

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/256774475>

# Controlled and Selective Area Growth of Monolayer Graphene on 4H-SiC Substrate by Electron-Beam-Assisted Rapid Heating

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY C · AUGUST 2013

Impact Factor: 4.77 · DOI: 10.1021/jp404483y

CITATIONS

5

READS

204

9 AUTHORS, INCLUDING:



Jeganathan Kulandaivel

Bharathidasan University

79 PUBLICATIONS 756 CITATIONS

SEE PROFILE



Parameshwari Ramalingam

Bharathidasan University

4 PUBLICATIONS 16 CITATIONS

SEE PROFILE



Veerabahu Ramakrishnan

Madurai Kamaraj University

179 PUBLICATIONS 1,504 CITATIONS

SEE PROFILE



Asokan Kandasami

Inter University Accelerator Centre

336 PUBLICATIONS 1,572 CITATIONS

SEE PROFILE

# Controlled and Selective Area Growth of Monolayer Graphene on 4H-SiC Substrate by Electron-Beam-Assisted Rapid Heating

P. Dharmaraj,<sup>†</sup> K. Jeganathan,<sup>\*,†</sup> V. Gokulakrishnan,<sup>†</sup> P. Sundara Venkatesh,<sup>†</sup> R. Parameshwari,<sup>†</sup> V. Ramakrishnan,<sup>§</sup> S. Balakumar,<sup>||</sup> K. Asokan,<sup>⊥</sup> and K. Ramamurthi<sup>‡</sup>

<sup>†</sup>Centre for Nanoscience and Nanotechnology, School of Physics, Bharathidasan University, Tiruchirappalli-620024, Tamil Nadu, India

<sup>‡</sup>Department of Physics and Nanotechnology, SRM University, Chennai-603203, Tamil Nadu, India

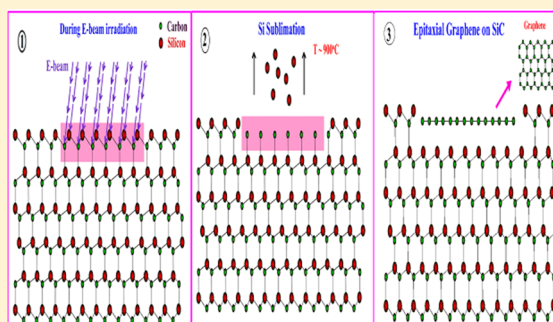
<sup>§</sup>Department of Laser Studies, School of Physics, Madurai Kamaraj University, Madurai-625021, Tamil Nadu, India

<sup>||</sup>National Centre for Nanoscience and Nanotechnology, University of Madras, Chennai-600025, Tamil Nadu, India

<sup>⊥</sup>Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi-110067, India

## Supporting Information

**ABSTRACT:** A facile method for direct and selective area conversion of 4H-SiC substrates into homogeneous epitaxial graphene is demonstrated by the irradiation of a low energy (5 keV) electron beam (e-beam). The localized interactions like scattering, excitation, and ionization between the primary electrons and the SiC surface result in Si–C bond breaking, and the excess kinetic energy of electrons is dissipated as heat that results in the selective sublimation of the Si ion favoring the formation of epitaxial graphene. The thickness of the graphene layer is precisely controlled by varying the e-beam energy and the irradiation time. The number of graphene layers increases with irradiation due to thermally induced Si sublimation over the depth of a few atomic layers depending on the incident energy of the e-beam. The Hall mobility of large area single layer graphene formed on the Si-face is  $\sim 6450 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  with a surface carrier density (n-type) of  $1.5 \times 10^{13} \text{ cm}^{-2}$ . Our results demonstrate that the e-beam irradiation technique is a viable route to define wafer scalable selective area graphene structures directly on semi-insulating 4H-SiC substrates for electronic applications.



## ■ INTRODUCTION

Graphene, a single layer of  $sp^2$ -carbon atoms densely packed in a honeycomb structure, is fascinating with its unusual conical band structure resulting in the relativistic linear dispersion relationship at low energies and the chiral nature of charge carriers. This provokes some unusual phenomena such as extreme high carrier mobility, room temperature quantum Hall effect, ambipolar tuning of conduction, and high thermal conductivity.<sup>1–3</sup> Such exotic properties have made it a significant material for fundamental advances and also a potential candidate for device applications. Over the past few years, various techniques such as mechanical exfoliation,<sup>1</sup> chemical vapor deposition (CVD) on catalytic transition metals,<sup>4</sup> epitaxial growth of graphene on SiC by thermal and laser treatment,<sup>5–8</sup> and certain chemical methods<sup>9</sup> have been employed to synthesize graphene. Although high quality graphene with better controlled layers in limited size can be produced through mechanical exfoliation and its high charge carrier mobility enhances ON current and fast switching, the zero band gap makes it difficult to turn OFF the transistor. However, the reported ON–OFF ratio is less than that of the real time transistors due to zero band gap and poor fabrication area.<sup>10,11</sup> Despite uniform wafer scale graphene being produced

using CVD, their polycrystalline nature scatters the charge carriers and inhibits device performance.<sup>12</sup> Chemically synthesized graphene is not suitable for electronic applications owing to its low yield and high defects.<sup>8</sup> In order to make graphene a suitable candidate for commercially viable high speed electronic applications, major obstacles must be overcome: first, effective band gap; second, scalable area; and finally, desired layer synthesis on a suitable substrate.<sup>13</sup> In principle, epitaxial graphene on SiC provides a potential system that overcomes the above obstacles due to its wafer scale growth and good epitaxial relationship. Generally, this method enables the growth of graphene on a scalable area with n-type majority charge carriers and a band gap of 200–400 meV attributed to the elimination of layer inversion symmetries and the layer–substrate interaction.<sup>14,15</sup> This empowers direct fabrication of graphene field effect transistors (GFETs) on SiC substrates<sup>16,17</sup> because the novel electronic properties of graphene can be well compromised by the semi-insulating nature of SiC. Practically, GFETs with a cutoff frequency of 300 GHz were realized by

