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Surface functionalization of epitaxial graphene on SiC by ion irradiation for gas sensing application

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Abstract:

In this work surface functionalization of epitaxial graphene grown on silicon carbide was performed by ion irradiation to investigate their gas sensing capabilities. Swift heavy irradiation using 100 MeV silver ions at four varying fluences was implemented on epitaxial graphene to investigate morphological and structural changes and their effects on the gas sensing capabilities of graphene. Sensing devices are expected as one of the first electronic applications using graphene and most of them use functionalized surfaces to tailor a certain function. In our case we have studied irradiation as a tool to achieve functionalization. Morphological and structural changes on epitaxial graphene layers were investigated by atomic force microscopy, Raman spectroscopy, Raman mapping and reflectance mapping. The surface morphology of irradiated graphene layers showed graphene folding, hillocks, and formation of wrinkles at highest fluence (2×10^{13} ions/cm²). Raman spectra analysis shows that the graphene defect density is increased with increasing fluence, while Raman mapping and reflectance mapping show that there is also a reduction of monolayer graphene coverage. The samples were investigated for ammonia and nitrogen dioxide gas sensing applications. Sensors fabricated on pristine and irradiated samples showed highest gas sensing response at an optimal fluence. Our work provides new pathways for introducing defects in controlled manner in epitaxial graphene, which can be used not only for gas sensing application but also for other applications, such as electrochemical, biosensing, magnetosensing and spintronic applications.

Keywords: Epitaxial graphene, Surface functionalization, Ion irradiation, gas sensors

Introduction:

Graphene with two-dimensional honeycomb lattice structure of sp^2 -bonded carbon atoms acts as excellent candidate for future nano electronics due to its outstanding properties such as long-range ballistic transport at room temperature, optical transparency, higher carrier mobility, electrical and thermal conductivity properties [1-3]. Graphene can be fabricated by different methods such as mechanical exfoliation of graphite [4], chemical exfoliation [5], chemical vapour deposition (CVD) [6] and epitaxial graphene (EG) grown on silicon carbide (SiC) [7]. Amongst all these techniques, growth of EG on SiC has several advantages. The wide band gap semiconductor SiC acts as a suitable substrate for not only various industrial applications but also provides wafer scale growth of epitaxial graphene [7]. On the contrary, graphene fabricated using chemical exfoliation technique suffers from lots of defects due to metallic impurities which alter electronic, electrochemical and redox properties of graphene [8]. Additionally, graphene grown using CVD technique on metal substrate requires transferring onto an insulating substrate for its industrial use and to date an efficient transfer process is not available [6]. Epitaxial graphene grown on SiC has fewer defects and does not require any additional transfer to another substrate. Hence, epitaxially grown graphene is free from processing pollutant, which alters electrical, mechanical and sensing property of graphene [9, 10]. Covalent functionalization and defects like vacancy defects, substitutional defects and topological defects introduced in controlled manner on the graphene surface, can further tailor and improve its electronic, sensing and magnetic properties. Functionalization of EG layer with polymers which create a type of sp^3 defects enhances electronic application of epitaxial graphene [11]. Doping of graphene with nitrogen introduces substitutional defects and provide a way for tailoring its electronic and chemical properties [12]. In addition, decorating EG with metals like Au and Pt increases its gas sensing ability [13]. Further band gap engineering and velocity renormalization is achieved by depositing Ti layer on graphene [14], while improved transistor performance is obtained by integration of EG with dielectric materials [15]. Graphene has also the ability of reconstructing its hexagonal carbon lattice into pentagons and heptagons near the defect sites under electronic beam irradiation [16]. These defects act as a tool for manipulating physical properties of graphene and result in device-based applications of graphene, such as FETs [17], RF transistors and amplifiers [18], sensors [19], detectors [20] and metrology [21].

Ion beam technology acts as a perfect tool to introduce defects in graphene due to its high uniformity, repeatability, single sided doping capability and ability to change the surface without affecting the bulk material. Previously, low energy ion implantation has been used to dope graphene using 50eV nitrogen ions at low temperature [22]. Swift heavy ion (SHI) irradiation is the process of irradiating materials with energy in the range of MeV. In SHI irradiation, electronic energy loss dominates over nuclear energy loss, contrary to nuclear energy loss domination during low energy ion implantation [23]. Previously, SHI irradiation has been used to study structural and electrical changes in graphene [24-26]. Kumar et al used silver ion irradiation with 100 MeV energy for graphene layer grown by CVD. They observed that up to 3×10^{11} ions/cm² fluence the defect density decreased compared to pristine sample as the annealing process reduced damage that occurred due to the irradiation [24]. However at fluence greater than 3×10^{11} ions/cm², the defect density increased due to domination of damages over the restoring action of the annealing process [24]. Change from n-doped to p-doped layer in single layer graphene was observed by Ochedowski et al following irradiation at glancing angle of incidence with 92 MeV energy [25]. Further, unzipping and folding of exfoliated graphene using SHI has been reported [26].

