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Selective area growth of Bernal bilayer epitaxial graphene on 4H-SiC (0001) substrate by electron-beam irradiation


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We report selective area growth of large area homogeneous Bernal stacked bilayer epitaxial graphene (BLEG) on 4H-SiC (0001) substrate by electron-beam irradiation. Sublimation of Si occurs by energetic electron irradiations on SiC surface via breaking of Si–C bonds in the localized region, which allows the selective growth of graphene. Raman measurements ensure the formation of homogeneous BLEG with weak compressive strain of ~0.08%. The carrier mobility of large area BLEG is ~5100 cm$^2$/V$\cdot$s$^{-1}$ with a sheet carrier density of $2.2 \times 10^{13}$ cm$^{-2}$. Current-voltage measurements reveal that BLEG on 4H-SiC forms a Schottky junction with an operation on mA level. Our study reveals that the barrier height at the Schottky junction is low (~0.58 eV) due to the Fermi-level pinning above the Dirac point. © 2014 AIP Publishing LLC.

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Graphene has garnered tremendous interest due to its unique properties including high electron mobility with low electronic scattering that make it a very promising candidate for next generation nanoscale electronics and photonics devices.$^1$ Several outstanding advancements in graphene fabrication technology have been explored including research grade mechanical exfoliation of graphite,$^2$ chemical vapor deposition,$^3$ thermal decomposition of SiC,$^4$ and chemical methods.$^5$ In particular, the thermal decomposition of SiC surfaces is presently being a very promising approach since it offers wafer scale growth of graphene layers, which is more compatible with the existing Si device technology.$^6$ Recently, we have demonstrated a facile approach to fabricate single layer (SLG) to few layer graphene (FLG) by exposing electron beam (e-beam) on desired area of SiC substrates by controlling the growth kinetics.$^7$ This method utilizes an e-beam that sublimates the localized Si ions on the topmost layer or even few atomic layers with reduced graphitization temperature (~1000 °C) as a consequence of bond-breaking and induces the selective formation of epitaxial graphene (EG) on SiC substrates. The number of graphene layers can also be varied as a function of irradiation time.$^7$ Further, this method extends the promise of graphene for nanoscale based integrated device applications. In order to design graphene-based field effect transistors, it is necessary to achieve a bandgap and scalable growth of graphene (to enhance the number of transistors per unit area) on desired substrates with highly reproducible features such as Bernal stacking (also known as AB stacking).$^6$ In particular, Bernal bilayer epitaxial graphene (BLEG) on the Si-face of SiC substrate is of particular interest since it has been shown to have an instinctive bandgap imposed by the interaction with SiC substrate.$^8$ Hence, it is of utmost important to understand the electronic and optical properties of Bernal stacked BLEG on SiC and their electron transport properties across the heterojunction for high frequency electronic applications.

In this letter, we demonstrate the selective growth of Bernal BLEG on 4H-SiC (0001) substrate and the nature of BLEG and SiC interface by low energy e-beam irradiation. A typical e-beam irradiation unit equipped with 3 kW electron gun produces electrons were focused directly on SiC substrates by using permanent or electromagnets. More information about the preparation of EG layers can be found elsewhere.$^7$ Briefly, the e-beam irradiation was performed in a high vacuum atmosphere (10$^{-6}$ mbar) at 5 keV energy with an electron emission current of ~20 mA, having fluency of ~10$^{23}$ e/cm$^2$ for the corresponding duration of 3 min. The heating and cooling rates rely on the acceleration and deceleration time of electron emission current, respectively. We employed a raster scanning of electron beam on SiC surface, the beam sweeps horizontally left-to-right and right-to-left in the next line at a steady rate over the desire area, for the fabrication of both large area and selective area EG layers. The surface features of the e-beam grown EG layers were examined using atomic force microscopy (AFM- Agilent 5500) and field emission scanning electron microscopy (FESEM-Carl Zeiss- Sigma). Stacking of layers, optical quality, thickness, strain, and uniformity of the EG layers were probed by confocal micro-Raman spectrometer recorded in the back scattering geometry using Lab Ram Horiba Raman spectrometer with an excitation wavelength of 532 nm. Near-edge X-ray absorption fine structure (NEXAFS) measurements at C K edge were performed in total electron yield mode at BL10D Pohang Accelerator Lab., Pohang, South Korea.

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Dharmaraj et al.  