Received: May 6, 2013

Revised: July 24, 2013

Published: August 19, 2013

epitaxial growth on SiC,<sup>17</sup> which are much faster than the Si transistors, and also, this method provides more than 40,000 transistors per sq.cm area.<sup>6</sup> In 1962, Badami et al.<sup>18</sup> introduced the mechanism of graphitization on SiC at the temperature range of 2000 °C. A decade later, monolayer graphite (graphene) on SiC substrate was fabricated by Si desorption over the temperature range of 800–1300 °C with poor quality having low carrier mobility.<sup>19</sup> Subsequently, epitaxial graphene on SiC was refined under different ambient circumstances by evaporating the Si atoms at its sublimation temperature to invoke the electronic applications.<sup>20</sup> However, the direct fabrications of high quality homogeneous epitaxial graphene on SiC with the desired number of layers still remain a challenging task.<sup>13</sup>

To date, two groups have grown graphene epitaxially on SiC substrates by irradiating with a low energy electron beam (e-beam). Huang et al.<sup>21,22</sup> have employed low energy (6–9 keV) pulsed electron irradiations in which the transfer of electron energy to atoms in SiC causes the ejection or sublimation of Si from the topmost layers and results in the nucleation of graphene. At low incident energies, e-beam induced ejection or sputtering events are relatively rare because the energy transfer mechanism is limited by the large mass mismatch between the electrons and the target nuclei. The minimum incident energy required for such ballistic ejection is called threshold energy of an atom.<sup>23–25</sup> For 4H-SiC, the threshold displacement energies for C and Si atoms are 17 and 25 eV, respectively, and its corresponding incident beam energies are 88 and 200 keV, respectively. Hence, the ejection of Si atoms requires more than 200 keV. Further, the incident energy of the e-beam with 200 keV and above converts the SiC crystal into amorphous Si.<sup>25</sup> There is some ambiguity about the mechanism of formation of graphene. Further, Go et al. have reported an epitaxial graphene with turbostratic nature, in which graphene layers are randomly rotated on the SiC substrate by continuous e-beam irradiation of 6H-SiC for 2 h.<sup>26</sup> However, the fabrication of controlled layers with a reliable growth process has not been demonstrated yet for the growth of epitaxial graphene on SiC using e-beam irradiation. Moreover, our literature survey has reflected that there has been no attempt to investigate the role of low energy and high current in the fabrication of graphene. Hence, our experiments were focused on finely tuning the e-beam energy between 3 and 10 keV with emission current up to 20 mA. A low energy e-beam is expected to introduce less damage to the surface compared to that with high energy e-beams. Highly reproducible epitaxial graphene can be fabricated using an optimized e-beam energy of ~5 keV. With a further increase of energy above 5 keV with high current (~20 mA), we observed that the SiC substrates experienced perturbation and broke into pieces due to thermal shock.

In this article, we explore a novel single step method for the fabrication of homogeneous epitaxial graphene on SiC by irradiation of a low energy e-beam over a short duration (in mins). In addition, this method facilitates the direct writing of graphene electronic structures without complex lithographic patterning and processing via direct conversion of SiC into homogeneous graphene by irradiating low energy electrons under vacuum conditions. Unlike in thermal annealing, Si sublimation may occur from the top layer or a few atomic layers of SiC because of the bond-breaking process on the localized area of SiC, which is controlled by e-beam energy and duration of irradiation. The formation and morphology of epitaxial graphene have been confirmed by atomic force microscope

(AFM) and field emission scanning electron microscope (FESEM) images. The number of layers and quality of graphene are systematically analyzed by micro-Raman spectroscopy. X-ray photoelectron spectroscopy (XPS) was used to confirm its electronic structure. The electrical properties are measured by the van der Pauw Hall measurement system.

## MATERIALS AND METHODS

Semi-insulating 4H-SiC substrates were used for the present study. Prior to placing the substrates into the chamber, it was cleaned in acetone followed by the RCA (1 and 2) cleaning procedure to remove the native oxides. SiC substrates with flat atomic surfaces were transferred into a high vacuum chamber and subjected to e-beam irradiation. Initially, the chamber was evacuated to the pressure of  $1 \times 10^{-6}$  mbar using molecular diffusion and rotary pumps. A typical e-beam evaporation unit equipped with a 3 KW electron gun produces electrons that were focused directly on SiC substrates by using permanent or electro magnets. The applied voltage to the tungsten filament was maintained to at 5 KV. The emission current was fixed for nonraster and finely tuned between 10 and 20 mA to raster the e-beam over the desired area of SiC substrates. Since the e-beam energy and irradiation time are precisely controllable, the sublimation rate of Si is tunable.

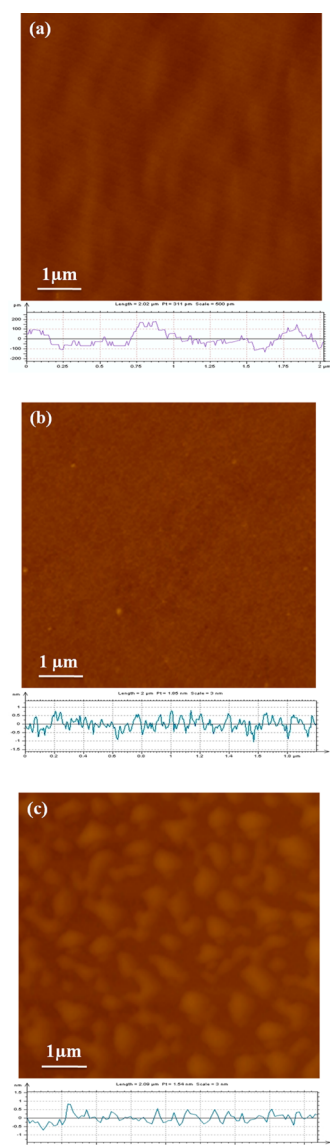
## CHARACTERIZATION METHODS

The surface morphology of the epitaxially grown graphene was examined using AFM (Agilent 5500) and FESEM (Carl Zeiss-Sigma). Micro-Raman spectra were recorded in back scattering geometry using a Lab Ram HR800 Raman spectrometer at the excitation wavelength of 632.8 nm with a spot size of ~1  $\mu$ m. The chemical composition was confirmed using XPS spectroscopy with an excitation photon energy of Al K $\alpha$  1486.7 eV. The electrical properties were measured by the van der Pauw Hall system (Ecopia).