However, despite high reproducibility and wider industrial applications of EG on SiC, SHI irradiation has never been employed to study structural changes in EG and subsequently investigate its applicability for sensing use. Since SHI is a powerful tool for altering the surface of graphene, in this work we investigated different types of defect generation in EG grown on 4H-SiC substrate and its application for gas sensing. Since we were interested to study defects in EG, we had chosen the fluence range from 6.6×10^{11} ions/cm² to 2×10^{13} ions/cm² in consideration of a previous study showing decrease in defect density up to 3.3×10^{11} ions/cm² in CVD grown graphene following 100 MeV SHI [24].

By studying irradiation induced defects in graphene, our ultimate aim is to control gas sensing ability of the irradiated samples. Gas sensing capabilities of epitaxial graphene in ppm and ppb range have been reported in the past [19, 27]. Defects like vacancy and substitutional defects create preferential bonding sites for adsorption of atoms and molecules, and can be exploited for enhancing gas and liquid sensing application of graphene [28]. Epitaxial graphene shows gas sensing due to physio-adsorption of gas molecules whereas defective graphene forms a bond with the gas molecules thereby resulting in increased sensing ability of graphene [29]. A theoretical study by Zhang et al showed that sensitivity and selectivity of graphene based gas sensors can be significantly improved by introducing defects in graphene [30]. In our work, the

gas sensing application of SHI irradiated epitaxial graphene on SiC is explored and reported for the first time to our knowledge.

In this study, Atomic Force Microscopy (AFM) and Raman spectroscopy showed that generation of various defects in epitaxial graphene depended on fluence of heavy ion irradiation. AFM images revealed hillocks and folding of single layer graphene due to formation of array of defects on graphene layer surface and SiC surface. Moreover, we have observed formation of wrinkles in the graphene at higher fluence. The gas sensing ability of EG was observed to increase with introduction of defects with SHI. Our work provides a new source for introducing and controlling defects in EG on SiC, which can be used not only for gas sensing application but also for other applications like electrochemical, biosensing, magnetosensing and spintronic applications.

Experimental

Growth of epitaxial graphene was performed on 4H-SiC (0001) at 2000°C and 1 atm argon pressure in an inductively heated furnace as described previously [31]. Swift ion irradiation on EG samples was done using 15 MV Pelletron Accelerator Facility (at IUAC, New Delhi, India). Silver ions with 100 MeV at 6.6×10^{11} , 2×10^{12} , 6.6×10^{12} and 2×10^{13} ions/cm² fluence were used for irradiation. The pressure in the irradiation chamber was of the order of 10^{-6} mbar and the average current was 2-particle nano ampere. The projected range, electron and nuclear energy loss were calculated using Stopping and Range of Ions in Matter (SRIM) software [32]. This calculation showed that the projected range of stable 100 MeV silver ion into graphene on SiC is 13.9 μm with nuclear energy loss (S_n) to be 0.0586 keV/nm and electron energy loss (S_e) to be 11.9 keV/nm resulting in S_e/S_n ratio of 203.

Atomic force microscopy in topological and phase mode have been used to study the graphene surface morphology and thickness uniformity. The AFM was performed using a Dimension 3100 AFM (Digital Instruments, Veeco, CA) operated in tapping mode. Fluence dependent damages in graphene were analyzed using Raman spectra taken with 488 nm laser excitation using Jobin Yvon Horiba Labram HR microscope with spot size of around 1 μm . Raman mapping was done with micro Raman set up with excitation laser of 532 nm and spatial resolution of $<1 \mu\text{m}$ to obtain detailed information about the defects generated after irradiation and also to determine the homogeneity of the defect distribution. To determine the number of graphene layers folded during irradiation, reflectance mapping was performed using micro

Raman spectrometer with the configuration described in reference [33]. Reflectance mapping is based on mapping the power of laser beam reflected from sample in micro Raman set up and can efficiently determine more than 10 graphene layers which is not possible by AFM [33]. However, due to limited resolution of reflectance mapping in comparison with AFM that has higher resolution in nanometer range, percentage of monolayer and bilayer graphene were calculated using AFM [33].

For gas sensing, firstly Ti/Au metal contacts were fabricated by magnetron sputtering on the irradiated graphene layer on SiC substrates. The as-prepared samples were glued onto TO8 16-pin headers in order to perform the gas testing. The current/voltage signals were transmitted from the metal contacts to the pins on the header. The gas testing was conducted with an in-house gas mixing systems and all measurements were done at room temperature. A Keithley 2100 Sourcemeter was used to measure the resistance. Before the testing, the sensors were flushed by a background gas composed of 80% nitrogen and 20% oxygen in order to stabilize the sensor baseline. The total flow rate was fixed at 100 ml/min and the same stabilizing method was used for the sensors between every gas exposure. Gas sensing capability of the irradiated samples was investigated for ammonia (NH_3) and nitrogen dioxide (NO_2). Sensors fabricated on pristine and irradiated samples at 6.6×10^{11} ions/cm², 2×10^{12} ions/cm² and 6.6×10^{12} ions/cm² fluences were exposed at room temperature to NH_3 gas for 1 h at 10 ppm and 50 ppm concentrations; and to NO_2 gas for 30 min at 10- and 50- ppm. A UV-LED of wavelength 365 nm was used for desorption of NO_2 .