FIG. 1. (a) Topographic AFM image of BLEG grown on the Si-face of 4H-SiC substrate. Insets show the step terraces of SiC substrate before the irradiation and (b) FESEM image of large size homogeneous BLEG on SiC.

using HOPG as reference sample for calibration. X-ray photoelectron spectroscopy (XPS) spectrum was performed to identify the bonding nature of the graphene using excitation photon energy of Al Kα, 1486.7 eV. The current-voltage characteristics were measured using semiconductor parameter analyzer connected with Keithely 2400 source meter. The electrical transport measurements were also carried out using van der Pauw Hall system.

Figure 1(a) shows the AFM image of 4H-SiC (0001) surface after exposing e-beam, revealing that the step terraces are not apparent any longer as the electron-irradiated region is homogeneously covered by graphene bilayer with a thickness of ~1.5 nm. Figure 1(b) shows the FESEM image of EG and demonstrates the maximum uniformity. The coverage of the homogeneous BLEG extends up to several hundred micro meters.

Figure 2 shows the Raman spectra of SiC samples after exposing the e-beam. The G band at 1580 cm⁻¹ is due to the first order scattering of E₂g phonon at the centre of the hexagonal Brillouin zone, which is a characteristic of sp² hybridized C atoms. The 2D band at 2685 ± 2 cm⁻¹ originates from the two phonon double resonance excitations closed to K point in the hexagonal Brillouin zone, and it is a distinctive signature of stacking dimension along the c-axis, electronic structure, and strain of graphene layers.⁹ If the stacking dimension of the graphene layer is Bernal, which yields four atoms per unit cell resulting in two bonding (π₁ and π₂) and two anti-bonding (π⁺ and π⁻) bands and the Raman scattering gives rise to four permissible intervalley double resonance process causes splitting of 2D band into four Lorentzian functions.⁹ Previously, it has been shown that the growth of Bernal stacked BLEG on the Si-face of the SiC substrates is highly difficult if the cooling rate is high as above 600 K/s, implying that the stacking dimension is distorted by the larger thermal expansion/contraction coefficient between graphene and SiC due to rapid cooling, resulting in rotationally disordered graphene layers with highly symmetric single Raman 2D band.¹⁰ However, in the present case, the asymmetric 2D band was well fitted with four Lorentzian peaks (shown in inset of Figure 2) that are evolved from the four allowable Raman transition processes occurring only in AB stacked graphene layers confirming the existence of the Bernal BLEG.¹¹ The interface layer (evidenced from Figure 4) plays an important role of maintaining the energetic stability of AB stacking when the carbon bilayers start to nucleate as it acts as a base material for the subsequent growth and also controlling the epitaxial relationship between the substrate and graphene.¹² Since the Raman 2D band shift is sensitive to the strain, the magnitude of the strain in the BLEG from its shift against the strain free Bernal graphene bilayers can be expressed as

\[ \epsilon = -\frac{\Delta \omega_{2\text{D}}}{0.817 \omega_{2\text{D}} \beta_{2\text{D}}} \]  

(1)

where \( \Delta \omega_{2\text{D}} \) is the shift of the Raman band position from strain free graphene bilayer, \( \omega'_{2\text{D}} \) is the band position of the strain free BLEG, 2680 cm⁻¹, and \( \beta_{2\text{D}} \) is the Gruneisen parameter (for BLEG, \( \beta_{2\text{D}} = 2.7 \)).¹⁴ From Eq. (1), the magnitude of the strain in this Bernal stacked BLEG grown by this method is \( \epsilon = -0.08\% \), which is likely to be originated from the lattice mismatch between the graphene (2.46 Å) and SiC (3.06 Å) substrate.¹³ Further, this compressive strain on the e-beam synthesized Bernal BLEG is much lower than that of graphene grown by other conventional thermal annealing (CTA) process, where \( \epsilon \) varies between ~0.3% and ~1.17% for a given cooling rate of 2–5 °C/s. This weak strain is attributed to the rapid cooling rate of ~500 K/s and also the elimination of step terraces since these facts are expected to induce more strain on graphene layers by e-beam assisted growth process. The Raman spectrum on delocalized area (unexposed area) exhibited nearly identical features with bare SiC that illustrates the growth of graphene occurred only on the irradiated region and is also strongly suggesting the feasibility for selective growth of graphene.