## RESULTS AND DISCUSSION

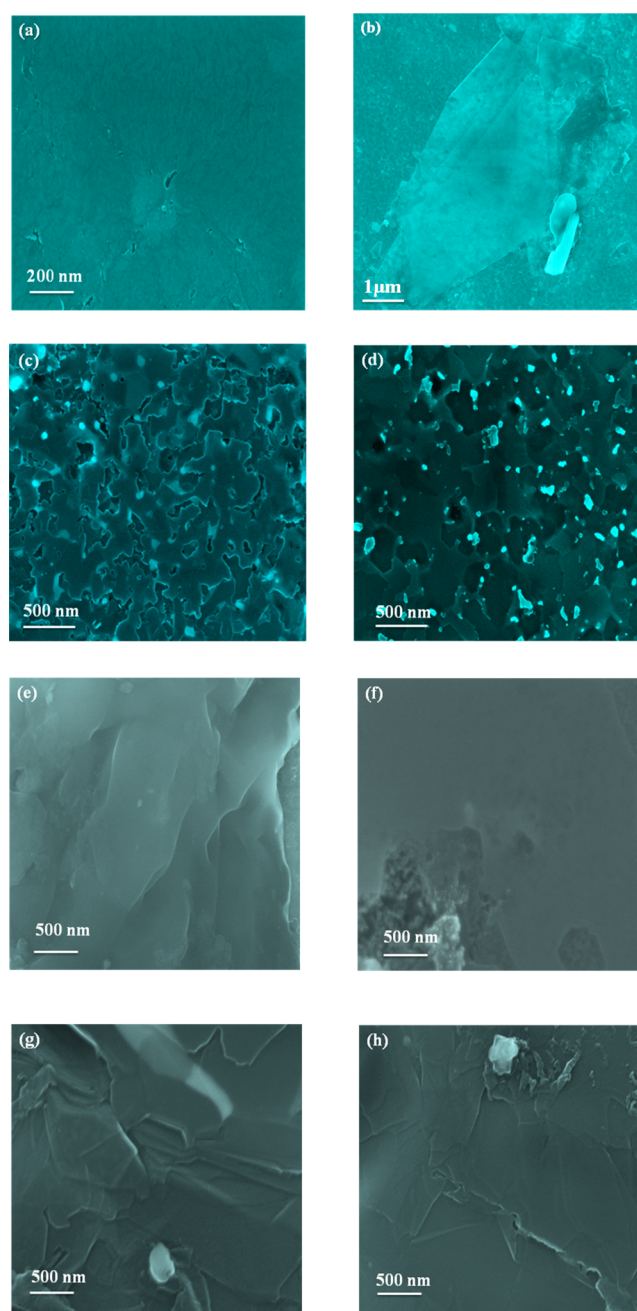
The surface morphology of the 4H-SiC sample, before and after e-beam irradiations, was effectively examined by AFM with noncontact mode. Figure 1a shows the AFM topographic image of the SiC surface after RCA cleaning. This ensures the uniform flat and step like terraces (roughness mean square of 0.10 nm) on pristine SiC which is free from native oxides. On exposing SiC to the e-beam, step terraces disappeared leaving the atomically flat surface. Figure 1b and c shows the topographic images of graphene formed on the Si-face and C-face, respectively, after 2 min of e-beam irradiation. The corresponding height profiles indicate the average thickness as ~3.5 Å on the Si-face. This provides clear evidence of the formation of uniform single layer graphene on the Si-face, whereas in the C-face, the average thickness is ~8 Å, which indicates the formation of bilayer graphene. The AFM topographic images show the homogeneity of the graphene layers having no distinguishable defects. However, the surface morphology and layer thickness were significantly affected with 4 and 5 min electron exposure time (Supporting Information, Figure S1).

The morphology and thickness of the layer were further investigated by FESEM. In practice, it is difficult to perform the imaging on semi-insulating SiC substrates due to their semi-insulating behavior ( $\rho > 10^5$   $\Omega$ -cm). Since graphene on SiC is highly conducting, it disperses the charge responsible for image breakdown, thus facilitating the capture of FESEM images. The



**Figure 1.** AFM topographic images of (a) the bare Si-face of 4H-SiC, (b) the 2 min irradiation of graphene on the Si-face, and (c) the 2 min irradiation of graphene on the C-face.

formation of graphene was found to occur for 30 s of e-beam irradiation in our experiment. Continuing the e-beam rastering further plays a vital role in the formation of uniform graphene and increase of graphene layers. Figure 2a shows a highly magnified image of single layer graphene on the Si-face. Rarely, few-layer graphene is also observed as shown in Figure 2b. This may be due to the nonuniform energy distribution over the substrate during e-beam rastering. The nonuniform rastering of the e-beam may strongly result in inhomogeneous graphene layers with less surface coverage. Nevertheless, the films are homogeneous over the irradiated area with >70% coverage of single layer graphene for 2 min of irradiation. Some fractals like graphene patterns were obtained after a second irradiation for 5 min. Repeated e-beam irradiation results in fractals like morphological graphene structure due to the  $sp^2$  based structural deformation (Supporting Information, Figure S2). Figure 2c and d shows the few-layer graphene on the C-face and clearly represents the presence of voids as well as nonuniform layers with some defects which are obviously