Results and Discussion

Topological AFM analysis represent how surface morphology changes with the experimental conditions. Reflectance maps and AFM images in Fig. 1 show the thickness uniformity and surface morphology of EG on SiC substrate before and after swift heavy ion irradiation with silver ions at 2×10^{13} ions/cm² fluence. Fig. 1(a) and (b) show reflectance maps of pristine and highest irradiated graphene, respectively on SiC over a $30 \mu\text{m} \times 30 \mu\text{m}$ area. For pristine sample (Fig. 1a) 99% of the surface covered by ML and bilayer graphene, and for irradiated sample (Fig. 1b) 26% covered by ML and bilayer graphene and the rest is multilayer graphene. The AFM images in Fig. 1(c) and (d) show the surface topography of graphene layer before and after irradiation on the same samples used for reflectance maps (parts a and b in Fig. 1). Fig. 1(d) shows hillocks, wrinkles and folding due to formation of multilayer graphene which can be

observed as change in contrast in comparison to pristine sample. Distinguishing different graphene layers based on change in contrast of AFM phase images has been previously reported [34, 35]. Based on AFM phase image (not shown) on pristine sample coverage of ML and bilayer graphene are 95% and 5%, respectively. Fig. 1(e) and (f) show higher magnification of the area in Fig. 1(c) and Fig. 1(d), respectively. Fig 1(f) shows hillocks, wrinkles and folding on surface of EG on SiC substrate.

Fig. 1. Reflectance map and AFM images of pristine and irradiated graphene. Reflectance map of (a) pristine, (b) irradiated graphene layer. The white spot in map (a) indicates multilayer graphene, most probably due to micropipe in the substrate. Topological AFM images of (c) pristine, and (d) irradiated graphene layer. (e) and (f) present higher magnification images from the areas in parts (c) and (d), respectively.

Zhao et al reported that rupturing of supported graphene requires energy S_e to be greater than the threshold of 6.5 keV/nm [36]. In this study, the provided S_e was 11.9keV/nm, and the graphene layers were ruptured. This resulted in folding of ML and bilayer graphene and consequently converting them to multi-layer graphene randomly distributed on the substrate. For the sample exposed to the highest irradiation, ruptured graphene layers are visible in the AFM images (Fig. 1(d) and Fig. 1(f)), as well as in the reflectance map, Fig. 1(b).

In SHI, when a fast moving ion passes along a straight-line trajectory perpendicular to the surface plane, an extremely localized energy release may lead to creation of single nanosized hillocks on the surface. Hillock formation has been reported previously [37-39] and their formation is explained by the thermal spike model [40] in which high-energy ion bombardment gives rise to a cylindrically shaped ion track of nanometric dimension along the ion path. This energy is transferred by electron – phonon coupling to the atomic system and causes localized heating along the ion track which results in transient thermal spikes that last for few picoseconds and gives rise to nanosized hillocks at the impact point of each ion [41]. Similar observation was reported earlier for mechanically exfoliated graphene following ~100 MeV SHI [26]. Additionally, we also observed wrinkles with non-uniform height, and mainly elongated in the $(11\bar{2}0)$ direction of the substrate, as shown in Fig. 1(f).

To determine fluence dependent defect formation on graphene surface, AFM study was done over scan areas of $1 \times 1 \mu\text{m}$ (Fig. 2) on samples irradiated at fluences 6.6×10^{11} , 2×10^{12} , 6.6×10^{12} and 2×10^{13} ions/cm². Figs. 2(a-c) show some structural defects which may represent the initial stage of formation of folding on the surface of graphene whose intensity increases with increasing the fluence. Surface roughness increased with increasing fluence, and the measured value using AFM for pristine and highest irradiated sample (2×10^{13} ions/cm²) are about 0.27 nm and 1nm, respectively. This increasing in roughness with increasing defects density agrees with previous report [42].

In the sample subjected to the highest fluence we can clearly observe wrinkles (Fig. 1(f) and 2(d)). Wrinkles are formed during the cooling process as a result of releasing compressive strain on graphene layers induced by thermal mismatch between the epitaxial graphene layer and SiC substrate [43]. At highest fluence (2×10^{13} ions/cm²) wrinkles are observed due to higher

temperature generated at higher fluence resulting in higher compressive strain, which leads to formation of wrinkles on the graphene surface [44].

Fig. 2. AFM height images of irradiated graphene samples, at (a) 2×10^{11} ions/cm² (b) 2×10^{12} ions/cm² (c) 6.6×10^{12} ions/cm² and (d) 2×10^{13} ions/cm² fluences. Scan size $1 \mu\text{m} \times 1 \mu\text{m}$.

