving the detector fixed. Inset is a schematic representation of reciprocal space. The scan in the figure is represented by the dashed arrow. Black filled circles correspond to peak positions of a single graphene layer. The filled triangle (red online) and square (blue online) indicate the positions of the SiC $[100]$ and sapphire $[110]$ peaks, respectively.