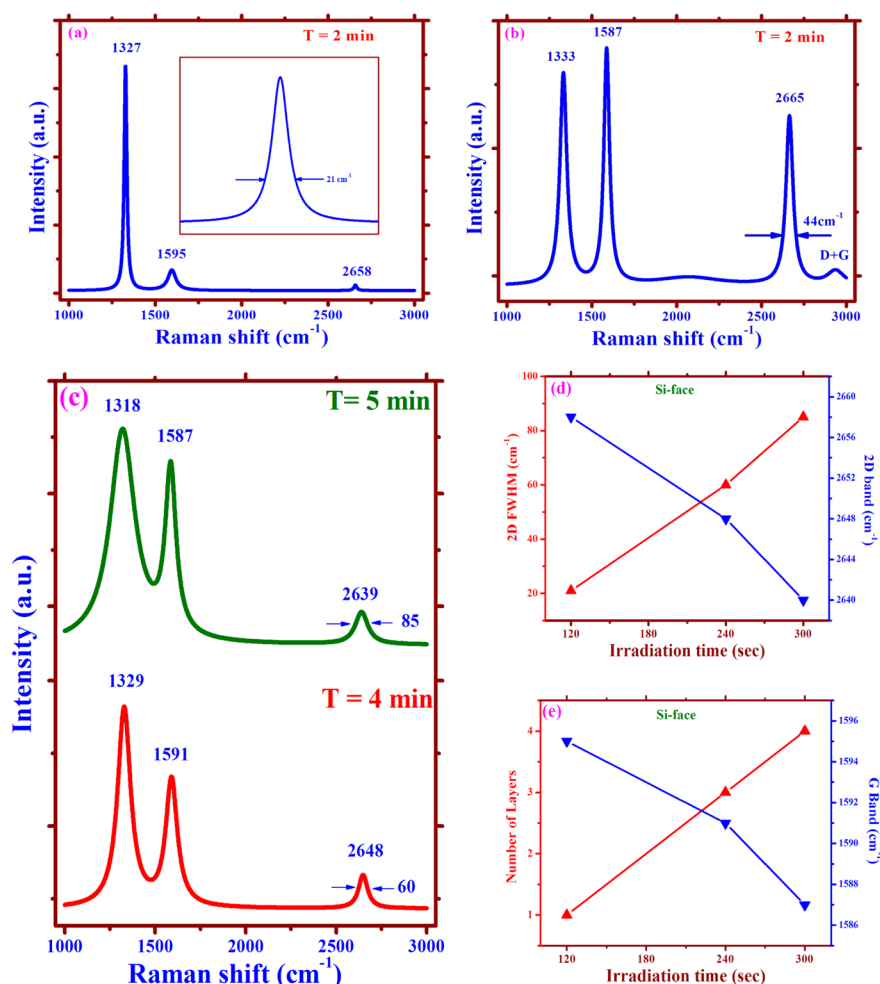


**Figure 2.** FESEM images of (a and b) 2 min irradiation on the Si-face, (c and d) 2 min irradiation on the C-face, (e and f) 4 min irradiation on the Si-face, and (g and h) 5 min irradiation on the Si-face.

absent in the Si-face. The surface energy of the C-face ( $300 \text{ erg/cm}^2$ ) is poor as compared to the Si-face ( $2220 \text{ erg/cm}^2$ ),<sup>16</sup> which may initiate an uncontrolled Si sublimation rate during the irradiation and induce the formation of inhomogeneities of graphene layers. The observed morphologies and layer thickness can be modified with the irradiation time (Figure 2e–h), thereby illustrating the sensitiveness and controllability of the number of layers.

Raman spectroscopy is used for identifying the number of layers, defects, and electronic properties of graphene. Figure 3a and b shows the typical Raman spectra obtained on both faces of SiC for 2 min of irradiation. For the Si-face, the prominent bands D, G, and 2D are located at  $1327$ ,  $1595$ , and  $2658 \text{ cm}^{-1}$ , respectively. For the C-face, similar bands are observed at  $1333$ ,





**Figure 3.** Raman spectra of samples with different irradiation times: (a) 2 min irradiation on the Si-face (the inset shows the FWHM of the 2D band), (b) 2 min irradiation on the C-face, (c) 4 and 5 min irradiation on the Si-face, (d) correlation between irradiation time and the 2D band, and (e) the G band as a function of irradiation time.

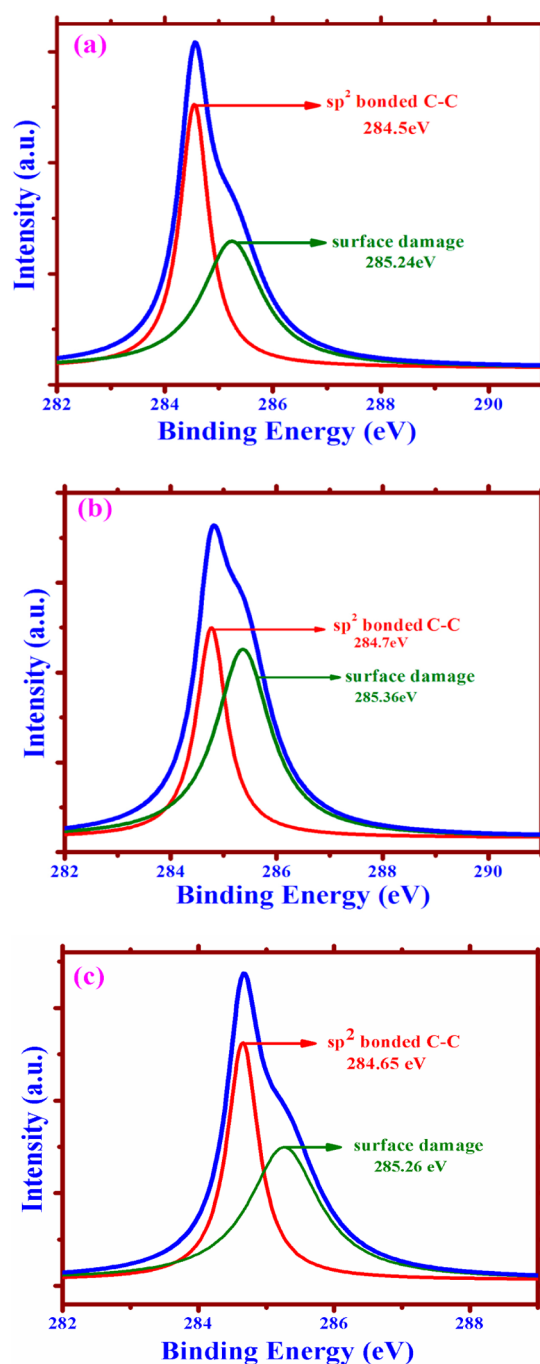
1587, and 2665  $\text{cm}^{-1}$ , respectively. The 2D band is attributed to the two phonon double resonance scattering process and does not require any defects to arise. Further, it is a sign of the electronic properties and stacking dimension of graphene layers. However, the existing defects in graphene would allow the double resonance scattering with one being elastic and the other inelastic leading to the D band. Hence, the wavenumber position of a D band is approximately half that of the 2D band and is sensitive to the excitation wavelength.<sup>7,27–29</sup> It is widely reported that the full-width-at-half-maximum (FWHM) of the 2D band for the single and bilayer epitaxial graphenes grown on SiC is  $\sim 60$  and  $95 \text{ cm}^{-1}$ , respectively, whereas in the case of mechanically exfoliated graphene (MEG), it is found to be 30 and  $45 \text{ cm}^{-1}$ , respectively.<sup>30</sup> However, in our case, the FWHM of the 2D band on the Si-face is measured to be  $21 \text{ cm}^{-1}$ , a lower value than the earlier reports, which strongly confirms single layer nature. However, in the case of the C-face, the broadening of the 2D band ( $44 \text{ cm}^{-1}$ ) occurs due to the existence of bilayer graphene. This might be due to the fact that the sublimation rate of Si on the Si-face induced by the e-beam is slower than that on the C-face due to its high surface energy and thus may provoke Si sublimation on the C-face about two atomic layers for the same irradiation time. The above results are in good agreement with MEG. Although the dominant G band intensity indicates good quality of graphene on the C-face,