Besides surface roughness, structural defects, hillocks and wrinkles, we also observed folding of graphene at all fluences. Fig. 3(a) shows graphene folding at 2×10^{12} ions/cm² over a scan area of $2 \times 2 \mu\text{m}$ which is seen more clearly over a scan area of $700 \text{ nm} \times 700 \text{ nm}$ as shown in Fig. 3(b). Smith et al reported that the minimum incident electron energy required to knock out a carbon atom from the graphene lattice is 86 keV [45]. Since an incident energy of 100 MeV was used in the current study, it is likely that carbon atoms were knocked out from the graphene lattice creating vacancy defects which further agglomerated into larger vacancy structures due to prolonged irradiation. A minimum energy of around 5-7 eV is required to form stable pentagon/heptagon defects in graphene from their regular hexagonal honeycomb like structure [46]. Additionally, Zhao et al reported that minimum 5 keV/nm electronic energy deposition is required to create other defects in graphene such as Stone–Wales defect, vacancy defects and local distorted carbon rings defects [36]. Since in this study, $S_e = 11.9 \text{ keV/nm}$, hence all such defects are likely to be present on the graphene surface. It has been shown previously that at glancing angle of incidence, folding is homogenous but at perpendicular angle

of incidence folding is inhomogeneous [26]. Moreover, Akcöltekin et al reported that multiple but aligned defects are formed during SHI, resulting in reconstruction of the carbon network along the ion track. They reported that chains of hillocks coincide exactly with the line of extended defects and results in unzipping the graphene along the ion track [26]. Due to this unzipping, graphene gets folded at many places along the ion track, which is seen in Fig. 3. However, the folding is inhomogeneous since the irradiation is done at normal incidence.

Fig. 3. AFM images of (a) folded graphene on SiC after irradiation at 2×10^{12} ions/cm² fluence (scan size $1 \mu\text{m} \times 1 \mu\text{m}$). (b) and (c) present higher magnification of points b and c in part (a).

Raman spectroscopy and reflectance mapping have been used to study the defect density and multiplicity of graphene folding on irradiated samples. Fig. 4(a-e) shows Raman spectra of pristine and irradiated graphene samples using a laser with excitation wavelength of 488nm. The spectra exhibit changes in D, G and 2D peak due to swift heavy ion irradiation. Monolayer pristine graphene is characterized by G peak around 1580 cm^{-1} and 2D peak around 2700 cm^{-1} [47].

Fig. 4. Raman spectrum of (a) pristine, and irradiated graphene on SiC at (b) 2×10^{11} ions/cm², (c) 2×10^{12} ions/cm², (d) 6.6×10^{12} ions/cm² and (e) 2×10^{13} ions/cm² fluences using a laser with excitation wavelength of 488nm. The structure of the left side of G peak for pristine graphene is due to the buffer layer and there is no D peak for pristine graphene.

The G peak is associated with the E_{2g} phonon mode at Brillouin zone center [48]. The breathing mode of six-atom rings gives rise to D peak around 1350 cm^{-1} , but requires defects for its activation and its intensity increases with increasing defects. It arises from transverse optic phonons around the K point [49]. The D peak in the pristine sample (Fig. 4(a) and 5(a)) is actually buried in the contribution of the buffer layer, which confirms the high quality of epitaxial graphene. This was also confirmed by the reflectance and AFM phase images, as grown graphene on SiC substrate was dominated by monolayer with some bilayer formation. The second order of the D peak is the 2D peak, which is allowed even in absence of defects since it

involves creation of two phonons with opposite momenta. Its intensity decreases with increase in defects [50]. The EG with single layer graphene is characterized by single Lorentzian 2D peak [47]. In case of bilayer, the 2D peak is broader and can be fitted by four Lorentzian peaks. However, the Raman spectrum of 5-layered graphene is hardly distinguishable from that of graphite [51]. Fig. 4 (b-e) shows that with increasing the ion fluence, the intensity around the D peak increases while that of the G peak decreases. The ratio $I(D)/I(G)$, sometimes called disorder parameter in graphene, serves as parameter for estimating the defect density [24]. Here $I(D)$ and $I(G)$ denote the peak intensities of the D and G peaks, respectively, and are obtained after fitting the D and G peak with Lorentzian functions. We found $I(D)/I(G)$ to increase with increasing fluence from approximately zero in pristine sample to 2.055 in the highest irradiated sample (2×10^{13} ions/cm²). Cancado et al suggested that defect formation in graphene can be divided into two stages on the base of $I(D)/I(G)$, with stage (i) and (ii) having low and high defect concentration, respectively [52]. In stage (i), $I(D)/I(G)$ increases monotonically with increasing defect density and varies according to the following formula:

$$I(D)/I(G) \propto 1/L_D^2, \quad (1)$$

where, L_D is average distance between defects. On the other hand, in stage (ii) $I(D)/I(G)$ decreases according to the equation