Figure 3 shows the normalized NEXAFS C K-edge spectra measured both in-plane and out-of plane to 2D graphene.
layers. For carbon materials, using the angle dependent NEXAFS C K-edge, one basically excites the electrons from the initial K-shell state into 1s to 2p states and extract information about the nature of chemical bonding.\(^{14}\) According to the dipole-transition selection rule, these spectral features can be attributed to C 2s 2p and higher derived states, respectively. The main spectral features are labeled as A\(_1\) to E\(_1\). The peak E\(_1\) is associated with higher derived states. Variation of the absorption intensity of NEXAFS C K-edge spectra with respect to the incident angle shows evidence of anisotropy in C 2p states. A broader shoulder in the pre-edge region shown in inset (\(\sim 283.5\) eV) aroused from unoccupied density of states of the \(\pi^*\) states along the \(MK\) high symmetry in the graphene band structure, which corroborates with the characteristics of graphitic bilayer (Bernal stacking).\(^{15,16}\) Specifically, the C K-edge spectra consist of a peak (\(\sim 285.3\) eV) shown as \(A_1\) at the edge threshold for transitions from the carbon 1s to \(\pi^*\) anti-bonding states, and peaks (287–305 eV) \(B_1\) to \(D_1\) corresponds to carbon 1s to \(\sigma^*\) transitions.\(^{15-17}\) In particular, a clear peak appearing at 291.6 eV is ascribed to an excitation of an electron from the carbon 1s to \(\sigma^*\) anti-bonding states.\(^{17}\) A peak at \(\sim 288\) eV is attributed to interlayer state transitions in graphene layers. These are the characteristics of EG on SiC substrate with Bernal stacking.

The observed C 1s spectrum is deconvoluted into three components as shown in Figure 4. The major component at 284.4 eV originates from the \(sp^2\) C–C bonding, which offers a strong manifestation for the formation of graphene.\(^{18}\) Another important aspect in the XPS spectrum is that a feature located at 285.6 eV may be attributed to interfacial carbon layers.\(^{5}\) It is widely established that formed EG layers on the SiC (0001) reside on a surface reconstructed carbon layer (interface layer) with (6,3 \(\times\) 6,3) R30° symmetry. Here, the top Si atoms of the SiC (0001) form partially bonds to the reconstructed carbon layer, partially they comprise amphoteric dangling bonds, which would acts as charged impurities and provide a Fermi level pinning (FLP) to the graphene layers.\(^{1,4}\)