the observed D+G band at  $2930 \text{ cm}^{-1}$  reveals the existence of surface damage on the epitaxial graphene over the C-face,<sup>31</sup> whereas it is not observed on the Si-face. FESEM images (Figure 2c and d) recorded on the C-face also clearly show the defect sites on epitaxial graphene layers in accordance with observations from Raman spectra. Furthermore, the FWHM of the D band on the Si-face ( $18 \text{ cm}^{-1}$ ) is very narrow as compared to that on the C-face ( $76 \text{ cm}^{-1}$ ), which reinforces the good crystalline quality of the Si-face (Supporting Information, Figure S3). Moreover, the controlled defining of graphene on the C-face is expected to be inflexible due to its poor surface energy. Hence, the characteristics of the Si-face rather than the C-face are concentrated, and the e-beam-assisted graphitization process of graphene on the Si-face was extended for 4 and 5 min of duration.

The prominent Raman band positions of the graphene with the irradiation time are shown in Figure 3c. The observed FWHM of the 2D band at 60 and  $85 \text{ cm}^{-1}$  confirms the tri- and tetra-layers of graphene, respectively. In Figure 3d and e, we present the number of layers as a linear function of irradiation time. It was realized that the stacking dimension of the hexagonally bonded carbon atoms upshifts the 2D band with decrease in the number of layers.<sup>5,30,32</sup> The variation of FWHM and position of the 2D band in response to the irradiation time is shown in Figure 3d. The shift toward lower wavenumber and

broadening of the 2D band with the irradiation time ensure the increase in number of layers. Further, this shift may be associated with the strain relaxation in the lattice as the effect of the substrate weakens. The G band is the result of first-order scattering of the  $E_{2g}$  phonon at the center of the hexagonal Brillouin zone and is a characteristic of  $sp^2$ -hybridized C–C.<sup>7,27,28</sup> As shown in Figure 3e, the G band down shifted (1595, 1591, and 1587  $\text{cm}^{-1}$ ) toward the bulk graphite (1575  $\text{cm}^{-1}$ ), which ensures the formation of single, tri-, and tetra-layers of graphene with irradiation times of 2, 4, and 5 min, respectively, and it corroborates with the earlier reports.<sup>30,32,33</sup> Therefore, we strongly conclude from the results of Raman spectra that the number of graphene layers increase linearly with irradiation time. This might be due to the fact that e-beam-assisted graphitization results in localized sublimation of Si atoms over a depth of few atomic levels depending on the time of irradiation. Further, the subsequent irradiation for 5 min results in the quenching of the 2D band intensity along with enhancement of D band intensity, thus confirming the deterioration of the crystalline quality of the pristine graphene layers (Supporting Information, Figure S3). It was also reported that the incident energies above 200 keV turns graphene into amorphous carbon,<sup>34</sup> and high energies of 1 MeV induce oxidation of graphene layers.<sup>35</sup> Further, Jones et al.<sup>36</sup> have assigned the D band to hydrogenation of graphene (graphane) as the peak vanished after annealing at  $\sim 543$  K for 30 min by the process of dehydrogenation. In order to corroborate the nature of the D band, Raman spectra were recorded for the samples annealed at 573 K under vacuum for 30 min, which show neither shifting nor diminishing of the D band (Supporting Information, Figure S3d). Thus, we ascertain that the D band is exclusively due to the defects in the graphene lattice and not from hydrogenation. Moreover, the hydrogenation process is less plausible since the experiments are conducted under high vacuum conditions in which no external hydrogen sources are involved. Therefore, we strongly conclude that the Raman D band arises from the defects scattering in graphene such as lattice defects, structural disorder, and physical damage induced by both the epitaxial relationship and electron irradiation but not necessarily with amorphization.

Figure 4 shows the C1s level XPS spectra of the epitaxial graphene measured on both the Si and C faces. These spectra are deconvoluted into two peaks in order to systematically analyze the surface modifications. For 2 min of irradiation on the Si-face, the main C1s peak observed at 284.5 eV (Figure 4a) originates from the  $sp^2$  bonding of the carbon layer that ensures the single layer graphene nature. Further, the C1s peak blue shifts to 0.15 eV for 4 min of irradiation and is observed at 284.65 eV (Figure 4c). The shift of the C1s peak to the higher energy side may be attributed to the change in hybridization with increasing irradiation time (Supporting Information). An additional peak at 285.24 eV can be attributed to surface damage or defects in the graphene layer. The observed C1s peak at 284.7 eV (Figure 4b) on the C-face corresponds to the characteristics of  $sp^2$  bonding in graphene and is blue shifted about 0.2 eV from its corresponding peak observed on the Si-face, which may be ascribed to the carbon vacancies in the graphene lattice.<sup>37</sup> The carbon vacancies are associated with the atoms at the edges of the few-layer graphene having nonfolded atomic arrangements, which may contain dangling bonds and unsaturated carbon atoms that are susceptible to ejection owing to its very low threshold energy compared to that of saturated carbon atoms.<sup>38</sup> The dominant surface damage peak in the C-