$$I(D)/I(G) \propto L_D^2. \quad (2)$$

The transition from stage (i) to stage (ii) is observed when the $I(D)/I(G)$ ratio is around 3 and L_D is in-between 2 to 5 nm using a 2.41eV (532 nm) laser excitation. In the present work, $I(D)/I(G)$ ratio increased to 2.055 at the highest fluence (2×10^{13} ions/cm²) and no decrease was observed with increasing fluence, thereby indicating that at all fluences stage (i) defect generation should be considered. Thus, as expected, the defects increase with increase in fluence which is evident both by increase in roughness (observed by AFM) and increase in $I(D)/I(G)$ ratio. Fig. 4 shows that the intensity of the 2D peak with respect to the G peak decreases with increasing fluence, and also the FWHM of the 2D peak increases at higher fluences suggesting conversion of monolayer graphene to multilayer graphene [51, 53]. This was further supported by the AFM, which shows that folding clearly appears in the irradiated sample (Fig. 1 and Fig. 3), resulting in formation of multilayer graphene [35]. Besides folding, decrease in intensity of 2D peak with respect to G peak could also be attributed to other factors such as doping. Ochedowski et al showed that SHI of exfoliated single layer graphene at 92 MeV with xenon ions resulted in doping of graphene and thereby increasing charged impurities [54]. Further, Ni

et al reported that increase in charge impurities results in decrease of 2D peak intensity with respect to the G peak [55]. In the present study, decrease in the intensity of 2D peak with respect to G peak upon irradiation maybe attributed to both conversion of monolayer graphene to multi-layer graphene and increase of charge impurities due to doping upon SHI. Fig. 4 also shows a red shift in 2D peak intensity of the irradiated samples in comparison to that in the pristine sample. Such shift could be due to the presence of tensile strain as previously reported [56].

Zandiatashbar et al used $I(D)/I(G)$ and $I(2D)/I(G)$ ratios to distinguish between sp^3 defect and vacancy defects [57]. They reported that if $I(D)/I(G) < 1$ and $I(2D)/I(G) > 1$, then it is a sp^3 defect region. On the contrary if $I(D)/I(G) > 1$ and $I(2D)/I(G) < 1$, then it is a vacancy defect region. Here $I(2D)$ represents peak intensity or the peak amplitude of the 2D peak which is obtained after fitting the 2D peak with Lorentzian function. In our study, at 6.6×10^{11} ions/cm² fluence, the $I(D)/I(G)$ and $I(2D)/I(G)$ are 0.630 and 1.1 respectively, which is indicative of sp^3 defect generation upon SHI. At higher fluences (2×10^{12} ions/cm², 6.6×10^{12} ions/cm² and 2×10^{13} ions/cm²) the $I(D)/I(G)$ ratio became greater than 1 and $I(2D)/I(G)$ became less than 1. At 2×10^{13} ions/cm² fluence, $I(D)/I(G)$ and $I(2D)/I(G)$ reached a maximum and minimum value of 2.055 and 0.50 respectively, which suggests vacancy defect generation upon SHI at higher fluences.

Along with the prominent peaks (D, G and 2D), the Raman spectra also show some additional peaks; D', D+D' and 2D' around 1620, 2950 cm⁻¹ and 3240 cm⁻¹ respectively. The D' peak originate from intra-valley double resonance process in the presence of defects. The D+D' peak also requires defects for its activation and arises from two phonons with different momentum [58]. The second overtone of D' is the 2D' mode, which does not require defects for its activation but arises from the process where momentum conservation is satisfied with two phonons with opposite wave-vectors [59]. In order to investigate the presence of D', D+D' and 2D' peaks in Raman spectra, and to investigate the homogeneity of the irradiated samples, we did Raman mapping on samples irradiated at 2×10^{12} ions/cm² and 2×10^{13} ions/cm² fluences using 532 nm laser in backscattering geometry. Each map contains 256 Raman spectra ordered on a grid with 300 nm pitch enclosed in a 4.5 x 4.5 μm square. The Raman spectrum obtained from pristine sample shows only the G, 2D and the 2D' peaks with clear contribution from the buffer layer (Fig. 5(a)). However, in the irradiated samples two additional peaks appear along with the D peak, D' and D+D' peaks, which are representative of significant defect concentrations in these samples (Fig. 5(b) –(c)) [58]. Raman mapping of the sample irradiated at 2×10^{12} ions/cm² fluence showed broadening of the 2D peak only in a few spectra, while the broadening was more often found in the spectra of the highest irradiated sample (at 2×10^{13}

ions/cm²). In addition, many Raman spectra obtained from the maps of both fluences (2×10^{12} ions/cm² and 2×10^{13} ions/cm²) show no contribution from graphene, indicating that in these regions the graphene and the underlying buffer layer has been removed from the substrate surface. The number of spectra with no graphene contribution is larger in the highest-fluence sample than the one at lower fluence.