Current-voltage characteristics of graphene and 4H-SiC (0001) junction were measured in air at 300 K as shown in Figure 5. The Ni (50 nm) and Au (50 nm) contacts have been deposited on SiC and graphene layers, respectively, by e-beam evaporation for electrical probing. The current transport measurement reveals a clear non-linear behaviour (rectifying), suggesting that a Schottky barrier is formed at the junction between the BLEG and SiC (shown in upper inset of Figure 5). A similar Schottky junction is also reported on EG formed by thermal annealing of SiC at elevated temperature (1400°C) under ultra high vacuum by Shivaraman \textit{et al.}\(^{19}\) The semilogarithmic plot of the I-V curve clearly (shown in Figure 5) demonstrates that
thermionic emission dominates current transport mechanism across the barrier and is governed by
\[ I = A^* T^2 \exp \left( -\frac{q\phi_{B0}}{k_B T} \right) \left[ \exp \left( \frac{qV}{\eta k_B T} \right) - 1 \right], \]  
(2)
where \( A^* \) is the effective junction area (0.03 nm²), \( A^* \) is the reduced effective Richardson constant (1.46 × 10⁶ Am²K⁻²), \( T \) is temperature (300 K), \( \phi_{B0} \) is the Schottky barrier height (SBH) at the junction between EG and SiC, \( k_B \) is the Boltzmann constant, \( q \) is the electronic charge, and \( \eta \) is the ideality factor. The observed slight deviation from linearity at high forward bias region can be ascribed to the presence of additional transport mechanism (such as thermionic field emission) or contribution of series resistance from the semiconductor. \(^2^0\) We follow the following equation to acquire the zero-bias SBH from extrapolation of \( I_s \) in semi-log forward bias curve:
\[ \phi_{B0} = \frac{k_B T}{q} \ln \left( \frac{AA^* T^2}{I_s} \right), \]  
(3)
where \( I_s \) is the saturation current (\( I_s \sim 0.4 \mu A \), which is extrapolated from semi-log forward curve). A zero-bias SBH of \( \sim 0.58 \text{ eV} \) is obtained from the experimental data using Eq. (3). SBH of the as-deposited graphene (DG) layers on SiC is widely calculated to be \( \sim 1 \text{ eV} \) using Schottky-Mott relation (\( \text{SBH} = \phi_g - \chi \), where \( \phi_g \) is the work function of graphene and \( \chi \) is the electron affinity of SiC) as due to the dearth of FLP. \(^2^1\) However, Sonde \textit{et al.} \(^2^3\) have shown that existence of interface dangling bonds in EG would lead to FLP above the Dirac point as it is adequate to reduce the SBH and gives rise to enhanced current leakage. The FLP originates by means of the interface charged impurities, residing at the interface between SiC (0001) and interface layer, as a result of broken bonds from the semiconductor surface during the surface reconstruction by e-beam irradiation, which forces the surface Fermi level to be locked or pinned at certain energy position and thus making Schottky-Mott relation invalid. This FLP dominates the band bending mechanism at graphene and SiC interface and effectively modulates the Schottky barrier height regardless of the work function of graphene. \(^2^4\) Based on our observations, we conclude that the interface dangling bonds could potentially lower the SBH due to the FLP. The difference in SBH (compared to as-deposited graphene) is well consistent with the Fermi level shift of \( \sim 0.4 \text{ eV} \) above the Dirac point owing to interfacial layer, which contains a high density of surface states ensuing the intrinsic behavior of electron doped graphene, as evidenced from angle resolved photoelectron spectroscopic measurements of BLEG band structure. \(^2^5\) A schematic energy band diagram of BLEG and SiC Schottky junction is shown in supplementary material (S4 (c)). The junction exhibits a nominal leakage current of \( \sim 30 \mu A \) under reverse bias and this might be a direct evidence of reduced SBH. The FLP can also be alleviated through hydrogen intercalation of EG at 900 °C which leads to the revolution of interface layer into free standing graphene layers wherein the covalent and amphoteric dangling bonds are expected to be plausibly terminated. \(^1^2\) We also calculated the ideality factor from the slope of the linear region in semi-log plot with the following relation:
\[ \eta = \frac{q}{k_B T} \frac{dV}{d \ln I}. \]  
(4)

Our Schottky diode exhibits an ideality factor of 4.5, which is analogous to the previous report. \(^2^1\) The ideality factor greater than unity can be ascribed to image force lowering, presence of additional transport mechanism (i.e., thermal field emission), or barrier inhomogeneities. \(^1^9\)\(^2^0\) Our BLEG based Schottky device exhibits high current operation under forward bias. The van der Pauw Hall transport measurements on large area BLEG samples (1 × 1 cm²) at room temperature show a high electron mobility and sheet carrier density of \( \sim 5100 \pm 300 \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1} \) and \( 2.2 \times 10^{13} \text{ cm}^{-2} \), respectively. We attribute this high mobility on the Si-face exclusively to the homogeneous growth of graphene layers and also the elimination of step terraces by this process as the step terraces likely to introduce typical scattering sources such as defects, long-range phonon, and electrical resistance, which are the dominant factors that influence the transport properties of graphene layers. \(^2^8\) Furthermore, e-beam assisted fabrication of graphene is a localized process, which significantly differs from the mechanism of CTA; \(^7\) this will open pathways for both selective and large area economically viable high-quality growth of EG. Additional information on the homogeneity, Bernal stacking, and band structure of BLEG are given in the supplementary material. \(^2^9\)

In summary, Bernal stacked BLEG on 4H-SiC (0001) substrates has been grown using low energy e-beam irradiation. Energetic electron irradiations on SiC break the bond in Si–C on the localized region, resulting in the reorganization of carbon atoms to form graphene layers owing to Si sublimation. Raman spectra substantiate the formation of homogeneous Bernal stacked BLEG with the maximum coverage over the irradiated area. High cooling rate and elimination of step edges play a vital role in the formation of uniform Bernal BLEG with a weak strain of \( \sim 0.08\% \). NEXAFS spectroscopic studies manifest the presence of transition states, 1 s to \( \pi^* \) and 1 s to \( \sigma^* \), in the sp² graphene lattice. BLEG on SiC interface forms a Schottky junction with rectifying properties.

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29See supplementary material at http://dx.doi.org/10.1063/1.4901074 for the selective area growth of Bernal bilayer epitaxial graphene on SiC by e-beam irradiation.