**Figure 4.** Deconvoluted XPS spectra of epitaxial graphene on (a) 2 min irradiation on the Si-face and (b) 2 min irradiation on the C-face, and (c) 4 min irradiation on the Si-face.

face at 285.36 eV indicates a highly defective C-face. Also, the FWHM of the C1s peak is 0.64 and 0.69 eV for Si- and C-faces, respectively, which is smaller than the reported values.<sup>5,39</sup>

As shown in Table 1, Hall mobility drastically decreases with the increase of irradiation time, and in turn, the number of layers increases. The maximum Hall mobility on the Si-face for single layer graphene is  $\sim 6450 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  with a surface carrier density of  $1.5 \times 10^{13} \text{ cm}^{-2}$ , whereas on the C-face it is  $3910 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  with a surface carrier density of  $3.8 \times 10^{13} \text{ cm}^{-2}$ . The observed low mobility on the C-face is controversial to the earlier reports.<sup>40</sup> The presence of the higher number defects on C-faces as compared to Si-faces, as evidenced from Raman, XPS

**Table 1. Room Temperature van der Pauw Hall Mobilities of the Samples Measured for Different Irradiation Times**

irradiation time (s)	mobility ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ )	carrier density ( $10^{13}\text{cm}^{-2}$ )	number of layers
120 (Si-face)	6450	1.5	1
120 (C-face)	3910	3.8	2
240 (Si-face)	3030	1.8	3
300 (Si-face)	1440	5.0	4

and FESEM analyses, will promote more scattering of charge carriers and subsequently diminish the carrier mobility on C faces. The Hall measurements on a number of monolayer samples with constant irradiation time of 2 min on the Si-face demonstrated the maximum mobility of  $\sim 6400\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  with the nominal variation of  $\pm 200\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which is less than 5%. Furthermore, the mobility of subsequent irradiation on preformed graphene samples is significantly reduced to  $\sim 1000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  compared to that of its pristine samples due to the formation of either defects such as bond distortion and carbon vacancies in graphene layers or carrier interactions but not necessarily because the vacancies will occur in all graphene layers that have saturated carbon atoms and a threshold energy of 88 keV.<sup>34,38</sup> It has been reported that an extended exposure of the e-beam during SEM could cause the degradation of electrical properties in exfoliated graphene.<sup>41</sup> In contrast, the degradation of electrical transport properties after SEM imaging is significantly less as the carrier mobility ( $\sim 6450\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for monolayer graphene on the Si-face) remains constant with an accuracy of  $\pm 25\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ . This might be due to the fact that the graphene grown on SiC is expected to be highly resistive against energetic irradiations such as X-rays and electrons owing to the epitaxial relationship with the SiC substrate. Also, the factors employed for SEM imaging such as electron energy (3–5 keV), emission current (150  $\mu\text{A}$ ), and scanning area (in  $\mu\text{m}$ ) are not violent enough to perturb the  $\text{sp}^2$  bonding nature of epitaxial graphene.

In this process, the formation of graphene by low energy e-beam irradiation could presumably be due to electron–electron interaction and its kinetic energy loss at the surface of the SiC substrate. In conventional thermal annealing of SiC under vacuum at very high temperature, the heat energy employed alone plays a decisive role in Si sublimation via bond breaking. Nevertheless, with the low energy e-beam, interactions like scattering, excitation, ionization, etc. between the primary electrons and SiC lattice are localized (due to the semi-insulating behavior of the SiC) and result in bond breaking of Si and C atoms, and the excess kinetic energy, acquired from the decelerated primary electrons, is dissipated as heat that results in Si sublimation.<sup>23,24</sup> It should be noted that the electronic excitations are delocalized in metals due to the presence of conduction electrons and would not result in bond breaking. Thus, Si–C bond breaking significantly reduces the desorption temperature of Si that favors Si sublimation ( $\sim 900^\circ\text{C}$ ) well below its graphitization temperature of  $1200^\circ\text{C}$  over the irradiated area and left behind a carbon rich surface that nucleates to form graphene layers. The SiC substrate experiences heat within a few milliseconds of the e-beam irradiation, and heat dissipates rapidly as the e-beam is withdrawn unlike in the thermal annealing process. Hence, the growth rate can be precisely controlled. The production of high quality graphene with better controlled layers is highly dependent on the precise control of growth parameters such as

incident energy, irradiation time, emission current, fluencies, and beam distribution. As the growth parameters are tunable, the uniform distribution of the e-beam over the SiC substrate is well controllable. However, the uniform distribution of the e-beam is desirable for future nanoscale graphene electronics. Further, a motorized precise translation or framework of electron optics can greatly improve the uniformity of beam distribution and defining area of e-beam for the writing of graphene on SiC for both large scale and nanoscale electronics. Therefore, this method is expected to be cost-effective for both large scale and microelectronics applications.

In summary, the fabrication of epitaxial graphene by the direct conversion of the 4H-SiC substrate using low energy e-beam irradiation is demonstrated. This simple and novel method is a feasible one for fabricating devices of graphene on SiC by focusing an e-beam onto the desired area. A physical mechanism for the formation of graphene under low energy e-beam is explained. Sublimation of Si atoms occurs only on the topmost layer or even at a few atomic layers because of the bond-breaking process on the localized area of SiC, which is responsible for the formation of the controlled layer of graphene on 4H-SiC under e-beam irradiation. Raman spectra confirm that the number of graphene layers increases linearly as a function of irradiation time. The electronic structure of the graphene layers is investigated by XPS spectroscopic techniques. The reproducible maximum Hall mobility of single layer graphene on the Si-face is  $6450\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  with a carrier density of  $1.5 \times 10^{13}\text{ cm}^{-2}$ . The number of layers and electronic properties are highly sensitive to the e-beam energy and irradiation time. Thus, scalable area, the defining structure, and controllable layers could be mastered by suitably regulating the rastering of the e-beam. On these grounds, the direct writing of graphene device structure on SiC is feasible without complex lithographic patterning.