Fig. 5. Raman spectrum obtained from Raman Mapping of (a) pristine, and irradiated graphene samples at (b) 2×10^{12} ions/cm² and (c) 2×10^{13} ions/cm² fluences using a laser with excitation wavelength of 532 nm. The structure of the left side of G peak for pristine graphene is due to the buffer layer and there is no D peak for pristine graphene.

The mean distance between defects in graphene (L_D , nm) and the intensity ratio between D and G peaks ($I(D)/I(G)$) are related by the quantitative formula [60]:

$$\frac{I(D)}{I(G)} = C_A \frac{(r_A^2 - r_S^2)}{(r_A^2 - 2r_S^2)} [e^{\pi r_S^2/L_D^2} - e^{\pi(r_A^2 - r_S^2)/L_D^2}] \quad (3)$$

where $r_S = 1$ nm, $r_A = 3.1$ nm, are the radii of "structurally disordered" area and "activated" area around ion induced defects, respectively. Depending on single impact of an ion on graphene, modification in graphene is governed by radii of two circular areas r_A and r_S measured from the impact point (with $r_A > r_S$). The region within r_S do not contribute much for activation of D band but the region in between r_S and r_A contributes strongly for its activation [60]. C_A is a constant representing electron-phonon interaction matrix elements and its value at green light excitation estimated from fit to data is ~ 4.2 [60]. The relation between defect density (n_D , cm^{-2}) and mean distance between defects (L_D , nm) is given by:

$$n_D = 10^{14} / \pi L_D^2 \quad (4)$$

Using equations (3) and (4), we calculated L_D and n_D of pristine and irradiated graphene on silicon carbide samples at fluences 2×10^{12} ions/ cm^2 and 2×10^{13} ions/ cm^2 , which are tabulated in Table 1. The values represent average Intensity ratio ($I(D)/I(G)$) of 10 Raman spectra from the 256 spectra measured during Raman mapping for each pristine and irradiated samples. Table 1 shows that with increase in fluence, intensity ratio ($I(D)/I(G)$) increases, the mean distance between defects (L_D) in graphene decreases and the defect density (n_D) increases. The calculations also show that this represents stage (i) of defect formation in graphene, which is in confirmation to the observations in Figure 4 where, $I(D)/I(G) \propto 1/L_D^2$. With increase in defect density, activated area also increases [60].

Table 1. Summary of Intensity ratio of D and G peak ($I(D)/I(G)$), mean distance between defects in graphene (L_D) and Defect Density (n_D) of Pristine and samples irradiated at fluence 2×10^{12} ions/ cm^2 and 2×10^{13} ions/ cm^2 of graphene on silicon carbide

Samples	$I(D)/I(G)^a$	L_D (nm) ^a	$n_D \times 10^{10}$ (cm^{-2}) ^a
Pristine	0.22 ± 0.007	22.36 ± 0.95	6.36 ± 0.81
2×10^{12} ions/ cm^2	1.12 ± 0.07	9.29 ± 0.27	36.90 ± 2.07
2×10^{13} ions/ cm^2	2.06 ± 0.09	6.05 ± 0.09	87.00 ± 2.59

^aErrors represents standard deviation in I(D)/I(G), L_D and n_D values deduced using 10 Raman spectra measured for pristine and irradiated samples.

In the sample irradiated at 2×10^{13} ions/cm², only about 17% of monolayer and about 9% of bilayer is observed due to multiple folding of graphene (Fig. 1(b) and Fig. 3). Table 2 shows percentage of different graphene layers present in pristine and sample irradiated at 2×10^{13} ions/cm² fluence. Also, reflectance map showed about 64% bare substrate in sample irradiated at fluence 2×10^{13} ions/cm². The bare SiC substrate observed in the irradiated samples is due to folding of monolayer graphene into bi-, tri- and multi- layered. This is also supported by Raman mapping results which show presence of bare substrate in irradiated samples but absent in pristine sample and also by AFM images which show folding of graphene (Fig. 3).

Table 2. Number of layers in pristine and irradiated graphene samples at fluences 2×10^{13} ions/cm² obtained from reflectance mapping.

Number of Layers*	Samples	
	Pristine sample	Sample irradiated at 2×10^{13} ions/cm ² fluence
Bare substrate	0	64
1	95	17
2	5	9
3	0.03	4.7
4	0.03	2.5
5	0.04	1.4
6	0.02	0.9
7	0.02	0.4
8	0.01	0.2
9	0	0.06
10	0	0.12