## ■ ASSOCIATED CONTENT

### ⑤ Supporting Information

AFM images taken on the Si-face for 4 and 5 min irradiation time; formation of fractal like graphene patterns; Raman spectra of bare 4H-SiC on the Si-face, comparison of the D peak on both faces for 2 min of irradiation time and 5 min of subsequent irradiation on preformed graphene on Si-face, before and after annealing of the graphene samples at 573 K; and the XPS survey scan and O 1s spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Phone: +91-431-2407057. E-mail: [kjeganathan@yahoo.com](mailto:kjeganathan@yahoo.com).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

K.J. thanks Department of Science and Technology (DST), Govt. of India for the financial support to develop the infrastructure facility under the scheme of FIST and Nano-mission (Contract No. SR/NM/NS-77/2008). P.D. thanks Mr. V. Purushothaman, Mr. M. Kanagaraj, and Mr. K. Prabakaran for their fruitful discussions. We thank Miss P. Sangeetha for experimental assistance with Raman spectroscopy.



## REFERENCES

- (1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.
- (2) Geim, A. K.; Novoselov, K. S. The Rise of Graphene. *Nat. Mater.* **2007**, *6*, 183–191.
- (3) Park, C.-H.; Yang, L.; Son, Y.-W.; Cohen, M. L.; Louie, S. G. Anisotropic Behaviours of Massless Dirac Fermions in Graphene under Periodic Potentials. *Nat. Phys.* **2008**, *4*, 213–217.
- (4) Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, L.; Tutuc, E.; et al. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* **2009**, *324*, 1312–1314.
- (5) Emtsev, K. V.; Bostwick, A.; Horn, K.; Jobst, J.; Kellogg, G. L.; Ley, L.; McChesney, J. L.; Ohta, T.; Reshanov, S. A.; Röhl, J.; et al. Towards Wafer-Size Graphene Layers by Atmospheric Pressure Graphitization of Silicon Carbide. *Nat. Mater.* **2009**, *8*, 203–207.
- (6) Sprinkle, M.; Ruan, M.; Hu, Y.; Hankinson, J.; Rubio-Roy, M.; Zhang, B.; Wu, X.; Berger, C.; de Heer, W. A. Scalable Templated Growth of Graphene Nanoribbons on SiC. *Nat. Nanotechnol.* **2010**, *5*, 727–731.
- (7) Yannopoulos, S. N.; Siokou, A.; Nasikas, N. K.; Dracopoulos, V.; Ravani, F.; Papatheodorou, G. N. CO<sub>2</sub>-Laser-Induced Growth of Epitaxial Graphene on 6H-SiC (0001). *Adv. Funct. Mater.* **2012**, *22*, 113–120.
- (8) Lee, S.; Toney, M. F.; Ko, W.; Randel, J. C.; Jung, H. J.; Munakata, K.; Lu, J.; Geballe, T. H.; Beasley, M. R.; Sinclair, R.; Manoharan, H. C.; Salleo, A. Laser-Synthesized Epitaxial Graphene. *ACS Nano* **2010**, *4*, 7524–7530.
- (9) Park, S.; Ruoff, R. S. Chemical Methods for the Production of Graphene. *Nat. Nanotechnol.* **2009**, *4*, 217–224.
- (10) Kim, K.; Choi, J.-Y.; Kim, T.; Cho, S.-H.; Chung, H.-J. A Role for Graphene in Silicon-Based Semiconductor Devices. *Nature* **2011**, *479*, 338–344.
- (11) Schwierz, F. Graphene Transistors. *Nat. Nanotechnol.* **2010**, *5*, 487–496.
- (12) Tsen, A. W.; Brown, L.; Levendorf, M. P.; Ghahari, F.; Huang, P. Y.; Havener, R. W.; Ruiz-Vargas, C. S.; Muller, D. A.; Kim, P.; Park, J. Tailoring Electrical Transport Across Grain Boundaries in Polycrystalline Graphene. *Science* **2012**, *336*, 1143–1146.
- (13) Gu, G.; Nie, S.; Feenstra, R. M.; Devaty, R. P.; Choyke, W. J.; Chan, W. K.; Kane, M. G. Field Effect in Epitaxial Graphene on a Silicon Carbide Substrate. *Appl. Phys. Lett.* **2007**, *90*, 253507.
- (14) Peng, X.; Ahuja, R. Symmetry Breaking Induced Band Gap in Epitaxial Graphene Layers on SiC. *Nano Lett.* **2008**, *8*, 4464–4468.
- (15) Zhou, S. Y.; Gweon, G.-H.; Fedorov, A. V.; First, P. N.; de Heer, W. A.; Lee, D.-H.; Guinea, F.; Costro Neto, A. H.; Lanzara, A. Substrate-Induced Bandgap Opening in Epitaxial Graphene. *Nat. Mater.* **2007**, *6*, 770–775.
- (16) Tzalenchuk, A.; Lara-Avila, S.; Kalaboukhov, A.; Paolillo, S.; Syvajarvi, M.; Yakimova, R.; Kazakova, O.; Janssen, T. J. B. M.; Fal'ko, V.; Kubatkin, S. Towards a Quantum Resistance Standard Based on Epitaxial Graphene. *Nat. Nanotechnol.* **2010**, *5*, 186–189.
- (17) Wu, Y.; Jenkins, K. A.; Valdes-Garcia, A.; Farmer, D. B.; Zhu, Y.; Bol, A. A.; Dimitrakopoulos, C.; Zhu, W.; Xia, F.; Avouris, P.; et al. State-of-the-Art Graphene High-Frequency Electronics. *Nano Lett.* **2012**, *12*, 3062–3067.
- (18) Badami, D. V. Graphitization of  $\alpha$ -Silicon Carbide. *Nature* **1962**, *193*, 569–570.
- (19) Bommel, A. J. V.; Crombeen, J. E.; Van Tooren, A. LEED and Auger Electron Observation of the SiC (0001) Surface. *Surf. Sci.* **1975**, *48*, 463–472.
- (20) Berger, C.; Song, Z.; Li, T.; Li, X.; Ogbazghi, A. Y.; Feng, R.; Dai, Z.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; de Heer, W. A. Ultrathin Graphite: 2D Electron Gas Properties and a Route Toward Graphene-Based Nanoelectronics. *J. Phys. Chem. B* **2004**, *108*, 19912–19916.
- (21) Huang, Q.; Chen, X.; Liu, J.; Wang, W.; Wang, G.; Wang, W.; Yang, R.; Liu, Y.; Guo, L. Epitaxial Graphene on 4H-SiC by Pulsed Electron Irradiation. *Chem. Commun.* **2010**, *46*, 4917–4919.
- (22) Huang, Q.; Guo, L.; Wang, W.; Wang, G.; Wang, W.; Jia, Y. P.; Jing-Jing, L.; Kang, L.; Chen, X. Raman Spectrum of Epitaxial Graphene on SiC (0001) by Pulsed Electron Irradiation. *Chin. Phys. Lett.* **2010**, *27*, 046803.
- (23) Krashennnikov, A. V.; Banhart, F. Engineering of Nanostructured Carbon Materials with Electron or Ion Beams. *Nat. Mater.* **2007**, *6*, 723–733.
- (24) Banhart, F. Irradiation Effects in Carbon Nanostructures. *Rep. Prog. Phys.* **1999**, *62*, 1181–1221.
- (25) Ishimaru, M.; Bae, I.-T.; Hirotsu, Y. Electron-Beam-Induced Amorphization in SiC. *Phys. Rev. B* **2003**, *68*, 144102.
- (26) Go, H.; Kwak, J.; Jeon, Y.; Kim, S.-D.; Lee, B. C.; Kang, H. S.; Ko, J.-H.; Kim, N.; Kim, B.-K.; Yoo, J.-W.; Kim, S. W.; Kim, Y.-W.; Kwon, S.-Y.; Park, K. Low Temperature Formation of Epitaxial Graphene on 6H-SiC Induced by Continuous Electron Beam Irradiation. *Appl. Phys. Lett.* **2012**, *101*, 092105.
- (27) Krauss, B.; Lohmann, T.; Chae, D.-H.; Haluska, M.; von Klitzing, K.; Smet, J. H. Laser-Induced Disassembly of a Graphene Single Crystal into a Nanocrystalline Network. *Phys. Rev. B* **2009**, *79*, 165428.
- (28) Das, A.; Pisana, S.; Chakraborty, B.; Piscanec, S.; Saha, S. K.; Waghmare, U. V.; Novoselov, K. S.; Krishnamurthy, H. R.; Geim, A. K.; Ferrari, A. C.; Sood, A. K. Monitoring Dopants by Raman Scattering in an Electrochemically Top-Gated Graphene Transistor. *Nat. Nanotechnol.* **2008**, *3*, 210–215.
- (29) Reina, A.; Jia, X.; Ho, J.; Nezich, D.; Son, H.; Bulovic, V.; Dresselhaus, M. S.; Kong, J. Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition. *Nano Lett.* **2009**, *9*, 30–35.
- (30) Ni, Z. H.; Chen, W.; Fan, X. F.; Kuo, J. L.; Yu, T.; Wee, A. T. S.; Shen, Z. X. Raman Spectroscopy of Epitaxial Graphene on SiC Substrate. *Phys. Rev. B* **2008**, *77*, 115416.
- (31) Guang, H.; Wong, S. L.; Tin, C.-C.; Luo, Z. Q.; Shen, Z. X.; Chen, W.; Wee, A. T. S. Epitaxial Growth and Characterization of Graphene on Free Standing Polycrystalline SiC. *J. Appl. Phys.* **2011**, *110*, 014308.
- (32) Röhl, R.; Hundhausen, M.; Emtsev, K. V.; Seyller, Th.; Graupner, R.; Ley, L. Raman Spectra of Epitaxial Graphene on SiC (0001). *Appl. Phys. Lett.* **2007**, *92*, 201918.
- (33) Tuinstra, F.; Koenig, J. L. Raman Spectrum of Graphite. *The J. Chem. Phys.* **1970**, *53*, 1126–1130.
- (34) Teweldebrhan, D.; Balandin, A. A. Modification of Graphene Properties due to Electron-Beam Irradiation. *Appl. Phys. Lett.* **2009**, *94*, 013101.
- (35) Kim, K.-J.; Choi, J.; Lee, H.; Lee, H.-K.; Kang, T.-H.; Han, Y.-H.; Lee, B.-C.; Kim, S.; Kim, B. Effects of 1 MeV Electron Beam Irradiation on Multilayer Graphene grown on 6H-SiC (0001). *J. Phys. Chem. C* **2008**, *112*, 13062–13064.
- (36) Jones, J. D.; Ecton, P. A.; Mo, Y.; Perez, J. M. Comment on “Modification of graphene properties due to electron-beam irradiation” [Appl. Phys. Lett. 94, 013101 (2009)]. *Appl. Phys. Lett.* **2009**, *95*, 246101.
- (37) Kim, S.; Zhou, S.; Hu, Y.; Acik, M.; Chabal, Y. J.; Berger, C.; de Heer, W.; Bongiorno, A.; Riedo, E. Room-Temperature Metastability of Multilayer Graphene Oxide Film. *Nat. Mater.* **2012**, *11*, 544–549.
- (38) Warner, J. H.; Rummeli, M. H.; Ge, L.; Gemming, T.; Montanari, B.; Harrison, N. M.; Buchner, B.; Briggs, G. A. D. Structural Transformations in Graphene Studied with High Spatial and Temporal Resolution. *Nat. Nanotechnol.* **2009**, *4*, 500–504.
- (39) Emtsev, K. V.; Speck, F.; Seyller, Th.; Ley, L. Interaction, Growth and Ordering of Epitaxial Graphene on SiC {0001} Surfaces: A Comparative Photoelectron Spectroscopy Study. *Phys. Rev. B* **2008**, *77*, 155303.
- (40) Yakes, M. K.; Gunlycke, D.; Tedesco, J. L.; Campbell, P. M.; Myers-Ward, R. L.; Eddy, C. R., Jr.; Gaskill, D. K.; Sheehan, P. E.; Laracuente, A. R. Conductance Anisotropy in Epitaxial Graphene



Sheets Generated by Substrate Interactions. *Nano Lett.* **2010**, *10*, 1559–1562.

(41) He, Y. H.; Wang, L.; Chen, X. L.; Wu, Z. F.; Li, W.; Cai, Y.; Wang, N. Modifying Electronic Transport Properties of Graphene by Electron Beam Irradiation. *Appl. Phys. Lett.* **2011**, *99*, 033109.