Fig. 6 (a) shows reflectance map obtained together with Raman mapping of the highest-irradiated (at 2×10^{13} ions/cm²) sample over a scan area of $4.5 \mu\text{m} \times 4.5 \mu\text{m}$. According to the reflectance map, up to 16 layers have been observed bunching in a hop after irradiation, but the map shown is restricted between 1 and 4 layers for better visibility. It is to be noted that about 56% of the area is not covered with graphene (according to the reflectance map and the Raman

spectra) and has only 10.5% and 5.8% of ML and bilayer graphene, respectively in this particular area. This hinders conventional plots of parameters obtained from the Raman spectra, but representative Raman spectra of monolayer, multi-layer graphene and bare SiC substrate taken from the same Raman map of the same irradiated sample are displayed in Fig. 6 (b). In the places covered with graphene, Raman mapping shows presence of D' peak along with D peak. At highest irradiated fluence, the $I(D)/I(D')$ ratio is 5.22 thereby indicating creation of vacancy defects. It has been previously reported that vacancy defects are created if $I(D)/I(D')$ is between 3.5 and 7 [59]. Creation of vacancy defects at highest fluence is also corroborated by the $I(D)/I(G)$ ratio (Fig. 4).

Fig. 6. (a) Reflectance Map of highest irradiated sample scanned over an area of $4.5 \times 4.5 \mu\text{m}$, illustrating formation of islands of multilayer graphene. The map is obtained during the Raman mapping. Up to 16 layers have been observed bunching in a hop after irradiation, but the reflectance map shown is restricted between 1 and 4 layers for better visibility, (b) Raman spectra of bare substrate (SiC), multi-layer graphene formed as a result of irradiation, and monolayer graphene in the sample irradiated at $2 \times 10^{13} \text{ ions/cm}^2$ fluence.

Fig. 6(b) shows that monolayer which is still presumably in contact with the substrate shows diminished 2D-peak intensity due to doping [55]. Broadening of 2D peak due to formation of multi-layer graphene can be seen besides reduced 2D, 2D' and G peak intensity in many multilayer spectra (Fig.5(c)). Additionally, we have observed that some multilayer spectrum exhibits some signatures of monolayer graphene, such as 2D intensity stronger than the G intensity, as well as symmetric (but significantly broader than true monolayer) single Lorentzian line-shape (Fig. 6(b)). These features are commonly observed in multilayer graphene grown on the C-face (000-1) of the SiC substrate, and are usually associated with presence of multiple layers, which are uncoupled. Also, complete absence of G and 2D peaks in bare substrate spectra show complete removal of graphene from the substrate in that area which is also observed in reflectance map due to multiple folding of graphene. Defects in graphene are used in many applications, and theoretical studies report better gas sensing capabilities in graphene with defects [29, 30]. We explored the gas-sensing capability of these irradiated samples. Fig. 7(a-c) shows the response of sensors fabricated on irradiated epitaxial graphene on SiC at room temperature towards 10 and 50 ppm NO_2 in a background of dry air. Schedin et.al, reported that graphene-based sensors could detect individual events when a gas molecule attaches or detaches from graphene surface [61], and Liu et al showed that since graphene is electronically low noise material, adsorbed molecules change local carrier concentration in graphene in steps of one electron leading to step-like change in resistance [62]. As-grown epitaxial graphene is n-type [63] and NO_2 is an oxidizing agent that withdraws electrons from graphene when adsorbed which results in increase in graphene resistance as seen in Fig. 7(a-c). The resistance increase with time due to NO_2 exposure and the slope of curve is proportional to the NO_2 concentration. We observed that the resistance approached steady state value within 30 minutes thereby showing equilibrium between adsorption and desorption. A previous study showed that desorption occurs for more than 12 h at room temperature. To reduce desorption time we used UV-LED irradiation and desorption was clearly visible in Fig. 7(a-c) as the

resistance rapidly recovers upon removal of NO₂. However, the initial resistance was not reached in the process of desorption which has also been reported previously and is likely due to strongly adsorbed or chemisorbed NO₂ [64]. Fig. 7(a-c) shows the normalized resistance versus time of sensors fabricated on irradiated graphene on SiC at 6.6×10^{11} , 2×10^{12} and 6.6×10^{12} ions/cm² fluences at room temperature to NO₂ gas flow in ppm range for an exposure time of 30 min. The results demonstrate the highest response of the sample at fluence 6.6×10^{11} ions/cm² in comparison to the other two fluences, 2×10^{12} and 6.6×10^{12} ions/cm². Decreasing response at higher fluences and lower response for pristine sample indicated the existence of an optimal fluence and consequently an optimal amounts of defects which maximize the gas sensing response towards NO₂.

Fig. 7. Response curve of sensor fabricated on irradiated graphene samples at 6.6×10^{11} ions/cm², 2×10^{12} ions/cm² and 6.6×10^{12} ions/cm² fluences, (a-c) exposed at 10 ppm and 50 ppm of NO₂ flow. (d-f) exposed at 10ppm and 50 ppm of NH₃ flow.

Figure. 7(d-f) show curve of normalized resistance versus time of irradiated graphene samples (at fluences 6.6×10^{11} , 2×10^{12} and 6.6×10^{12} ions/cm²) at 50 and 10 ppm NH₃ flow for an exposure time of 1 hour. NH₃ is a strong electron donor for graphene and thereby result in a decrease of the resistance when NH₃ is adsorbed on graphene. This is also seen in Fig. 7(d-f) [65]. Our pristine sample does not show any response towards NH₃ gas, but all the irradiated samples show such a response. The sample irradiated at 6.6×10^{11} ions/cm² fluence showed the

best responses of 4% and 24% at for 10 and 50 ppm of NH₃ gas, respectively. The sensitivity is defined as:

$$S = ((R - R_0) / R_0) \times 100,$$

where R is resistance under test gas exposure and R₀ is resistance in carrier gas. At higher than 6.6×10¹¹ ions/cm² fluences the response was observed to decrease with increase in fluence, similar to the response for NO₂ gas. A previous study showed that both sp³ and vacancy defects increase the gas-sensing response [66]. In our study, at higher fluences besides vacancy defects, other defects such as graphene folding and presence of higher area of bare substrate might contribute to reduced sensing capabilities. Pearce and co-workers reported that multi-layer graphene on SiC shows less sensing response compared to monolayer graphene due to higher number of charge carriers in the uppermost layer which are screened from electron donation of SiC substrate [19]. The reason for decrease in response with increase in fluence after 6.6×10¹¹ ions/cm² fluence is due to more conversion of monolayer graphene to multi-layer which is shown by our Raman and reflectance mapping results. Also, Raman mapping and reflectance mapping results show increased bare SiC area at higher fluences showing complete detachment of graphene due to multiple folding of graphene layer. Due to increase in bare SiC area with increase in fluence, the effective area of graphene for gas sensing reduces which results in a decreasing sensing capability.

Table 3. Sensitivity of pristine and irradiated samples at fluences 6.6×10¹¹, 2×10¹² and 6.6×10¹² ions/cm² towards the flow of NO₂ and NH₃ at concentrations 10 and 50 ppm. The sensitivity is calculated as percentage of resistance change as explained in text.

Gases	Samples	Sensitivity (%) at concentration	
		10 ppm	50 ppm
NO ₂	Pristine	5.5	23.1
	6.6×10 ¹¹ ions/cm ²	22.74	52.99
	2×10 ¹² ions/cm ²	19.2	40.24
	6.6×10 ¹² ions/cm ²	18.09	22.74
NH ₃	Pristine	0	0
	6.6×10 ¹¹ ions/cm ²	4.45	23.89
	2×10 ¹² ions/cm ²	2.11	7.39
	6.6×10 ¹² ions/cm ²	2.21	6.3

Table 3 shows the sensitivity at concentrations 10 and 50 ppm of sensors fabricated at pristine and at varying fluences for NO₂ and NH₃ gas. It is shown that the sensitivity of pristine sample to NO₂ is 5.5% and 23% at 10 and 50 ppm, respectively. The highest sensitivity of 23% and 53% was detected for NO₂ gas in sample irradiated at 6.6×10^{11} ions/cm² fluence. At higher fluences, sensitivity further decreases. The sample irradiated at 6.6×10^{11} ions/cm² fluence showed also the best sensitivity of 4% and 24% at 10 and 50 ppm for NH₃ gas. The sensitivity was observed to decrease beyond 6.6×10^{11} ions/cm² fluence for both test gases. Among the investigated fluences, the defects introduced upon irradiation at fluence 6.6×10^{11} ions/cm² seem to fit best for gas sensing applications. In our future work, we are planning to explore further gas sensing behavior of irradiated graphene on SiC around this optimized fluence (6.6×10^{11} ions/cm²) and also to explore gas sensing capabilities of irradiated samples in lower concentration range (less than 10 ppb).

Conclusion

In this study, we irradiated EG on SiC substrate with 100 MeV of Ag ions to investigate structural and morphological changes and investigate their gas sensing capabilities. The AFM study on irradiated graphene layer showed formation of hillocks, wrinkles, and folding of graphene which results in formation of multi-layer graphene due to unzipping of graphene and bunching of graphene fragments. Wrinkles were observed at the highest fluence (2×10^{13} ions/cm²). Raman spectroscopy showed increase in defect density with increasing fluence. Additionally, Raman and reflectance mapping showed high percentage of multi-layer graphene formation and bare SiC presence in samples irradiated at higher fluence. Our results also show formation of sp³ defects at low fluence and vacancy defect generation at high fluence on irradiated samples. Gas sensing capabilities of pristine and irradiated samples for NO₂ and NH₃ gases showed an initial increase in sensing response with maximum at 6.6×10^{11} ions/cm² fluence, which then decreased upon increasing fluence. This results indicated the existence of an optimal fluence and consequently an optimal amount of defects which maximize the gas sensing response towards NO₂ and NH₃ gases. The reason for decrease in response with increase in fluence after 6.6×10^{11} ions/cm² fluence is due to more conversion of monolayer graphene to multi-layer which has less sensing response in comparison with monolayer graphene. This work

could provide new pathways for increasing sensing capabilities of epitaxial graphene by introducing defects in controlled manner using ion beam technology.

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